

UNIT – 1

LESSON – 1

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1.0 AIMS AND OBJECTIVES

The aims and objectives of this lesson are to learn and to discuss the structural features of different types of inorganic chains and cage structures.

1.1 INTRODUCTION

Some non-metals have the tendency to resemble carbon in certain properties. This chapter discusses one such property of nonmetals. Nonmetals other than carbon have also the tendency to form chains, rings and cages. Most metals show less tendency to form compounds of this type, and the length of the chains and size of the rings thus formed are restricted. However, the ease with which both metals and nonmetals and combinations of the two form clusters has only been recognized in the last decade. This branch of chemistry has seen a rapid growth.

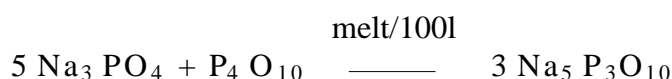
Carbon has the tendency to form extensive stable chains and hence we study the organic chemistry, as a separate branch. This phenomenon is not common in the remainder of the periodic table. Silicon and related nonmetals

have the tendency of form chains, to a limited extent. There is no thermodynamic barrier to the formation of long chain silanes, $\text{Si}_{(n)}\text{H}_{(2n+2)}$. Their synthesis and characterizations are difficult tasks. Si-Si bonds are weaker than C-C bonds. Silanes are very highly reactive. At 400°C , Si_2H_6 decomposes much faster than C_2H_6 .

$2\text{Si}_2\text{H}_6 + 7\text{O}_2 \longrightarrow 4\text{SiO}_2 + 6\text{H}_2\text{O}$. This reaction is kinetically favoured. Compounds of silanes from $n=1$ to $n=8$ have been isolated, including both straight chain and branched-chain compounds. A number of Polysilane polymers have been isolated. The chemistry of germanes is similar to silanes. Nitrogen, phosphorous and Sulphur form chains. Chain length up to 8 atoms of nitrogen are known. They are highly explosive. In the case of sulphanes, chains up to 8 sulphur atoms have been obtained. P_2H_6 is well known P_3H_5 is well characterized. Oxygen forms no chains longer than three atoms, O_3 and its anion O_3^- and a few compounds are known, for e.g., bis (perfluoroalkyl) trioxides such as $\text{F}_3\text{C}(\text{O})\text{O}(\text{C})\text{O}(\text{C})\text{F}_3$. Allotropes of both 'S' and 'Se', are known in which helical chains of great length are present. Sulphur chains are instable with respect to S_8 (Cyclic). The chain form of 'Se' is stable. Red 'P' is polymeric and is thought to have chains of pyramidal 'P' atoms. Polyhalide ions are stable, for e.g., I_3^- .

1.2.1 HETERO CATENATION:

The phenomenon of hetero catenation or chains built up of alternating atoms of different elements, is well known. Silicons, $(\text{R}_2\text{SiO})_n$ and polyphosphazenes $(\text{PN}(\text{OR})_2)_n$ are hetero catenated polymers, having wide application. The simplest hetero catenated compounds are those formed by the dehydration of acids or their salts. Simple acid phosphate salts on heating give rise to pyrophosphates, for e.g., $(\text{P}_2\text{O}_7)^{-4}$. The general formula of polyphosphate may be given as : $(\text{P}_n\text{O}_{3n+1})^{-(n+2)-}$; $n=2$, it is known as diphosphate, $n=3$ - triphosphate etc.,



condensed poly phosphates such as sodium triphosphates, are largely used as detergents.

Silicate Minerals

Silicon forms a very large number of compounds containing heterocatenated anions. The silicates make up of various minerals. About three fourths of the earth crust is silicon and oxygen. The majority of silicate minerals are insoluble, because they have an infinite ionic structure and because of the Si-O bond. Silicate structures have been solved by X-ray crystallographic methods:

- i) The electro negatively difference between 'Si' and 'O' is equal to 1.7. This suggests that the bonds are 50% ionic and 50% covalent.
- ii) The structure may be considered both by ionic and covalent methods. The radius ratio of $\text{Si}^{+4}:\text{O}^{-2}$ is 0.29, which suggests that 'Si' is four coordinate. It is surrounded by four oxygen atoms at the corners of a tetrahedron. 'Si' in $(\text{Si O}_4)^{-4}$ may be assumed to be SP^3 hybridized (3s and three 3P orbitals) and hence silicates are based on $(\text{Si O}_4)^{-4}$ tetrahedral units.
- iii) The SiO_4 tetrahedra may exists as discrete units or may polymerize into larger units by sharing corners, i.e., by sharing oxygen atoms.
- iv) The 'O' atoms are often close packed or nearly close packed. Close packed structures have tetrahedral and octahedral holes and metal ions can occupy either tetrahedral or octahedral sites depending on their size. Al^{3+} can fit into either octahedral or tetrahedral site. Thus Al can replace either octahedral or tetrahedral site. Thus Al can replace either a metal in one of the holes or a silicon atom in the lattice. This is particularly important in the aluminosilicates.

Classification of Silicates

- i) **Ortho Silicates:** A wide variety of minerals contain discrete $(\text{SiO}_4)^{4-}$ tetrahedra. They have the general formula $\text{M}_2(\text{SiO}_4)$ (M=Be, Mg, Fe, Mn or Zn). $\text{M}(\text{SiO}_4)$ M-Zr. These silicates share no corners.

In Zn_2SiO_4 (Willemite) and Be_2SiO_4 (Phenacite) Zn and Be have a 'CN' of 4; Zn and Be occupy tetrahedral holes. In Mg_2SiO_4 , Mg has a CN of 6 and occupies octahedral holes. Zr SiO_4 is a gem stone. Zr has a CN of 8. The structure is not close packed. The garnets are minerals with discrete tetrahedra; are used as red gem stones. Its formula is $\text{M}_3\text{M}_2(\text{SiO}_4)_3$ M(II) = Mg, Ca or Fe (II); Me(III) may be Fe(III), Cr or Al. These are 8 coordinate.

ii) Pyrosilicates

Two tetrahedral units are joined by sharing the 'O' at one corner and the unit is $(\text{Si}_2\text{O}_7)^{6-}$. This is the simplest of the condensed silicate ions. The name pyro comes from the similarity in structure with pyrophosphates like $\text{Na}_4\text{P}_2\text{O}_7$.

Pyrosilicates are rare, for e.g., Thortveitite $(\text{Sc}_2(\text{Si}_2\text{O}_7))$ Si-O-Si bond angle is 180° in this compound and it changes upto 133° .

The coordination number of the metal changes from 6 to 7 and then to 8, with increase in size of the metal. Structural studies show no difference in the lengths of the bridging and terminal Si-O bonds.

Cyclic Silicates

If two oxygen atoms per tetrahedron are shared, ring structures of formula $(\text{Si}_n\text{O}_{3n})^{2n-}$ may be formed. Rings containing, three, four, six and eight tetrahedral units are known. But those with three and six are the most. The cyclic ion $\text{Si}_3\text{O}_9^{6-}$ occurs in wollastonite, $\text{Ca}_3(\text{Si}_3\text{O}_9)$. The $\text{Si}_6\text{O}_{18}^{12-}$

occurs in beryl, $\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18})$. In beryl the Si_6O_{18} units are aligned one above the other, leaving channels. Na^+ , Li^+ and Cs^+ are commonly found in these channels, and because of the channels the mineral is permeable to gases consisting of small atoms or molecules e.g., helium. Beryl and emerald are gemstones. Beryl is found with granite and usually forms pale green crystals, which are six sided prisms. Emerald has the same formula as beryl, but it contains 1-2%Cr, which gives it a strong green colour.

Chains Silicates:

Pyroxenes are simple chain silicates. These are formed by the sharing of oxygen atoms on two corners of each tetrahedron, with other tetrahedra. This gives the formula $(\text{Si O}_3)_n^{2n-}$. A large number of important minerals form chains, but there are a variety of different structures formed because the arrangement of tetrahedra in space may vary and thus affect the repeat distance along the chain. The most common arrangement repeats after every second tetrahedron for e.g., in spodumene, $\text{Li Al} [(\text{Si O}_3)_2]$, enstatite $\text{Mg}_2 [(\text{Si O}_3)_2]$ and diopside, $\text{Ca Mg} [(\text{Si O}_3)_2]$. $\text{Ca}_3 [(\text{Si O}_3)_3]$ has a repeat of three, and others are known with repeat units 4,5,6,7,9 and 12.

Double chains can be formed when two simple chains are joined together by shared oxygens. These minerals are amphiboles. They have different formulae, due to several ways of forming double chains, for e.g., $[(\text{Si}^2\text{O}_5)_n]^{2n-}$, $[(\text{Si}_4\text{O}_{11})_n]^{6n-}$, $[(\text{Si}_6\text{O}_{17})_n]^{10n-}$ etc., Asbestos minerals are the best known amphiboles. These have the structural units $(\text{Si}_4\text{O}_{11})_n^{6n-}$. Amphiboles always contain – OH groups, which are attached to the metal ions. The Si-O bonds in the chains are strong and directional. Adjacent chains are held together by metal ions present. Pyroxenes and amphiboles cleave readily parallel to the chains, forming fibres. For this reason, they are called fibrous minerals. The cleavage angles for pyroxenes and amphiboles are different. Example are tremolite $\text{Ca}_2\text{Mg}_5 [(\text{Si}_4\text{O}_{11})_2] (\text{OH})_2$ and crocidolite $\text{Na}_2\text{Fe}_3\text{Fe}_2 [(\text{Si}_4\text{O}_{11})_2] (\text{OH})_2$ (. (blue asbestos).

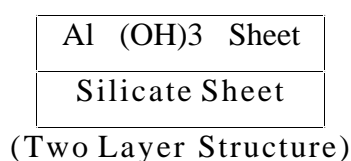
The mineral chrysotile $\text{Mg}_3(\text{OH})_4(\text{Si}_2\text{O}_5)$ is white asbestos and is a sheet silicate. Asbestos causes lung cancer.

Sheet Silicates

When SiO_4 units share three corners the structure formed is an infinite two dimensional sheet of empirical formula $(\text{Si}_2\text{O}_5)_n^{2n-}$ within the Si-O sheet bonds are strong but much weaker forces hold each sheet to the next one. These sheets cleave into thin sheets. These consist of two or three layers joined together. Examples are

- (i) Clay minerals (Kaolinite)
- (ii) White asbestos
- (iii) Micas (Muscovite)
- (iv) Montmorillonites (fullers earth, bentonite).

consider the formation of a two layer structure. If a Si_2O_5 layer is placed along side a layer of $\text{Al}(\text{OH})_3$, then many of the 'O' atoms will coincide. The 'OH' groups in $\text{Al}(\text{OH})_3$ can be removed and an electrically neutral two layer structure is formed. These double layers stacked parallel give the mineral kaolinite, which has the formula $\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$. It is a white solid and formed by the decomposition of granite.



Three Dimensional Silicates

Sharing all four corners of a SiO_4 tetrahedron results in a three dimensional lattice of formula SiO_2 (quartz, tridymite, cristobalite etc.). These contain no metal ions, but three dimensional silicate structures in which some of the Si^{+4} ions are replaced by Al^{3+} , plus an additional metal

ion. This gives an infinite three dimensional lattice and the additional cations occupy holes in the lattice. The cations are usually the larger metal ions like K^+ , Na^+ , Ca^{+2} or Ba^{+2} . The smaller ions Fe^{3+} , Cr^{3+} and Mn^{2+} which are common in chain and sheet silicates do not occur in three dimensional silicates because the cavities in the lattice are too large. Replacement of one quarter or one half of the 'Si' atoms are quite common. These give structures, $M[Al Si_3 O_8]$ and $M[Al_2 Si_2 O_8]$. Such replacements gives rise to the minerals.

- i) Feldspars
- ii) Zeolites
- iii) Ultramarines

Granite is made up of feldspars. We have orthoclase feldspars:

- a) Orthoclase $K[Al Si_3 O_8]$
- b) Celsian $Ba[Al_2 Si_2 O_8]$

Plagio Clase:

- a) Albite $Na[Al Si_3 O_8]$
- b) Anorthite $Ca [Al_2 Si_2 O_8]$.

The ortho clases are more symmetrical than are Plagio Clases. K^+ and Ba^{2+} are just the right size to fit into the lattice while Na^+ & Ca^{2+} being smaller, cause distortion.

Zeolites:

Zeolites have a much more open structure, than the feldspars. The anion skeleton is penetrated by channels, giving a honeycomb like structure. These channels are large enough to allow them to exchange certain ions. They can also absorb or lose water, and other small molecules without the structure being broken. Zeolites are often used as ion- exchange materials and as molecular sieves. Natrolite, $Na_2[Al_2 Si_3 O_{10}] 2H_2O$ is a natural ion exchanger. Permutit water softeners use sodium zeolites. Zeolites take Ca^{2+}

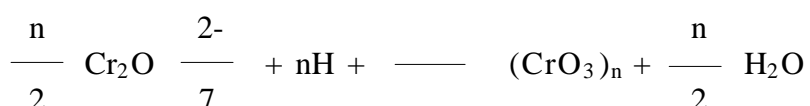
from water and replace them by Na^+ . Zeolites can absorb CO_2 , NH_3 and Et OH, Zeolites have been employed to separate branched chain hydrocarbons from straight chain hydrocarbons.

The mineral lapis lazuli has a fine blue colour. It contains ultramarine $\text{Na}_8[(\text{Al Si O}_4)_6]\text{S}_2$, in which the colour is produced by the polysulphide ion. Ultra marines do not contain water.

The ultramarines are now produced synthetically is obtained by heating kaolinite, Na_2CO_3 and S in the absence of air.

1.2.2 ISOPOLY AND HETEROPOLYANIONS

Transition metals in their higher oxidation states are similar to nonmetals with corresponding group numbers. For e.g., V and P in VO_4^{3-} and PO_4^{3-} , CrO_4^{2-} and SO_4^{2-} , MnO_4^- and ClO_4^- . The analogy may be extended to poly anions, such as $\text{Cr}_2\text{O}_7^{2-}$. Polymensation of some metal anions occurs spontaneously, upon acidification. At low P1+ CrO_4^- is converted into $\text{Cr}_2\text{O}_7^{2-}$. When $\text{Cr}_2\text{O}_7^{2-}$ is treated with concentrated sulphuric acid red chromium (VI) oxide, chromium acid is formed.



The structure of CrO_3 consists of infinite linear chains of CrO_4 tetrahedra. The vanadate ion, VO_4^{3-} exists in extremely basic solution. Under dilution and low pH, protonation yields monomers (VO_2^+). When solutions are more concentrated ($\text{V}_2\text{O}_7^{4-}$) and higher vanadates are obtained. The polymerization of vanadate, molybdate and tungstates ions forming isopoly anions have been extensively studied. In the condensation process, the coordination number changes from 4 to 6 and the basic building block in the polymerization process becomes an octahedron of six oxygen atoms, surrounding each metal atom. The resulting octahedra may link either by sharing an apex or edge (rarely a face) due to the relaxation of electrostatic

repulsion, in the larger octahedra. As a result, the structures tend to be small clusters of octahedra, in the discrete poly anions, culminating in infinite structures in the oxides. When the edge sharing occurs, the structure may be stabilized, if some distortion occurs such that the metal ions move away from each other. It might be expected that the smaller the metal ion, the less the repulsion and the larger the number of edge sharing octahedra per unit. This is found to be true V^{5+} (68pm), Mo^{6+} (73pm), W^{6+} (74 pm), Nb^{5+} (78pm) Ta^{5+} (78pm) and the most common edge shared poly anions are, $(V_{10} O_{28})^{6-}$, $(Mo_7O_{24})^{6-}$, $(Mo_8 O_{26})^{4-}$ $(W_6 O_{19})^{2-}$, $(W_7O_{24})^{6-}$, $(Nb_6 O_{19})^{8-}$ and $(Ta_6 O_{19})^{8-}$. To form larger polyanions such as $(W_{12} O_{42})^{12-}$ edge sharing must give to rise to apex sharing.

The isopoly an ions may be considered to be portions of a closest packed array of oxide ions with metal ions occupying the octahedra holes. The edge sharing array found in $(V_{10} O_{28})^{6-}$ consists of ten octahedral stacked. This is the largest stacked octahedra isopoly anion cluster compatible with metal-metal repulsions, and the remaining edge shaped structures represent portions of this unit.

Elements other than V, Nb, Ta, Mo and W do not form isopoly anions. Al^{3+} , Ga^{3+} , I^{7+} may have appropriate radii for isopoly anion formation. But they form, sheets or three dimensional frame works. The reason given is as follows. The terminal oxygen atom in the isopoly anion is strongly π bonded to a transition metal such as Mo(VI) or W(VI). The metal ion is displaced in the direction of the terminal oxygen; due to this effect. Metal ions such as Al^{3+} and Ga^{3+} are poor π acceptors. Thus their terminal oxygen atoms are not stabilized, and this leads to chain structures. Due to π bonding the terminal oxygen atoms of the transition metal polyanions are stabilized and have less affinity for adjacent metal units.

In aprotic media, new poly anions have been obtained for e.g., When $[(n-Bu)_4N] OH$ and $[(n-Bu)_4N] [H_3 V_{10} O_{28}]$ are mixed in acetonitrile, a new isopoly vanadate, $[V_5 O_{14}]^{3-}$ is formed. It is the first example of a poly

oxoanion cage that is built from corner shared tetrahedra. When $[\text{n Bu}_4\text{N}] [\text{H}_2\text{V}_{10}\text{O}_{28}]$ is refluxed in acetonitrile, CH_3CN is found to be suspended in a $(\text{V}_{12}\text{O}_{32})^{-4}$ basket.

Heteropolyanions

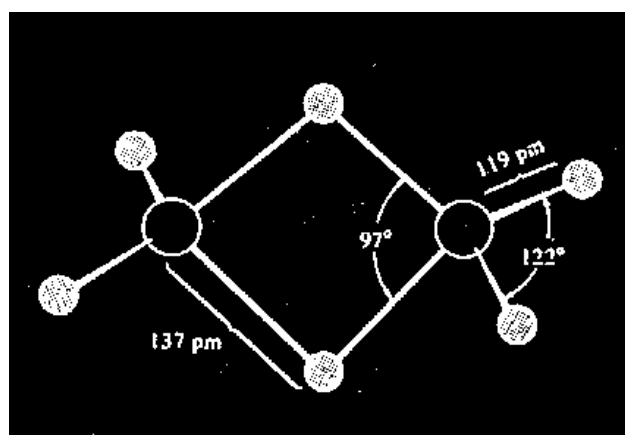
It has been found that there is a cavity in the center of a metatungstate ion. This cavity is surrounded by a tetrahedron of four oxygen atoms. This cavity is sufficiently large to accommodate a relatively small atom like P(v), As(V), Si (IV), Ge(IV), Sn (IV) or Zr (IV). The 12-tungsto heteropoly anions are of general formula $[\text{X}^{\text{n}+}\text{W}^{12}\text{O}_{40}]^{(8-\text{n})-}$ similar molybdo heteropoly anions are also known. For e.g., when a solution containing phosphate and molybdate is acidified, the ion $(\text{PMo}_{12}\text{O}_{40})^{3-}$ is formed P-O bonds are not broken in this process. The product anion contains the PO_4^{3-} in the $\text{MO}_{12}\text{O}_{36}$ cage. Between 35 and 40 hetero atoms are known to form heteropoly anions and their corresponding acids. Large hetero atoms such as Ce (IV) and Th (IV) are found icosahedrally coordinated in salts such as $(\text{NH}_4)_2 \text{H}_6 \text{Ce Mo}_{12} \text{O}_{42}$. It is unique in as much as pairs of MoO_6 octahedra share faces to form Mo_2O_9 groups which are corner connected to each other 6 molybdo heteropoly acids form with hetero atoms Te(VI), I(VII) and tripositive metal ions such as Rh(III). All these heteroatoms prefer an octahedral coordination sphere, which can be provided by a ring of six M_6O_6 octahedral. The isopoly and heteropoly anions may be considered small chunks of metal oxide lattice. For selective oxidation of organic molecules, these may be used as catalysts. As anions they show very low surface charge densities and low basicities. Hence molybdate (-2) ion and 12-tungsto phosphate (-3) ion have lower basicities than perchlorate ion. Mn^{2+} binds weakly to a terminal oxygen atom of $(\text{H}_2\text{W}_{12}\text{O}_{40})^{6-}$ and the anion functions as a monodentate ligand.

Co in $[(\text{Si W}_{11}\text{O}_{39}) \text{Co} (\text{H}_2\text{O})]^{6-}$ is 6 coordinate, the heteropoly anion functions as a pentadentate ligand. $(\text{W}_6\text{O}_{19})^{2-}$ has been studied using O^{17} NMR spectroscopy. The spectm gives three signals corresponding to twelve bridging oxygen atoms, one signal for encapsulated oxygen and one for terminal oxygens.

Fig.1.2(a) and (b) Bonding and structure of tetraborane, B_4H_{10} . (From Mutterties, E.L. The Chemistry of Boron and Its compound; Wiley: New York, 1967. Reproduced with permission.)

1.2.3 CAGES

The bonding and structures of boranes are of great interest. They are different from all other hydrides. These compounds are electron deficient. Diborane (B_2H_6) has 12 valency electrons (3 from B and 6 from H atoms). Electron diffraction studies indicate that the compound has B-H-B bridges. The two bridging H-atoms are in a plane perpendicular to the rest of the molecule, and prevent rotation between the two 'B' atoms. Specific heat measurements confirm that the rotation is hindered. Four of the H atoms are in a different environment than the other two. This is confirmed by Raman spectra and by the fact that diborane cannot be methylated beyond $Me_4 B_2 H_2$, without breaking the molecule into $B Me_3$. The terminal B-H distances are the same. These are assumed to be normal covalent bonds. These are (2C-2e) two centre-two electron bonds. The structure is shown in fig 1. Each of the bridging B-H-B linkages then involves a delocalised three centre bonds. Each 'B' is SP^3 hybridised.

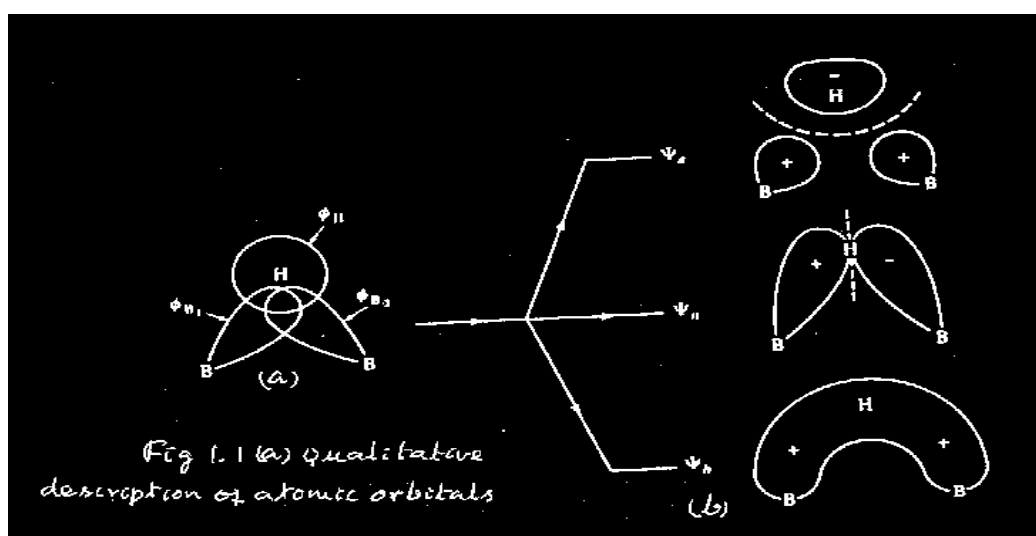


The appropriate combinations of three orbital wave functions, ϕ_{B_1} , ϕ_{B_2} (SP^3 hybrid orbitals) and ϕ_H ('s' orbitals), give rise to three molecular orbitals (M_O)

$$\Psi_b = \frac{1}{2} \phi_{B1} + \frac{1}{2} \phi_{B2} + \frac{1}{\sqrt{2}} \phi_H$$

$$\Psi_n = \frac{1}{\sqrt{2}} \phi_{B1} - \frac{1}{\sqrt{2}} \phi_{B2}$$

$$\Psi_a = \frac{1}{2} \phi_{B1} + \frac{1}{2} \phi_{B2} + \frac{1}{\sqrt{2}} \phi_H$$



Ψ_b = bonding MO, Ψ_a = antibonding MO and Ψ_n = nonbonding. Each bridging bond thus consists of a bonding MO containing two electrons. Thus all the twelve electrons in B_2H_6 have been accounted for fig.1.1(a) and (b) give qualitative description of atomic orbitals and three centre MO orbitals respectively $B_{10}H_{14}$ is quite stable in air. B_4H_{10} is formed by slow decomposition of B_2H_6 . In addition to terminal and bridging of B-H bonds B_4H_{10} contains a direct B-B bond. Tetraborane undergoes both symmetric and unsymmetric cleavage. Fig 1.2(a) and (b). Fig 1.3 gives bonding and structure of B_4H_{10} . Larger bases spit off BH_3 groups:



small hard Lewis bases (NH_3) - result in unsymmetrical cleavage - splits of BH_2^+

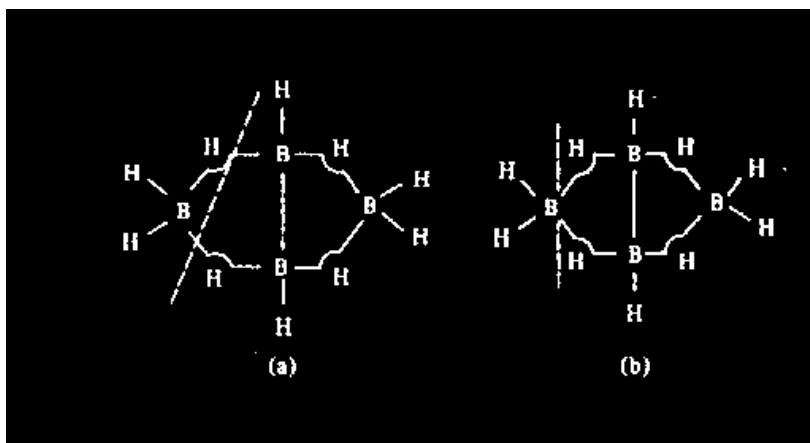
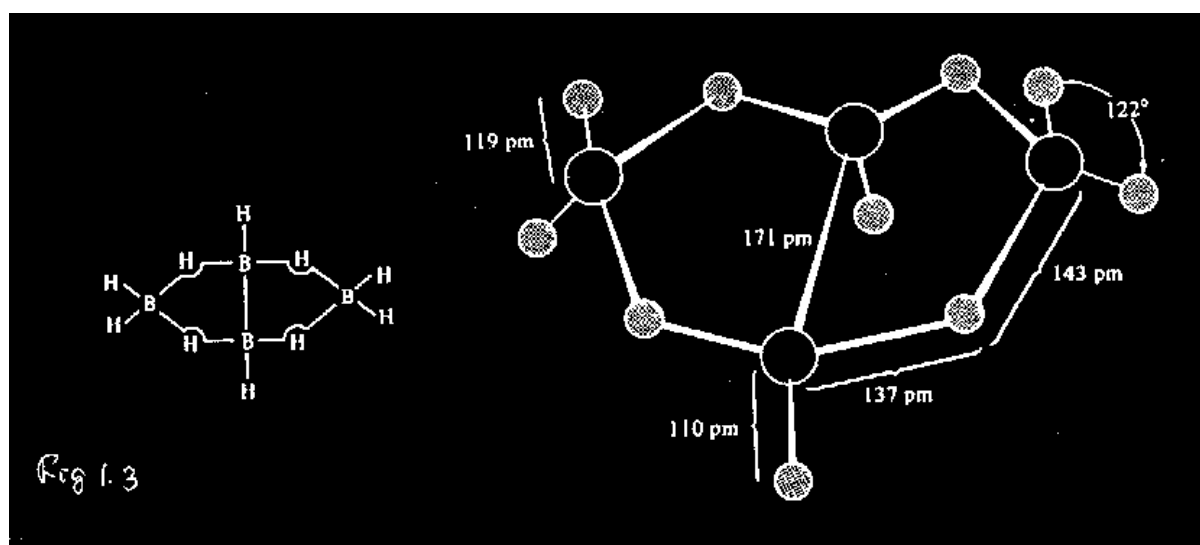
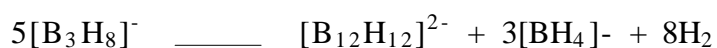


Fig 1.2 Symmetric (a) and Unsymmetric (b) Cleavage of Tetraborane

$[\text{B}_{12}\text{H}_{12}]^{2-}$ is a highly symmetric borohydride. It is obtained from B_3H_8^- ion.



The $[\text{B}_{12}\text{H}_{12}]^{2-}$ is a regular icosahedron of atoms, each of the twenty faces being an equilateral triangle. All of the H atoms are external to the boron icosahedron and are attached by terminal B-H bonds. The structure involves several canonical forms. Both two electron, two centre B-B and two electron, three centre B-B-B bondings are involved. Several boranes may be considered as fragments of a B_{12} icosahedron (or of the $[\text{B}_{12}\text{H}_{12}]^{2-}$ ion) in

which extra hydrogen atoms are used to "sew up" the unused valences around the edge of the fragment. For e.g., decaborane ($B_{10}H_{14}$), may be considered as a $B_{12}H_{12}$ framework from which B_1 and B_6 have been removed, leaving "dangling" three centre bonds that are completed with hydrogen atoms to form B-H-B bridges. (B_6H_{10} (hexaborane) is a pentagonal prism. Experimental work has shown that the icosahedrons of $[B_{12}H_{12}]^{2-}$ is merely the upper limit of a series of deltahedra $(B_nH_n)^{2-}$ (from $n=4$ to $n=12$). If all the vertices of the deltahedron are occupied, as in the $[B_nH_n]^{2-}$ series, the structure is called a 'closo' (closed structure). The number of vertices in the deltahedron will be one less than the number of bonding pairs in the framework. This theory is called 'Wade's rules'. For the closo series the number of framework electrons equals $2n+2$. Consider $(B_{12}H_{12})^{2-}$ to count framework electrons. Each 'B' has one of its valence electrons tied up with the 'exo' B-H bond and it has thus two to contribute to the framework, giving a total of $2n$ (in this case 24 electrons) from the 'B' atoms. No neutral B_nH_n species are known, but an array of dianions, obeying the $2n+2$ are known.

The 26 electrons ($2 \times 12 + 2$) are just the number required to fill all the bonding molecular orbitals in $[B_{12}H_{12}]^{2-}$ and this corresponds to 13 ($n+1$, $n=12$) electron pairs as expected for an icosahedron. If a B atom is removed from a vertex of the closo structure, a cup-like or nest like structure remains. Such structures are called 'nido' (nest). The nido structures obey the framework formula $2n+4$. Consider B_5H_9 .

Five exo B-H groups will contribute two electrons each, and the four extra 'H' atoms will contribute 4 electrons and thus the total will be $10+4=14$ electrons ($2n+4$, $n=5$). This corresponds to 7 pairs ($n+2$) and the geometry will be derived from an octahedron ($n-1$ vertices). The structure is thus a square pyramid nido form derived from the closo octahedron. If two vertices are missing, the resulting framework is called "arachno" (spider's web). These obey the formula $2n+6$ ($n+3$ electron pair). B_5H_{11} (penta borane) has arachno structure. In arachno series the extra H atoms form endo B-H bonds. In hypso (net) series the rule is $2n+8$. Some borane derivatives, fit it into this scheme. For a regular deltahedron having 'n' vertices there will be $n+1$ bonding

molecular orbitals. The number of electrons that can occupy these Mos will be $2n+2$. This gives the highly symmetric closo structure.

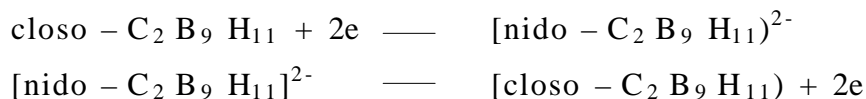
Carboranes:

The systems $C_2B_{10}H_{12}$ is isoelectronic with $[B_{12}H_{12}]^{2-}$ and can be synthesized from decarborane and alkynes using diethyl sulphide as solvent.



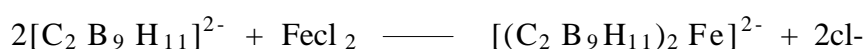
The acetylene may be unsubstituted or substituted, in which case, the compound is known as 1,2-dicarba-closo-dodeca borane or orthocarborane and is isoelectronic and iso structural with $[B_{12}H_{12}]^{2-}$. It is stable to both heat and air, but it isomerises at high temperatures to the 1,7 (meta or 'neo' isomer) and the 1,12 (Para isomer). The mono carboranes are known in closo, nido and arachno structures.

Thus



In the anion $[C_2B_9H_{11}]^{2-}$, each of the three 'B' atoms and the two carbon atoms on the open face of the cage directs an orbital (SP^3) toward the apical position occupied formerly by the 12th boron atom. Further these orbitals contain a total of six electrons.

Hence this anion $[C_2B_9H_{11}]^{2-}$ has a resemblance to cyclopentadienide anion. This anion could be considered isoelectronic with $C_5H_5^-$ and should be capable of acting as a Π ligand in metallocene compounds. Hawthorne succeeded in synthesizing metalla carboranes.



This has structure similar to ferrocene.

Self Check Exercise m- 1

- 1) What is heterocatenation?
 - b) Discuss the different types of silicates and their structures.
-
- 2) Describe with examples, the isopoly anions.

Self Check Exercise – 2

- 1) Discuss the structures of molybdates and tungstates
- 2) Elucidate the structure of diborane
- 3) Discuss in detail the structures of boranes and explain the terms, closo, nido and arachno with examples.

1.3 Let us Sum Up

Heterocatenations, like heteropoly and isopoly anions and their structures are discussed various types of silicate minerals and how SO_4 tetrahedra could form different types of structure sare indicated. Boron cage compounds, wades rules and closo nido and arachno spieces are also described.

1.4 Points for Discussions

- i) Silicates ad their structures
- ii) Isopoly and heteropoly anions – structures and uses
- iii) Boranes – Closo nido & arachno species the different formulae as $2n+2$, $2n+4$, $2n+6$ and $2n+8$

1.5 References

Concise Inorganic chemistry – V edition – J.D.Lee – Blackwell.
Publishing – Noida- Delhi – 2005.

LESSON -2

CONTENTS

- 2.0 AIMS AND OBJECTIVES
- 2.1 INTRODUCTION
- 2.2 METAL CLUSTERS
 - 2.2.1 TYPES OF METAL CLUSTERS
 - 2.2.2 ORGANOMETALLIC CLUSTERS
- 2.3 Let us Sum Up
- 2.4 Points for Discussion
- 2.5 References

2.0 AIMS AND OBJECTIVES

The aims and objectives of this lesson are to learn about the different types of metal clusters and their structures.

2.1 INTRODUCTION

Compounds containing metal-metal bonds are as old as chemistry itself. Calomel was known to chemists of India as early as 12th century. The dimeric nature of mercurous ion was confirmed only later. It was only some 30-35 years ago that the study of other metal-metal bonds began in earnest; yet this branch of inorganic chemistry has grown at a phenomenal rate.

Metal cluster compounds can be conveniently classified into two classes:

- i) Polynuclear carbonyls, nitrosyls and related compounds
- ii) Halide and oxide complexes

The second class will be discussed here. The two classes have un related chemistry. Metal atoms in class.

- i) Have formal oxidation states -1 to +1, while those in
- ii) are found in higher formal oxidation states, +2 to +3.

The transition metals (late transition metals) typically form class

i) Clusters, while those on the right side of the periodic table (early second and third row transition metals) tend to form class II clusters. Atoms having large energies of atomization (hence very high m-pts and b-pts) form metal clusters. Thus the most refractory metals (Zr, Nb, Mo, Tc, Ru, Rh, Hf, Ta, W, Os, Ir and Pt) have the greatest tendency to form metal clusters. Effective overlap of d-orbitals appears necessary for stabilizing metal clusters. Excessive contraction of the 'd' orbitals will destabilize the metal clusters. Hence large charges (very high oxidation states) on the metal atoms are unfavourable for the formation of metal clusters. In first row transition metals, the 'd' orbitals are relatively small and metal cluster formation is not favoured.

i) Dinuclear Compounds

The best studied compound is $(\text{Re}_2 \times 8)_2^-$ ion; obtained by reducing

Perrhenate with H_3PO_2 in the presence of $x^- 2 \text{ReO}_4$ $\xrightarrow[\text{H}_3\text{PO}_2]{\text{Hx}}$ $(\text{Re}_2 \times 8)^{2-}$;

$x = \text{Cl, Br, I, NCS}$.

It has two unusual features. Re-Re bond distance is 224pm compared with an average of 275pm in rhenium metal, and 248pm in $\text{Re}_3 \text{Cl}_9$. The unexpected features in this ion is the eclipsed configuration of the chlorine atoms. But chlorine atoms are expected to lie at distances of 330pm, i.e., the staggered configuration would be preferred. According to Cotton, the Z-axis of the ion is taken as the line joining the two Re atoms. Each Re atom is bonded to four 'Cl' atoms in a square planar array. We may consider the Re-Cl bonds to involve $d\text{sp}^2$ hybrids on each metal (using dx^2-y^2 orbitals). The metal dZ^2 and P_z orbitals lie along the bond axis and may be hybridized to form one orbital directed toward the other rhenium atom and a second orbital

directed in the opposite direction. The former can overlap with the similar orbital on the second 'Re' atom to form a ' σ ' bond, the second dZ^2 -pz hybrid orbital forms an approximately a non-bonding orbital. The dx_z and dy_z orbitals of each rhenium atom can overlap to form two Π bonds. The dxy orbitals on each Re atom can overlap "sideways" forming a ' δ ' bond (delta). overlap of the dxy orbitals can only occur if the chlorine atoms are eclipsed. If the chlorine atoms are staggered, the dxy orbitals do not overlap. The eight d electrons (Re^{3+} , d^4) from two 'Re' atoms occupy σ bonding (2), two Π bonds (4) and delta bond (2) ing orbitals to form the quadruple bond; hence the complex is diamagnetic. The model accounts for the strength of the bond, the short Re-Re distance and the eclipsed configuration.

The isoelectronic $(Mo_2 Cl_8)^{2-}$ is known. Both Re (III) and Mo(III) form a large series of carboxylate complexes of formula $Re_2(RCO_2)_2 \times 4$ etc, and $Mo_2(RCO_2)_4$. Structurally these are related to $(Re_2 \times 8)^{2-}$.

$[Re_2 Cl_8]^{2-}$ (having qudruple bond) has all its bonding Mos filled up i.e $\sigma^2 \Pi^4 \delta^2$ (bond order = 4). δ and δ^* are nearly non-bonding.

Tungsten forms a series of compounds $W_2 Cl_4 (OR)_4 R_2$ (R=Me, Et), with a W=W double bond. These ditungsten compounds have bond orders 4, 3, 2 and 1 Cu(II) and Cr (II) in the 1st transition series form acetate complexes. These are diamagnetic. Cu-Cu bond in Cu (II) acetate is only a weak single bond resulting from pairing the odd electron in each copper atom. Cr-Cr bond in its acetate complex, is stronger than Cu-Cu bond. Cr-Cr distance is shorter in the complex than in the metal. These suggest that the Cr complex has a qudruple bonds (weak). But the lengths of the qudruple bonds in Mo-Mo and W-W are uniform.

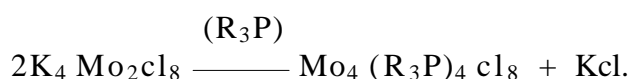
$(RO)_6 M_2$ e.g. $W_2 (OR)_6$ are known. $W \equiv W$ is found in these complexes ($\sigma^2 \Pi^4$). This undergoes addition reactions with halogens (Cl_2 , Br_2 , I_2). $W_2 (O-i-Pr)_6$ dimerises to $W_4 (o-i-Pr)_{12}$ - analogous to cyclobutadiene - a fluxional molecule.

Trinuclear Clusters:

$[(\text{ReCl}_3)_3]$ contains three metal atoms. Each rhenium atom is bonded to other two 'Re' atoms directly by metal-metal bonds, and indirectly by a binding halogen ligand. In addition each, rhenium atom in the triangular array is coordinated by two more halide ligands above and below the plane defined by the three rhenium atoms. Each Re (III) has d^4 configuration which would lead to a paramagnetic complex, if only metal-metal single bonds were present. The complexes are diamagnetic, however which implies that each Re atom is doubly bonded to its Re neighbour. Re_3 cluster is persistent in many chemical transformations.

Tetra Nuclear Clusters :

$\text{W}_4(\text{OR})_{12}$ is a tetra nuclear cluster which is formed by the dimerisation of $\text{W}_2(\text{OR})_6$. The tetrameric $\text{W}_4(\text{OR})_{16}$ has also been synthesised. $\text{W}_4(\text{OR})_{16}$ is saturated, containing W-W single bonds. Quadruply bonded dinuclear compounds can also dimerise to give tetrameric molecules



Four member ring containing Mo is formed. The resulting four membered ring is not square. Bond length measurements indicate, that there are alternating single and triple Mo-Mo bonds. Tetranuclear cluster units (rhombohedral Mo_4), connected by oxygen atoms and forming infinite chains, are found in $\text{Ba}_{1.14}\text{Mo}_8\text{O}_{16}$.

Hexa Nuclear Clusters

Clusters of six, Mo, Nb or Ta atoms are known. There are two types. In the first an octahedron of six metal atoms is coordinated by eight chloride

ligands, one on each face of the octahedron. This is found in "Molybdenum dichloride", $\text{Mo}_6\text{Cl}_{12}$, better formulated as $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$. Each Mo (II) atom can use its four electrons to form four bonds with adjacent Mo atoms and can form dative bonds from the four chloride ligands. $(\text{Mo}_2\text{Cl}_8)^{4-}$ and $(\text{Mo}_6\text{Cl}_8)^{4-}$ have a cubic arrangement of chloride ions, Nb and Ta form hexanuclear clusters. These have octahedron of metal atoms, but they are coordinated by twelve halide ligands, along the edges. The structures are complicated. The metal atoms are surrounded by a distorted square prism of four metal and four halogen atoms. These compounds are electron deficient (as boranes)– there are fewer pairs of electrons than orbitals to receive than orbitals and so fractional bond orders of $2/3$ are obtained.

Chevrel Phases

Ternary molybdenum chalcogenides, $\text{M}_x\text{Mo}_6\text{X}_8$, are called chevrel phases and are polynuclear clusters having unusual structures. These have interesting electrical and magnetic properties. PbMo_6S_8 is a super conductor below 13.3K. This has an octahedral cluster of Mo atoms, surrounded by a cubic cluster of S atoms, which in turn is surrounded by a cubic lattice of lead atoms.

2.2.2 Organometallic Clusters

Poly nuclear carbonyls such as $\text{B}_3\text{H}_7[\text{Fe}(\text{CO})_3]_2$ and complexes of the type $\text{Rh}_6(\text{CO})_{16}$ may be classified as organometallic clusters. The structures of these cages or clusters can be predicted by 'Wade's rules' (Closo, nido or arachno) using $2n+2$, $2n+4$ and $2n+6$ formulae.

Consider the Molecule:

$\text{B}_3\text{H}_7[\text{Fe}(\text{CO})_3]_2$, for which $n=5$. The three BH units and the two $\text{Fe}(\text{CO})_3$ units contribute 2 electrons each and the four extra H atoms contribute 1 electron each (total 14 electrons).

$$\begin{array}{rcl}
 2 \text{ Fe (Co)}_3 & = & 2 \times 2 = 4 \\
 3 \text{ BH} & = & 3 \times 2 = 6 \\
 4 \text{ H} & = & 4 \times 1 = 4 \\
 \hline
 & & 14 \\
 \hline
 \end{array}$$

Since $n=5$, there are $2n+4$ framework electrons and we predict a nido structure for the same. Molecule has a square pyramidal structure. This results from the substitution of 2 BH units by 2Fe (Co)₃ units in B₅H₉.

Consider Rh₆(Co)₆: $n=6$. Each of the six Rh(Co)₂ contributes 1 electron to the framework, 4Co molecules provide 8 electrons.

$$\begin{array}{rcl}
 6 \text{ Rh (Co)}_2 & = & 6 \times 1 = 6 \\
 4 \text{ Co} & = & 4 \times 2 = 8 \\
 \hline
 & & 14 \\
 \hline
 \end{array}$$

We have 14 framework electrons in $2n+2$ formula ($n=6$; $2 \times 6+2=14$). Hence the complex has a close structure. There are two terminal CO groups per 'Rh' and four bridging 'CO' groups. Which span alternate triangular faces [p-(cymene)₃ - R_μ₃S₂]²⁺ has 48e⁻s close structure. This can be reduced to a nido structure (50e⁻s).

Self Check Exercise – 1

1. What are closo, nido and arachno structures? and explain wade's rules with examples.
2. Discuss in detail the different types of clusters.

Self Check Exercise – 2

- 1) Show how wade's rules can be applied to organo metallic clusters. Compare with 18e rule for carbonyls.

2.3 Let us Sum Up

Metal clusters of different types such as tetra nuclear and polynuclear structures are discussed in detail. The application of wade's rules to metal clusters is indicated organo metallic clusters such as $\text{Rh}_6(\text{CO})_6$ and the application of $2n+2$ rule is also discussed.

2.4 Points for Discussion:

1. Metal clusters – types and structures
2. Wade's rules
3. Organo metallic clusters.

2.5 References:

1. Concise Inorganic chemistry – J.D.Lee 5th edition
2. Inorganic chemistry – Huhecy et al Pearson Education – Asia.

UNIT –II
LESSON – 3

BORAZINES – PHOSPHONITRILIC COMPOUNDS

CONTENTS

- 3.0 AIMS AND OBJECTIVES
- 3.1 INTRODUCTION
- 3.2 BORAZINES
 - 3.2.1 SYNTHESIS OF BORAZINES
 - 3.2.2 STRUCTURE AND PROPERTIES OF BORAZINES
- 3.3 PHOSPHONITRILIC COMPOUNDS
 - 3.3.1 SYNTHESIS OF PHOSPHAZENES
 - 3.3.2 STRUCTURAL STUDIES
 - 3.3.3 PHOSPHAZENE POLYMERS
- 3.4 Let us Sum Up
- 3.5 Points for Discussion
- 3.6 References

3.0 AIMS AND OBJECTIVES

In this Lesson the Synthesis of Borazines and the synthesis of phosphazenes are discussed. The structures of borazines and phosphazenes are also discussed.

After going through this lesson you should be able to compare the structure of Borazines and Phosphazenes with benzene and other ring systems.

- Understand the 'd' orbital participation in the phosphazenes structure.
- Develop interest in doing research in the fields of Phosphazenes and their applications.

3.1 INTRODUCTION

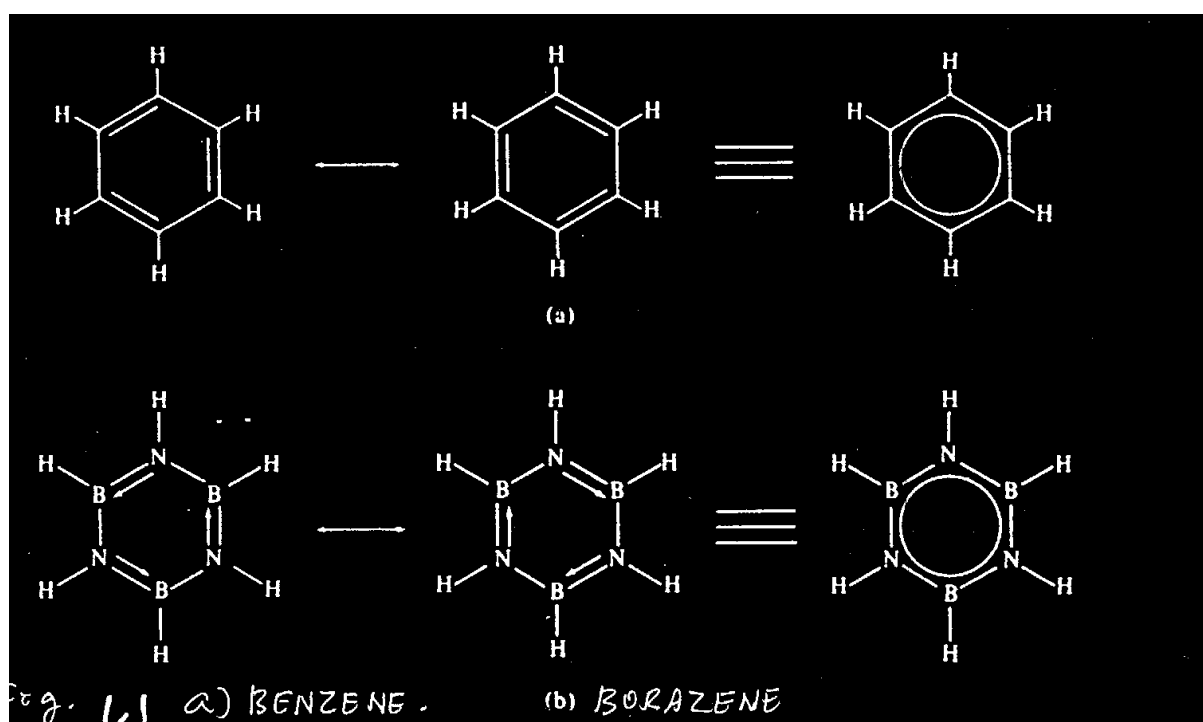
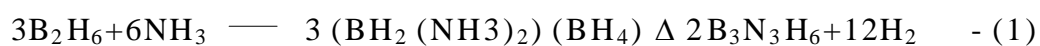
The most important ring system of organic chemistry is the benzene ring, either as a separate entity or in polynuclear hydrocarbons such as

naphthalene, anthracene and phenanthrene. Inorganic chemistry has two analogues of benzene $B_3N_3R_6$ and trimeric cyclophosphazene compounds, $P_3N_3X_6$. Alfred Stock synthesised borazine early in this century. He was the first to study compounds such as boranes, silanes and other similar nonmetal compounds. He perfected vacuum line techniques for the handling of air and moisture sensitive compounds invaluable to the modern inorganic chemist.

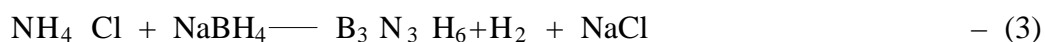
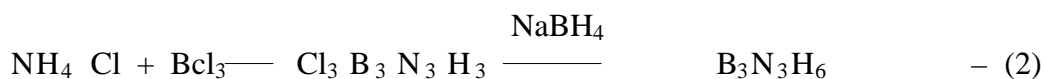
3.2 BORAZINES

3.2.1 SYNTHESIS OF BORAZINES

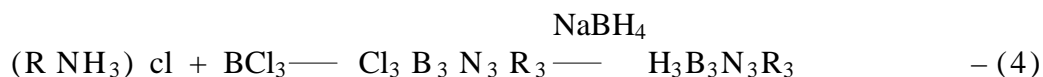
Stock synthesized borazine by heating the adduct of diborane with ammonia.



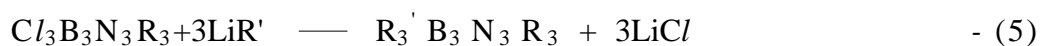
More efficient of syntheses are:



N or B substituted borazines may be made by appropriate substitution on the starting materials prior to the synthesis of the ring



or substitution after the ring has formed



Borazine is isoelectronic with benzene, as B=N is with C=C (Fig 1.1). Physical properties of borazine and benzene are similar. The physical properties of alkyl-substituted derivatives of benzene and borazine are remarkably similar. For example the ratio of the absolute boiling points of the substituted borazines to those of similarly substituted benzene is constant. This similarity led to a labeling of borazine as "Inorganic Benzene". This is a misnomer because the chemical properties of borazine and benzene are different.

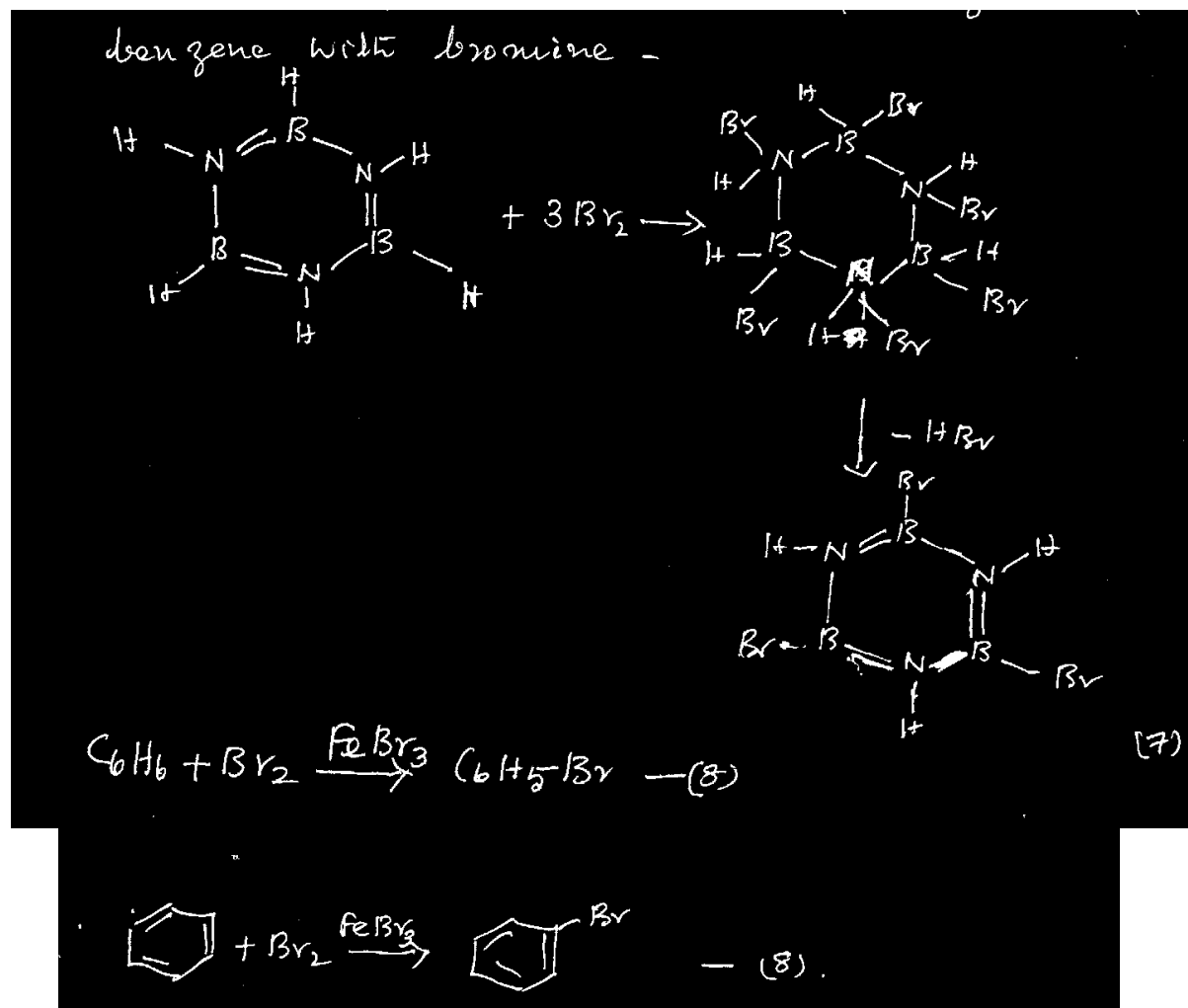
3.2.2 STRUCTURE AND PROPERTIES OF BORAZINE

In both benzene and borazine the Π electrons are delocalized over all of the ring atoms. Because of the electro negativity difference between Boron and Nitrogen, more electron density is located on the nitrogen atoms. Due to this partial localization, the Π bonding is weakened in the ring. Each nitrogen receives more σ -electron density from the neighboring boron than it gives away as a Π -donor.

The net effect is that the charge density on the nitrogen increases. Besides nitrogen retains its basicity and boron its acidity. Borazine is more reactive than benzene and undergoes addition reactions. Benzene does not undergo addition reaction with



One can compare the reactions of borazine and benzene with bromine.



It is of interest to note that borazine resembles benzene in forming arene - metal complexes, thus the hexa methyl borazine complex $B_3N_3(CH_3)_6$ $Cr(CO)_3$ has been reported and closely resembles, $C_6(CH_3)_6$ $Cr(CO)_3$ but is thermally less stable.

The ring metal dissociation energy of the borazine complex is about one half that of the arene complex.

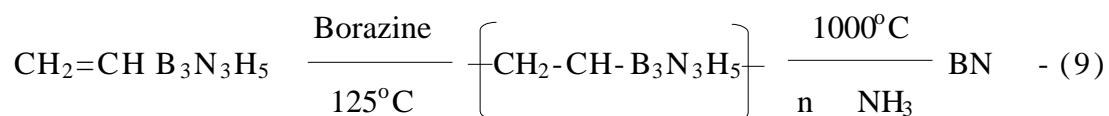
Self Check Exercise – I

Note: Please do not proceed unless you attempt the question, and write your answer in the space below.

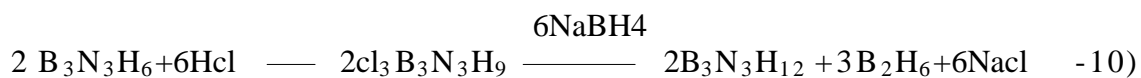
1. How are the following synthesised?

(a) Borazine and benzene (b) Bromo Derivatives of borazine and benzene.

Borazine analogues of naphthalene and related hydrocarbons have been made by pyrolyzing borazine or by passing it through a silent discharge. Related four membered rings $R_2B_2M_2R_2^1$ and $R_4B_4M_4R_4^1$ are also known boron nitride ceramics has been synthesized from borazine derivative $(CH_2=CH)B_3N_3H_5$, which is polymerised and decomposed to give boron nitride



Benzene may be hydrogenated to give cyclohexane. But hydrogenation of borazine results in polymeric materials of indefinite composition. Cycloborazine $B_3N_3H_{12}$ is obtained by the reduction of the chloro derivative.



Boraxine, $H_3B_3O_3$ is isoelectronic with borazine. (Prepared by the explosive oxidation of B_2H_6). Boraxine is planar and has even less Π delocalization than borazine $B_3P_3(Ph)_3$ has also been prepared 'B' and 'P' have similar electro negativities compared to B and N and therefore polarization is less extensive in this compound than borazine and is considerably aromatic.

Self Check Exercise – 2

- a) Compare the properties of borazine and benzene, on the basis of their structures.
- (b) How would $B_3P_3(Ph)_3$ react with Br_2 ?
Please do not proceed till you attempt the above questions. The space below is for your answer.

3.3 PHOSPHO NITRILIC COMPOUNDS**3.3.1 SYNTHESIS OF PHOSPHAZENES**

The Phosphazenes are cyclic or chain compounds that contain alternating phosphorus and nitrogen atoms with two substituents on each phosphorus atom. The three main structural types are cyclic trimer (Fig 1.2), cyclic tetramer (Fig 1.3) and the oligomer or high polymer (Fig 1.4). A few cyclic pentamers and hexamers are also known. The alternating single and double bonds in the figures are written for convenience but should not be taken literally.

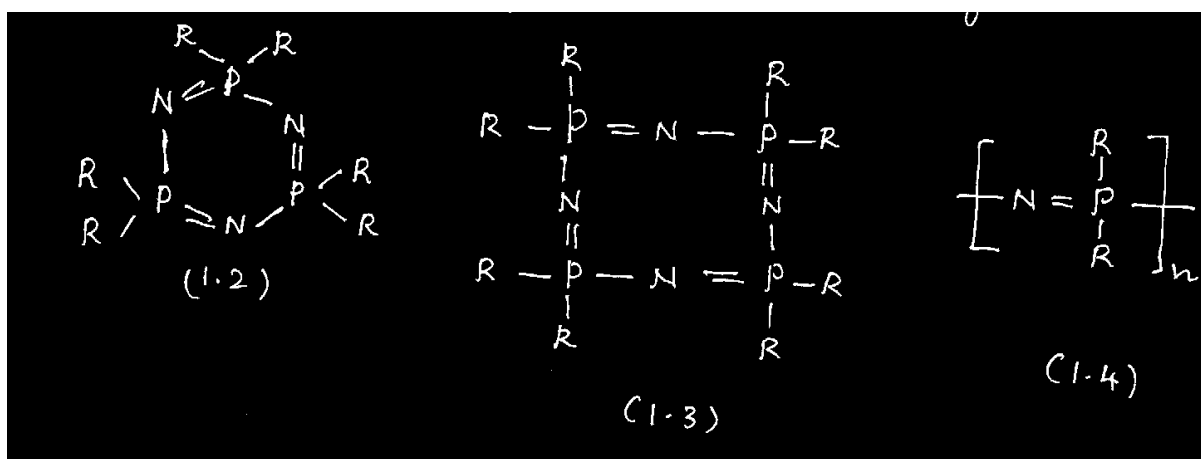
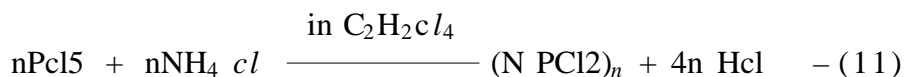


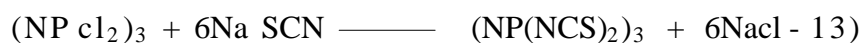
Fig. 1.2, 1.3, 1.4

Hexachlorocyclotriphosphazene ($NPCl_2$)₃, is a key intermediate in the synthesis of many other phosphazenes and is manufactured commercially on either a large or a small scale, it is readily prepared by the reaction

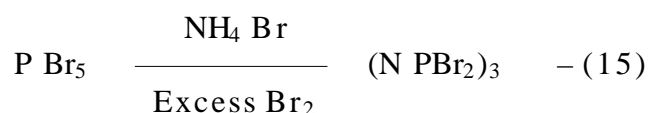


This reaction produces a mixture of $(\text{NPcl}_2)_n$ species with $n = 3,4,5$ and low polymeric linear species. Favorable conditions give 90% yields of the $n=3$ or 4 species, which can be separated easily.

The compound $(\text{NP Cl}_2)_3$ undergoes substitution reactions with groups like, OH, OR, NR_2 , NHR, or R, to give fully or partially substituted derivatives.



The mechanisms of these reactions are not fully understood, but in general they appear to involve SN_2 attack on 'P' by an anion. Bromo compounds may be prepared in the same manner.



The fluoride may be prepared indirectly by fluorination of the chloride.



Self Check Exercise – 3

1. How are different types of phosphazenes synthesised?
2. Why excess bromine is added in reaction (15)

Please do not proceed till you attempt the above questions.

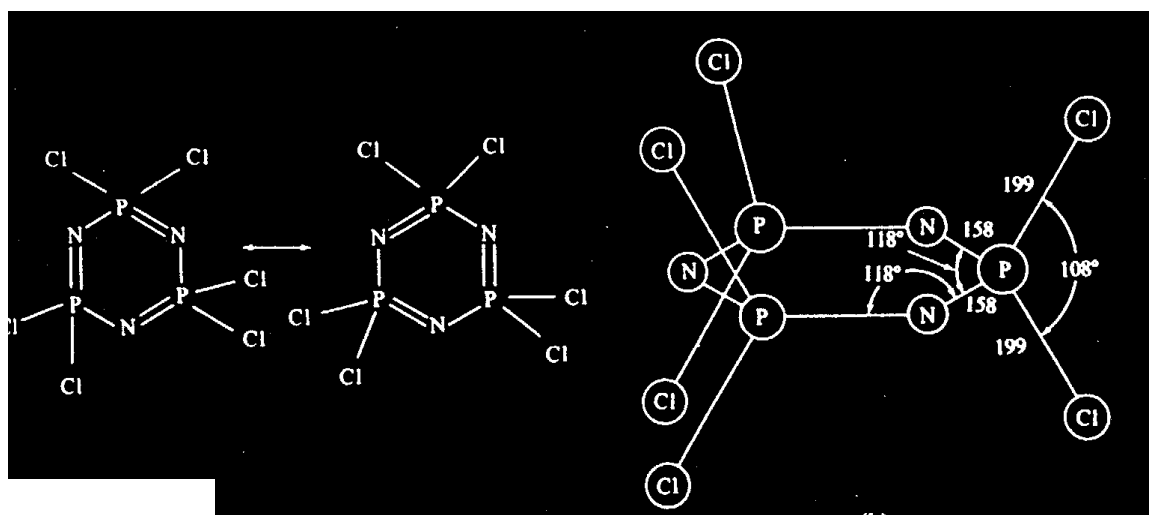


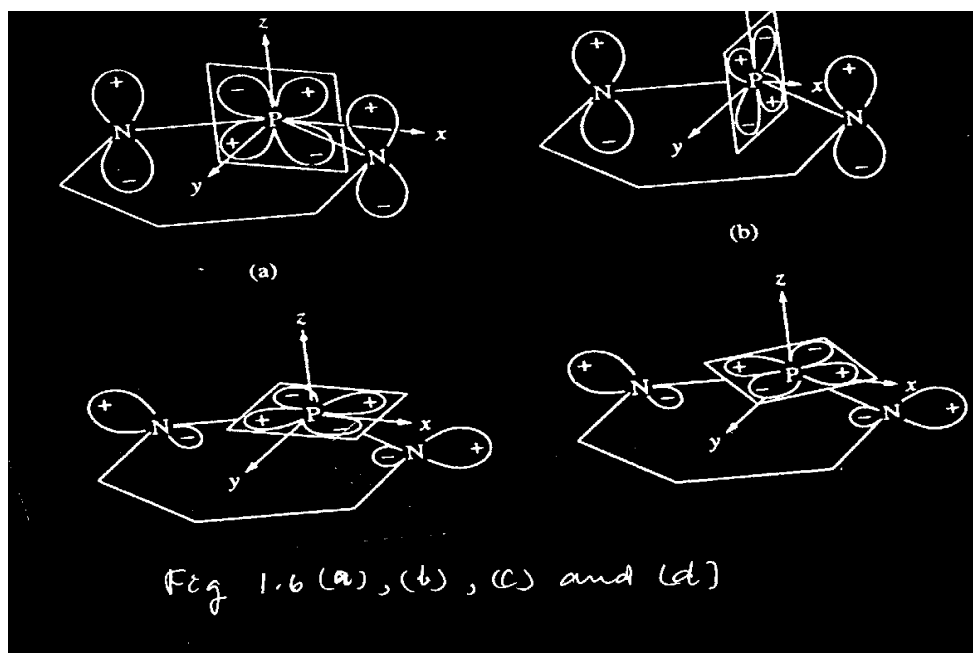
Fig. 1.5 (a) & (b)

3.3.2 STRUCTURE STUDIES

The halide trimers consist of planar six membered rings. The bond angles are consistent with SP^2 hybridization of the nitrogen and approximately SP^3 hybridization of the phosphorous. Two of the SP^2 orbital of nitrogen, containing one electron each, are used for ' σ ' bonding and the third contains a lone pair of electron. This leaves one electron for the unhybridised P_z orbital.

The four SP^3 hybrid orbital (containing four electrons) of phosphorous are used for ' σ ' bonding leaving a fifth electron to occupy a 'd' orbital. Resonance structures can be drawn like benzene ring indicating aromaticity (Fig 1.5a). The Planarity of the ring, the equal P-N bond distances and the shortness of the P-N bonds, and the stability of the compounds suggest delocalisation. All phosphazenes are not planar. This does not make them less stable. Phosphazenes are much more difficult to reduce. Unlike in benzene π -bonding in cyclophosphazenes involves d and p orbitals Craig and Paddock suggested the following model. The dxz orbital of the phosphorous atom overlaps with the p_z orbital of the nitrogen atom adjacent to it (Fig 1.6a). As a result of the 'g' symmetry of the 'd' orbitals an inevitable mismatch in the signs of the wave functions occur on the trimer, resulting in a node which reduces the stability of the dolocalished molecular orbital. The dyz orbital

which is perpendicular to the dxz , can also overlap with the p_x orbital of nitrogen, but in this case no nodal surface results (Fig 1.6b). There may be in-plane π bonding between the sp^2 non bonding orbital of nitrogen and the $dx^2 - y^2$ and for $dx^2 - y^2$ orbital of the phosphorous (fig 1.6c and 1.6d).



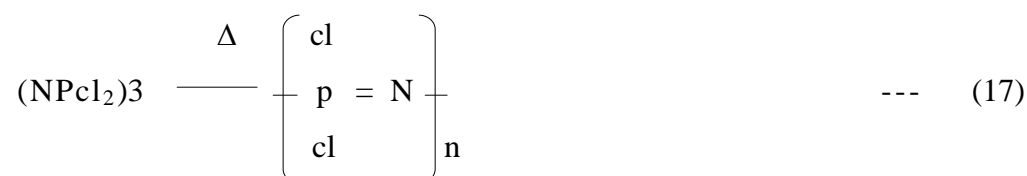
The structure of tetrameric phosphazenes is more flexible than these of the trimers. The structure of $(NPF_2)_4$ is planar, but others are found in a variety of conformations (tub, boat, chair, crown, saddle and structures in between). Inter molecular forces play a major role in these structures. The use of 'd' orbital removes the restrictions of the Huckel rule $(4n+2)$ π electrons for aromaticity. Thus the model due to Craig predicts that the tetramer is stabilized by delocalisation unlike cyclo,octatetraene)

Self Check Exercise 4

- 1.(a) Discuss the structures of phosphazenes on the basis of 'd' orbital participation of the 'P' atom.
- 1.(b) is delocalisation possible in the trimer? Please do not proceed till you attempt the above questions. The space below is for your answers.

3.3.3 PHOSPHAZENE POLYMERS

Phosphazenes can be polymerized. Their polymers have advantages over carbon-based polymers polyolefin's and polyesters. However commercial application is not well developed as silicones $(R_2SiO)_n$. Trimeric-chloro phosphazenes can be polymerized thermally.



If this is done carefully, extensive cross linking does not take place and the polymer ($n=15,000$) remains stable in organic solvents, similarly:



can be obtained. By varying the nature of the side chain 'R' various elastomers, Plastics, films and fibres have been obtained. They are flexible at low temperatures and water and fire resistant. Some R groups like $R=CH_2CF_3$ in OR group in the above reactions are water repellent and do not interact with living and promise to be useful in fabrications of artificial blood vessels and prosthetic devices.

Self Check exercise -5

1. How are phosphazene polymers obtained? Indicate their uses.

Space for answers

3.4 Let us Sum Up

- (i) The synthesis of borazine is indicated.
- (ii) The planarity of benzene is compared with that of borazine.
- (iii) The synthesis of phosphazenes and their structures are discussed.
- (iv) The importance of $d\pi - p\pi$ bonding in phosphazenes is discussed.
- (v) polymeric phosphazenes and their uses are also indicated.

3.5 Points for discussion.

- I (i) In the case of borazines compare its synthesis with benzene (ii) Planarity of benzene ring to the compared with that of borazine (iii) Compare the properties especially using electronegativities of B and N.
- II (i) In the case of Phosphazenes, the 'd' orbital participation of 'P' atom in forming dII-PII bonding decides its aromaticity (ii) The synthesis of polymeric phosphozenes and their uses to be discussed.

3.6 References

1. Advanced Inorganic Chemistry, A comprehensive Text-F, Albert Cotton and G.Wilkinsonwiley Eastern Limited– New Delhi-3rd Edition1972.
2. Inoragnic Chemistry – 4th Ed James E, Huheey, Ellen. A. Keiter Richard L. Keiter – pearson Education Asia 4th Ed, Reprint, 2002.

LESSON – 4**SULPHUR – NITROGEN RING COMPOUNDS****CONTENTS**

- 4.0 Aims and objectives
- 4.1 Introduction
- 4.2 Sulphur – Nitrogen Compounds
 - 4.2.1 Synthesis of S-N Compounds
 - 4.2.2 Structural studies
 - 4.2.3 One – Dimensional conductors

4.0 AIMS AND OBJECTIVES

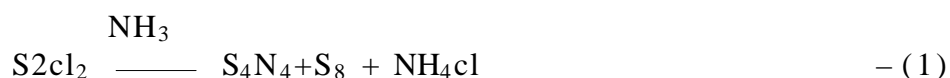
In this lesson the synthesis, of sulphur-nitrogen compounds and the Syntheses of some derivatives of sulphur- nitrogen compounds are discussed. After studying this lesson you would be able to understand the bonding in S-N Compounds. Learn the application of S_4N_4 in forming $(SN)_x$ which behaves like a super conductor.

4.1 INTRODUCTION

Compounds which contain sulphur-nitrogen rings were known in the last century, but many new ones have been prepared in the last decade. It is currently an area of considerable interest.

4.2 SULPHUR NITROGEN COMPOUNDS**4.2.1 Synthesis of S_4N_4 :**

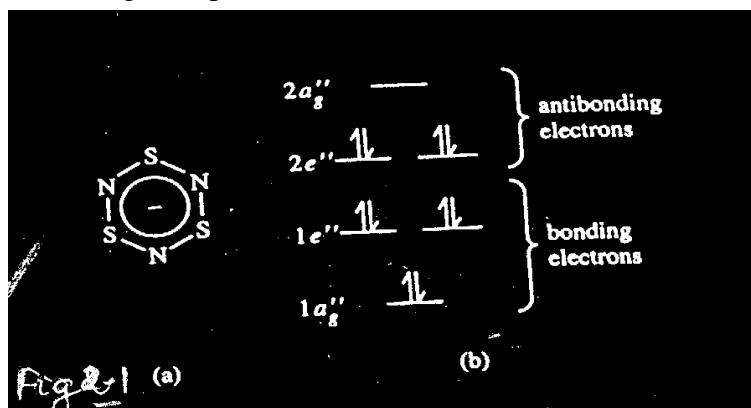
The ammonolysis of S_2Cl_2 , either in solution or in an inert solvent or heated over solid ammonium chloride yields tetra-sulphur, tetra-nitride.



The product is a bright orange solid insoluble in water but soluble in some organic solvents. The crystals are reasonable stable to attack by air,

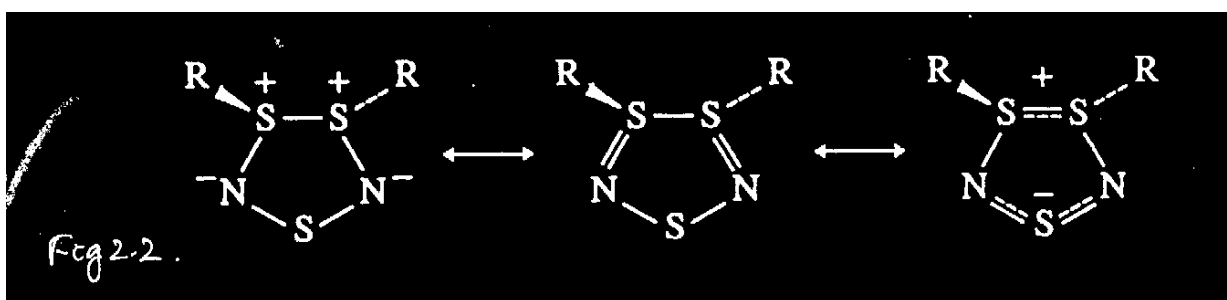
they are explosively sensitive to shock or friction. Reduction of S_4N_4 with metallic potassium or sodium oxide gives S_3N_3 (Fig 2.1a).

Reduction of S_4N_4 with Sn (II) chloride produces tetrasulphur tetraimide isoelectronic with S_8 . When S_4N_4 is heated under pressure in a solution of CS_2 , containing sulphur S_4N_2 is formed.



4.2.2 STRUCTURAL STUDIES OF S-N COMPOUNDS

It is impossible to write a simple Lewis structure for S_4N_4 . A cage structure for S_4N_4 has been suggested. This structure contains two pairs of non-bonding sulphur atoms at a distance of about only 258pm, considerably shorter than the sum of the vanderwall's radii (360pm). All of the S-N bond distances within the ring are approximately equal (162pm) and has 12 π electrons and this indicates considerable delocalisation. The molecule S_4N_2 has half-chair conformation. The molecule $S_3N^{-}_3$ has a planar six membered ring. It has 10 π electrons instead of six (Fig 2.1b). Still the Huckel rule is obeyed ($4n+2$) rule and the system is expected to be aromatic. Four of the π electrons occupy antibonding orbitals.



and this weakens the S-N bond.

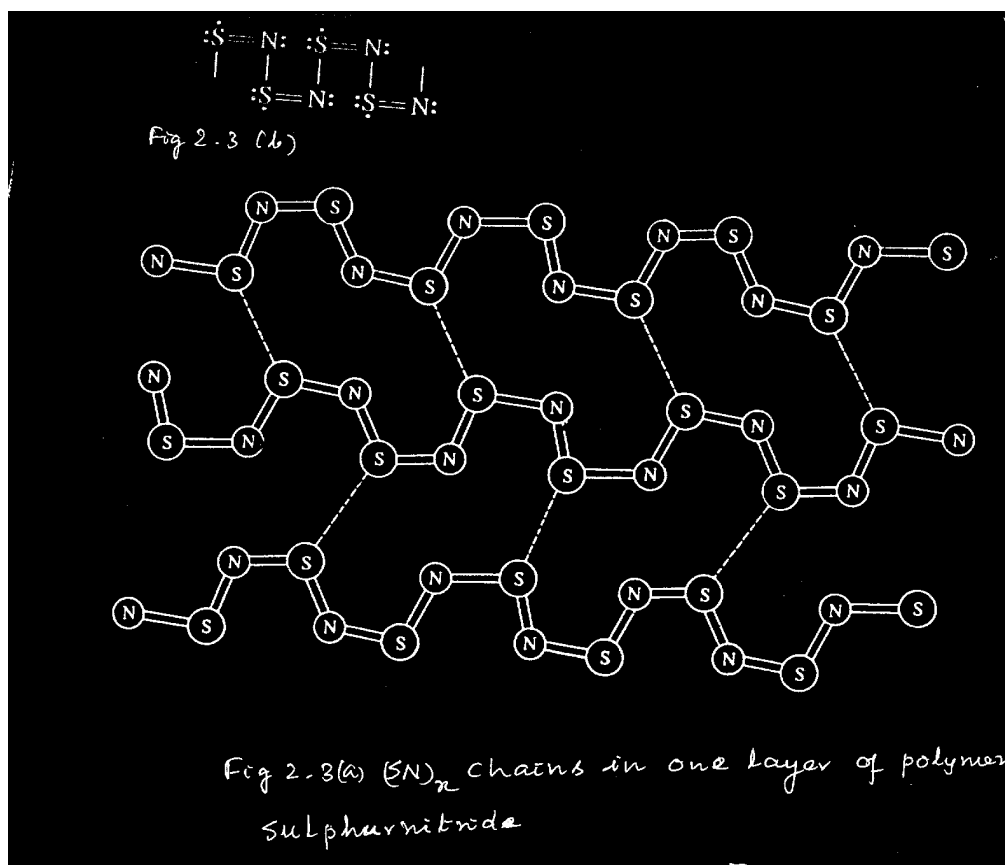
Sulphur – nitrogen compounds have often unpredictable structures, for example the compound $Ph-SN=S=NSPh$ is considered to have resonance structures (Fig 2.2). This is based on the fact that the separation between end sulphur atoms is only 329pm (compared to vanderwal's sum of 360pm).

4.2.3 ONE DIMENSIONAL CONDUCTOR

Polymeric sulphur nitride (also called polythiazyl), $(SN)_x$ has some physical properties of a metal. It is prepared from S_4N_4 .

$$\text{S}_4\text{N}_4 \xrightarrow{\text{Ag}} \text{S}_2\text{N}_2 \longrightarrow (\text{SN})_x$$
 The S_4N_4 is pumped in a vacuum line over silver wool at 220°C , where it polymerize slowly to a lustrous golden material. It has a conductivity near that of mercury at room temperature and it becomes a super conductor at low temperatures below (0.26K). X-rays studies indicate that the SN chains have the structure shown in Fig (2.3a). This chain can be generated from adjacent square planar S_2N_2 molecules. The S-N bonds in this starting material have a bond length of 165.4pm, intermediate between single (174pm) and double (154 pm) SN bonds.

For the $(\text{SN})_x$ chain many resonance structures can be drawn. The single structure (Fig 2.3 b) has single bond double bond resonance system, with nine electrons on each sulphur atom. Every S-N unit has thus one antibonding Π^* electron. The half filled over lapping Π^* orbitals will combine to form a half-filled conduction band in much the same way as half-filled 2s orbitals on a mole of Lithium atoms, form a conduction band. This conduction band lies only along the direction of the $(\text{SN})_x$ fibres, the polymer is thus a one dimensional conductor.



Self Check Exercise – 1

1. Give the synthesis of S_4N_4 and $S_3N_3^-$.
2. All of the S-N bond distances within the ring are equal and what does it indicate?
3. How does $(SN)_x$ behave like a one dimensional conductor?

Model answer for Self – Check exercise – 1

1. S_4N_4 is obtained from S_2Cl_2 by ammonolysis.
2. S-N bond distances (162pm) are equal and it has 12- Π electrons, obeys Huckel rule-aromatic.
3. Π^* half-filled orbitals overlap forming conduction band in one dimension.

4.3 Let Us Sum Up

The synthesis of S_4N_4 is discussed. The molecule S_3N_3 has a planar structure and obeys Huckels rules. $(SN)_x$ behaves like a one dimensional conductor the conduction is explained.

4.4 Points for Discussion:

- (i) The molecule $S_3N_3^-$ has a planar six membered ring structure and has 10 Π electrons. The system obeys Huckel's rule.
- (ii) The over lapping of Π^* orbital (half-filled) in $(SN)_x$ leads to one dimensional conduction.

4.5 References

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LESSON – 5

CONTENTS

- 5.0 AIMS AND OBJECTIVES
- 5.1 INTRODUCTION
- 5.2 METALLIC STATE
 - 5.2.1 FREE ELECTRON THEORY
 - 5.2.2 BAND THEORY
- 5.3 LET US SUM UP
- 5.4 POINTS FOR DISCUSSION
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5.0 AIMS AND OBJECTIVES

In this lesson the conductivity of metals can be understood on the basis of free electron theory and band theory.

The behaviour of semi conductors is discussed on the basis of band theory.

After going through this lesson you would be able to

- Understand the electrical properties of metals.
- The electrical conductivity of semiconductors can be understood.

5.1 INTRODUCTION

Metals have the following characteristics properties (1) high reflectivity (2) high electrical conductance, decreasing with increasing temperature (3) high thermal conductance (4) Mechanical properties such as strength and ductility. An explanation for these properties, and for their variations from one metal to the other, must be derived from the structural and electronic nature of metal. The electrical conductivities of semiconductors can be understood on the basis of band theories.

5.2.1 FREE ELECTRON THEORY

At the beginning of the twentieth century, a bold guess was made by Drude regarding the electronic structures of metals. The resulting free electron theory was made by Lorentz a few years later and is known as Drude-Lorentz theory of metals. The basic assumption of this theory is that a metal crystal consists of positive metal ions whose valence electrons are free to move between the ions as if they constituted an electron gas. The crystal is then pictured to be held together by electrostatic forces of attraction between the positively charged ions and the negatively charged electron gas. It is further assumed that the electrons are free to move throughout the entire crystal subject only to the laws of classical mechanics. The mutual repulsion between negative electrons is ignored in this theory and the potential field due to the positive ions is assumed to be completely uniform. Thus the electrons can move from place to place in the crystal without change in their energy. The electrons collide occasionally with the atoms and have velocities determined at constant temperature according to the Maxwell-Boltzmann distribution laws. This model of a metal is highly successful in explaining many properties of metals. For example if an external electric field is applied to metal, the negatively charged electrons are accelerated towards the positive pole of the field. The resulting current is limited by electron atom collisions and is proportional to the applied voltage gradient according to Ohm's law. The opaqueness of metals for all wavelengths of light is explained by the ability of a free electron to oscillate in the electromagnetic field of the incident light beam regardless of its frequency. Similarly a free electron once excited to a higher energy by the absorption of energy, can return to its former energy by reemitting light of the same frequency in all directions.

Because only light rays directed towards the surface can get out of the crystal, this interaction appears as a reflection of the incident light and accounts for the so called metallic luster.

Success of the Free Electron Theory

1. It is used to verify Ohm's law.

2. It is used to explain the electrical and thermal conductivities of metals.
3. It is used to explain the optical properties of metals.

Breakdown of classical theory

1. From the classical free electron theory the value of specific heat of metal is given by $4.5 \times R$, where R is the gas constant. But experimental value is nearly equal to $3R$. According to classical free electron theory, the value of electronic specific heat is equal to $\frac{3}{2}R$. But actually it is $0.01R$ only.
2. We cannot explain the electrical conductivity of semi conductors or insulators using this model.
3. Ferromagnetism cannot be explained by this theory.
4. The photo electric effect, compton effect and the black body radiation cannot be explained by the classical free electron theory.

Self-Check Exercise – 1

1. As the temperature increases the electrical resistance of a metal increases – explain.
2. Indicate the failures of the classical free electron theory.

Please do not proceed until you attempt the above questions. The space below for your answer.

Special features of quantum free electron theory.

1. Quantum concepts are followed. That is, the distribution of electrons in a solid is determined by Femi-Dirac distribution.
2. The wave nature of electrons is taken into account.

3. The physical properties of solids depend on the number of free electrons available at the fermi energy level. Thus the fermi level electrons play an important role in determining the various properties of a solid.
4. The correct values of electrical conductivity, thermal conductivity, specific heat, optical absorption, ferromagnetic susceptibility are determined by quantum free electron theory of solids.
5. Quantum free electron theory is not only applicable for metals (conductors) but also for semiconductors and insulators.
6. Thus the correct pictures of atoms and molecules and their electron distributions and bonds are identified only from the quantum free electron theory of solids.

Electron in a Metal

Consider problem for a three dimensional metal in which the electrons move in all directions so that three quantum numbers n_x, n_y , and n_z are needed, corresponding to the resolution of the motion into components along three perpendicular axes x, y , and z . For simplicity we will take the potential energy of the electron to be zero inside the metal and infinite outside. So that the problem is just an extension of the one dimensional problem. Therefore with a cubically shaped block of metal of sides 'a' the permitted energy levels can be written as

$$E_n = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad \dots (A)$$

where n_x, n_y , and n_z can each take any number from the set 1,2,3,... etc., irrespective of what numbers the others take.

Similarly the wave function

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{a^3}} \sin \left[\frac{n_x \pi x}{a} \right] \sin \left[\frac{n_y \pi y}{a} \right] \sin \left[\frac{n_z \pi z}{a} \right] \dots (B)$$

The three quantum numbers n_x , n_y and n_z are required to specify completely each stationary state. It should be noted that the energy E depends only on the sum of the squares of n_x , n_y and n_z .

Consequently there will be in general several different wave functions having the same energy. For example the three independent stationary states having quantum numbers

(2,1,1), (1,2,1) and (1,1,2) for n_x , n_y and n_z have the same energy $6h^2/8ma^2$ such states and energy levels are said to be degenerate and the corresponding wave functions are Ψ_{211} , Ψ_{121} , Ψ_{112} .

On the other hand if there is only one wave function corresponding to a certain energy, the state and the energy level are said to be non-degenerate. For example,

The ground state with quantum numbers (1,1,1) has the energy $3h^2/8ma^2$ and no other state has this energy.

The degeneracy breaks down on applying a magnetic field or electric field to the system.

Electron Energies in metals and fermi energy

The expression for the energy values given in equation (A) corresponds to the permissible energy values that the valence electrons in a metal may have, but it is essential to know what energies the electrons actually possess. For a piece of metal of macroscopic dimensions, say a centimeter cube, the

energy of the ground state ($n_x = n_y = n_z = 1$) is of the order of 10^{-15} eV and hence may be taken to be zero for all practical purposes.

Also the maximum spacing between consecutive energy levels is less than 10^{-6} eV. So the distribution of energy levels may be regarded as a continuum.

If a plot is made for a large range of energy values such that the individual E_n values are so close together that they can be shown as a continuum and the number of states per interval of energy, $N(E)$ increases parabolically with increasing E as shown in figure (3.1(a)).

The dashed line shows the nature of the change in electron energies that occurs on heating to room temperature.

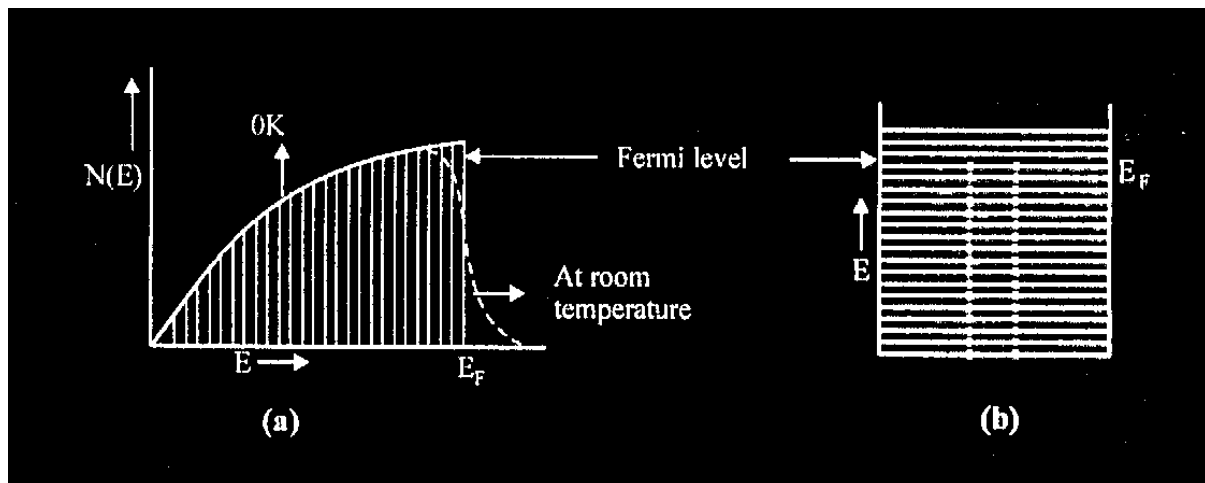


Fig 5.1

Figure 5.1 (a) The distribution of energy states as a function of energy E
 (b) Filling of energy levels by electrons at 0 K

(a). Fermi energy

The valence electrons tend to occupy the lowest available energy states. However because of the mutual interactions among all the electrons

that form the electron gas, it is necessary to consider that all the electrons are in a single system and that the Pauli Exclusion Principle applies.

According to Pauli exclusion Principle only two electrons can occupy a given state specified by the three quantum numbers (n_x , n_y and n_z), one with spin up and other with spin down (i.e., with opposite spins).

As a result of this principle, at 0 K the electrons fill all the states upto a certain maximum energy level, E_{\max} called the fermi level or fermi energy 'E'. All quantum states in the energy levels above E_F are empty (figure 3.1(b)). Thus the fermi level is a boundary line which separates all the filled states and empty states at 0 K in a metal.

Thus in a metal the energy of the highest filled state at 0 K is called the fermi energy 'E_F' or fermi level. The magnitude of E_F depends on how many free electrons there are. At 0 K all states upto E_F are full and states above E_F are empty.

5.2.2 Band or Zone theory of Solids

Energy bands in solids (quantitative treatment)

In an isolated atom, the electrons are tightly bound and have discrete sharp energy levels. When two identical atoms are brought together the energy levels of each atom which are initially the same are split into two, one higher and one lower than the corresponding levels of the separated atoms.

The splitting only becomes appreciable when the wave functions of the electrons on different atoms begin to overlap considerably; at a given distance it is therefore greatest for the outermost electrons and least for the inner electrons.

If more atoms are brought together more levels are formed and for a solid of 'N' atoms, each of the energy level of an atom splits into N levels of

energy. The levels are close together that they form an almost continuous band.

The width of this band depends on the degree of overlap of electrons on adjacent atoms and is again largest for the outermost atomic electrons. The bands appear only when the distance between two atoms is very small. That is the bands are formed in solid only.

For example, when the distance between two sodium atoms is about 5\AA the splitting of energy levels is maximum and bands appear. But when the distance between sodium atoms is about 20\AA the splitting of energy levels is minimum and there is no band formation and hence there is no solid formation.

The electrons can take only the energy values which are in the band.

The gap between two allowed band is called forbidden energy gap (or) band gap since the electron cannot take the values of energy which are in the forbidden energy gap. Normally we are interested in the valence (outermost energy) band, formed by valence electrons since these are responsible for electrical, thermal and optical properties of solids. Above the valence band there is conduction band which has no electrons at 0 K.

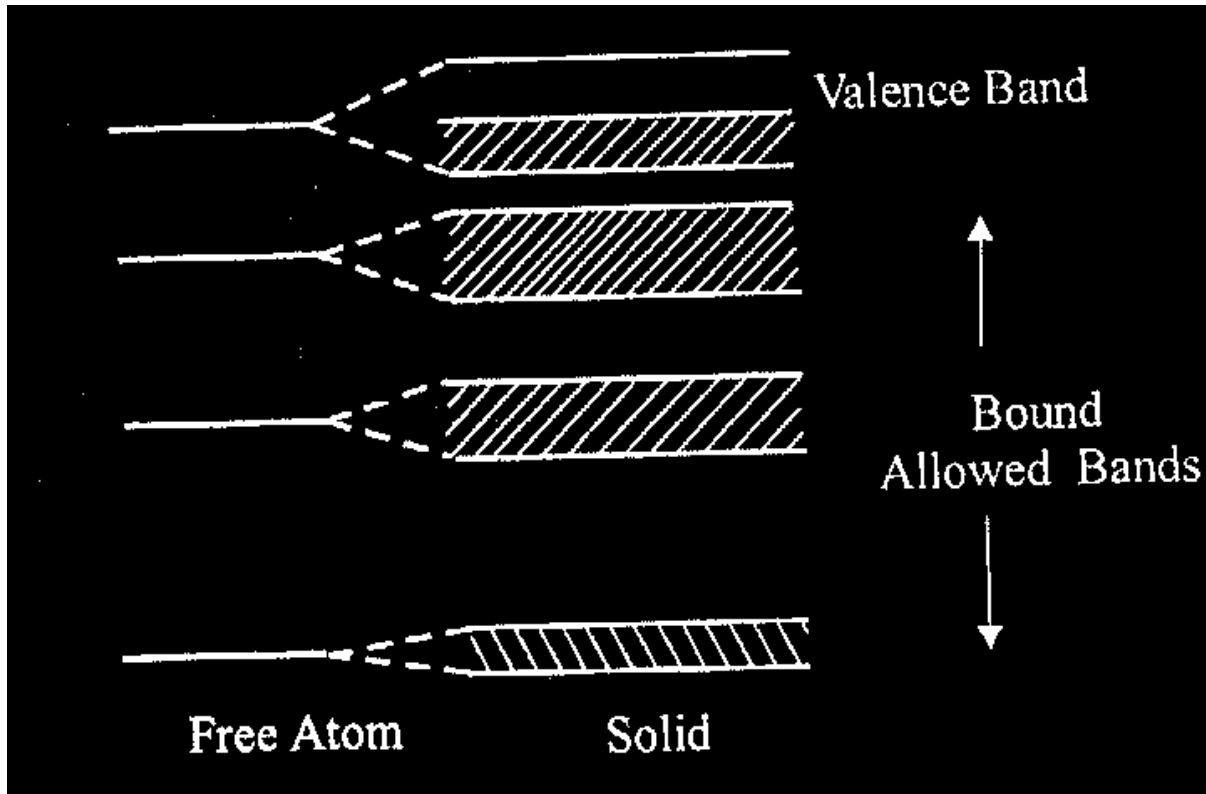


Fig. 5.2

Figure 5.2. Energy levels of an isolated atom and the energy bands in the solid.

Figure 3.2 shows the energy levels of an isolated atom and solid which is the collection of N atoms. We can see that the allowed bands and the energy gap between the allowed bands. Thus the bands are formed in solids only and are due to overlapping of wave functions of different states and the consequent energy level splitting.

Distinguish between conductors, semiconductors and insulators on the basis of band theory of solids.

In a solid the outermost allowed band formed by valence electrons is called the valence band and is fully or partially filled. Since the valence

electrons are alone determining the properties of the material, the remaining lower allowed bands consisting of bound electrons are not considered.

The band that is above the valence band and empty at 0K is called the conduction band and is partially filled by free electrons which are generally unbound valence electrons generated by thermal excitation or electric field.

The band gap or forbidden gap is the energy interval between the maximum energy of the valence band and the minimum energy of the conduction band. In conductors, there is no meaning for band gap. But in insulators and semiconductors, the value of band gap plays an important role in determining the carrier concentration or electrical conductivity of different materials.

Solids can be classified on the basis of their band structure as conductors, semiconductors and insulators.

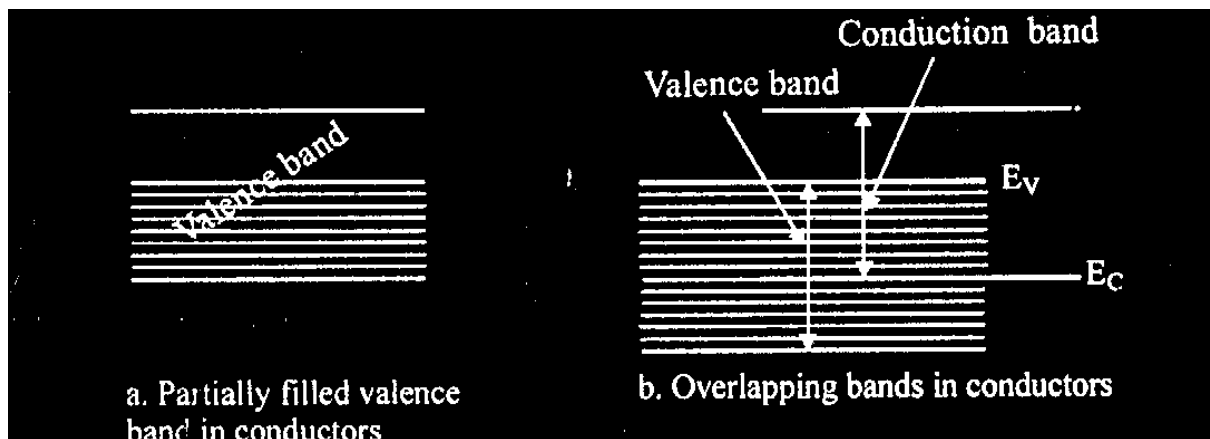


Fig. 5.3 Schematic band structure of conductors

Conductors are those solids which have vacant electron energy states immediately above the highest filled level of the valence band. This can happen in two ways. In the first case, the valence band is only partially filled as in figure 5.3 (a). The electrons here can respond to an externally applied field by acquiring extra velocity and moving into higher energy states. In the

second case, a full valence band overlaps the conduction band as shown in figure 3.3(b) so that the forbidden gap is zero. Monovalent metals such as the alkali metals have one electron per atom in the outer most shell and the outer most energy bands are half filled in these metals. Divalent metals such as magnesium have overlapping conduction and valence bands. Therefore they can also conduct even if the valence band is full. The band structure of trivalent metals such as Aluminium is similar to that of monovalent metals. Thus there is no meaning for band gap in conductors.

Semiconductors are those materials which have an energy gap of about 2 to 3 eV or less. When the energy gap is 2eV or less an appreciable number of electrons can be excited across the gap at room temperature. So semiconductors conduct much better than insulators at room temperatures but still orders of magnitude poorer than metals which have no forbidden gap. By adding impurities or by thermal excitation we can increase the electrical conductivity in semiconductors. Figure 5.4 (a) shows the band structure of silicon.

Insulators are those materials which have an energy gap more than 3eV. It has been estimated that millions of volt/m of electrical potential would be necessary to accelerate an electrons sufficiently to jump the forbidden gap. The other possibility for a transition is that electrons cross the gap by thermal excitation. At room temperature the number of electrons that can be thermally excited across the gap in insulators such as Diamond turns out to be extremely small. Figure 3.4 (b) shows the band structure of diamond.

So the conductors are the materials having enormous electrical conduction; the insulators are the materials in which practically there is no electrical conduction and the semiconductors are the materials in which the electrical conduction is in between the electrical conduction of conductor and insulator.

Electron in a periodic potential (Origin of band gap and effective mass of electrons)

While the Sommerfeld theory discussed earlier accounts satisfactorily for electrical conductivity in most metals, it failed to explain why other substances that also contain free electrons have virtually no conductivity and are considered to be excellent insulators. A solution to this problem is given by the Zone theory or Band theory of solids. The effect of the periodic lattice field on the motion of the electrons leads to the zone or band theory of solids, which is of the greatest importance for understanding the structures and properties of metals, alloys and non-metallic solids.

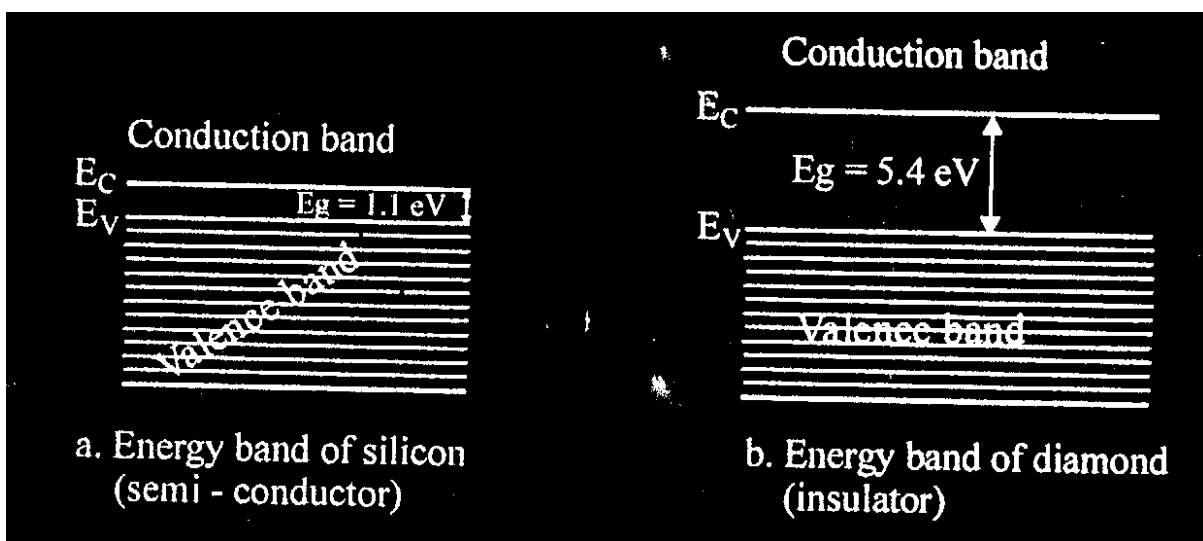


Figure 5.4 band structures of semiconductor and insulator

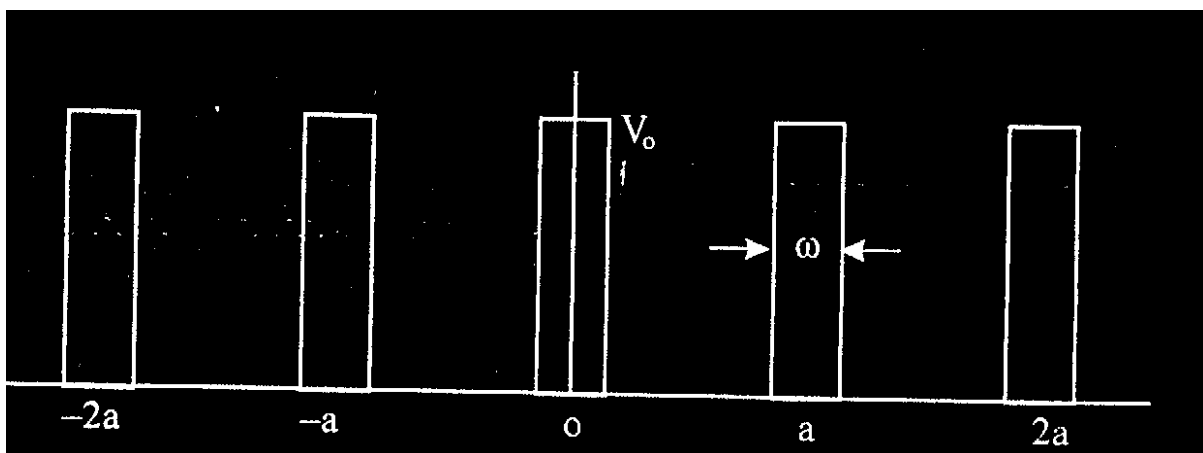


Fig.5.5 One dimensional periodic potential

According to zone theory, the electrons move in a periodic field provided by the lattice. The potential of the solid varies periodically with the periodicity of space lattice and the potential energy of the electron is zero near the nucleus of the +ve ion in the lattice and maximum when it is half way between the adjacent nuclei which are separated by the interatomic spacing distance 'a' (Figure.3.5). This model was first postulated by Kronig and Penny. So taking this model and solving the Schrodinger equation for this case, we can find the existence of energy gap between the allowed values of energy of electron.

So if we use classical theory, we can get a parabola when we plot the curve between the electron's energy and its momentum. In the figure.3.6 (a) instead of momentum 'P'

the wave vector k is used since $P = \hbar k = \frac{\hbar}{2\pi} \frac{2\pi}{\lambda} = \frac{\hbar}{\lambda}$. Thus the 'k'

is directly proportional to momentum 'P'. Since the curve is a parabola, we can infer that the energy varies continuously.

But by Kronig-Penny model, we can get a parabola with some discontinuities in it as shown in figure.3.6(b). Thus we have allowed bands and forbidden energy gap between the allowed bands.

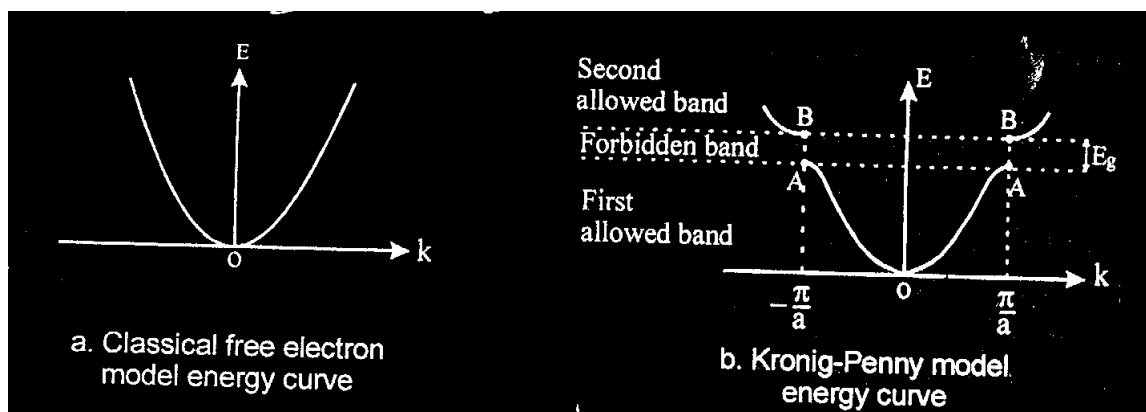


Figure 5.6 Energy Vs momentum curve

Self check exercise –2

1. How does the band theory explain the conductivity of semi conductors?
What are intrinsic semi conductors?

Self check exercise - 2

Model Answer:

(i) Ge and SI are intrinsic semi conductors. Their band gaps are low and hence even at ordinary temperatures free electrons are present in the conduction band and has appreciable conductivity compared to insulators.

5.3 Let us Sum Up

(i) The free electron theory and band theory of metals and their applications are discussed. (ii) Quantum free electron theory is discussed. (iii) Fermi energy is explained (iv) The conductors, semiconductors and insulators are compared using band theory (v) Kroning-Penny model is indicated.

5.4 Points for discussion:

1. The free electron theory of metals as suggested by Drude and Lorentz successfully explained properties of metals such as electrical conductivity, increase of electrical resistance with temperature and metallic luster.
2. It failed to explain the values of specific heats of solids
3. The modified quantum free electron theory gives the correct values of electrical conductivity, thermal conductivity, specific heats of metals.
4. The quantum free electron theory can be applied to metals as well as semiconductors and insulators.

5.5 References

1. Advanced Inorganic Chemistry – A comprehensive Text (3rd Ed).
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LESSON - 6

CONTENTS

- 6.0 Aims and Objectives
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6.0 AIMS AND OBJECTIVES

The study of imperfections has a two fold purpose, namely

- (i) A better understanding of them and how they affect material properties
- (ii) Exploration of possibilities of minimizing or eliminating these defects.

The term imperfection or defect is generally used to describe any deviation from the perfect periodic array of atoms in the crystal.

6.1 INTRODUCTION

In an ideal crystal, the atomic arrangement is perfectly regular and continuous throughout. But real crystals are never perfect; lattice distortion and various imperfections, irregularities or defects are generally present in them. The mechanical, electrical and magnetic properties of crystalline solids, particularly metals and alloys are profoundly affected by the imperfections in the crystals.

6.2.1 Point Defects

1. Point imperfections are also called zero dimensional imperfections. One or two atomic diameters is the typical size of a point imperfection.
2. In a crystal lattice, point defect is one which is completely local in its effect, e.g., a vacant lattice site.
3. The introduction of point defect into a crystal increases its internal energy as compared to that of the perfect crystal. Further they produce distortions inside the crystal structure.
4. They change the electrical resistance of a crystal.
5. If a point defect is a vacancy, then there is no bonding. Hence the value of the mechanical strength at that point is reduced.
6. Similarly if an impurity atom is present instead of the original atom, in the lattice, there must be some strain due to the different size of the impurity atom.
7. Point defects are created during crystal growth and application of thermal energy, mechanical stress or electric field. Further they are created by irradiating the crystal by x rays, microwaves and light.

Different types of point imperfection are described below:

a. Vacancies

A vacancy or vacant site implies an unoccupied atom position within the crystal lattice. In other words, vacancies are simply empty atom sites. Vacancies may be single, two or more of them may condense into a divacancy or tri-vacancy.

It may be shown by thermodynamic reasoning that lattice vacancies are a stable feature of metals at all temperatures above absolute zero. Vacancies exist in a certain proportion in a crystal in thermal equilibrium leading to an increase in the randomness of the structure.

The every day industrial processes of annealing, homogenization, precipitation, sintering, surface hardening, oxidation and creep, all involve to varying degrees, the transport of atoms through the lattice with the help of vacancies.

Vacancies may occur as a result of imperfect packing during the original crystallization or they may arise from thermal vibrations of atoms at elevated temperatures, because as thermal energy is increased there is a higher probability that individual atoms will jump out of their position of lowest energy.

The atoms surrounding a vacancy tend to be closer together, thereby distorting the lattice planes.

Schottky defect

1. Ion vacancies are called Schottky defects.
2. A pair of one cation and one anion can be missing from an ionic crystal. The valency of the missing pair of ions should be equal to maintain the electrical neutrality. So these are normally generated in equal numbers of anion and cation vacancies in a crystal.
3. When vacancies are created by movements of an anion and one cation from positions inside the crystal to positions on the surface of the crystal, a Schottky defect is said to have been formed.
4. This type of point defect is dominant in alkali halides.

b. Interstitial Defect

1. An interstitial defect arises when an atom occupies a definite position in the lattice that is not normally occupied in the perfect crystal.
2. In interstitialcies, atoms occupy vacant positions between the atoms of the ideal crystal. The interstitial atom may be lodged within the crystal structure, particularly if the density of packing (or) packing fraction is low.
3. Interstitialcy produces atomic distortion or strain because interstitial atom tends to push the surrounding atoms further apart, unless the interstitial atom is smaller than the rest of the atoms in the crystal.
4. By giving enormous stress (or) compressive force to a crystal, some of the parent atoms dislodge from their lattice sites and occupy the voids or interstitials present in the lattice. These type of imperfections are called self interstitial imperfections.

Frenkel defect

1. In the case of ionic crystals, an ion displaced from the lattice into an interstitial site is called a Frenkel defect.
2. As cations are generally the smaller ions, it is possible for them to get displaced into the void space present in the lattice. Anions do not get displaced like this, as the void space is just too small for their size.
3. A Frenkel imperfection does not change the overall electrical neutrality of the crystal. The point imperfections in silver halides and calcium fluoride are of the Frenkel type.
4. Frenkel and Schottky defects together are called 'Intrinsic defects'.

c. Impurities

1. Impurities give rise to compositional defects.
2. A controlled addition of impurity to a very pure semiconductor crystal is the basis of producing many electronic devices like diodes and transistors. Addition of pentavalent and tetravalent impurity atoms in silicon or germanium crystal increases its electrical conductivity.
3. Foreign atoms generally have atomic radii and electronic structures differing from those of the host atoms and therefore act as centers of distortion.
4. Basically there are two types of impurity defects.
A substitutional impurity refers to a foreign atom that substitutes for or replaces a parent atom in the lattice as shown in fig. 4.1(a).
5. In the case of semiconductor technology aluminium and phosphorous doped in silicon are substitutional impurities in the crystal. Further during the production of Brass alloy, the zinc atoms are doped in copper lattice. Here the zinc atoms are called substitutional impurities. In ionic solids, for example in sodium chloride, the substitution of Na^+ by Li^+ produces a substitutional impurity.

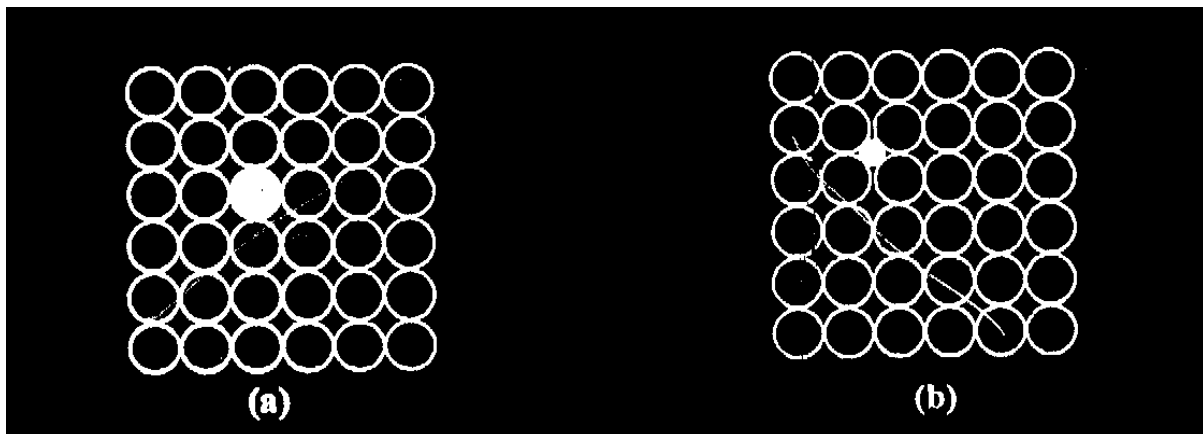


Fig. 6.1 (a) Substitutional Impurity (b) Interstitial Impurity

An interstitial impurity is a small sized atom occupying the void space in the parent crystal, without dislodging any of the parent atoms from their sites as shown in figure 4.1 (b). An atom can enter the interstitial or void space only when it is substantially smaller than the parent atom. For example in FCC iron, the atomic radius of iron atom is equal to 2.25\AA . The carbon atoms with atomic radius equal to 0.777\AA can occupy the octahedral void spaces in FCC lattice as interstitial impurities, But the carbon atom radius is greater than the radius of the void and so a strain is produced there. Addition of carbon atom upto 1.7% in Iron increases its mechanical strength.

d. Electronic defects

1. Electronic defects are the result of errors in charge distribution in solids. These defects are free to move in the crystal under the influence of an electrical field, there by accounting for some electronic conductivity of certain solids and their increased reactivity.
2. For example if we take zinc oxide, the zinc ions can occupy interstitials and this leads to a large number of positive charges at that place.
3. In some places if zinc ions are missing, then in that places there is a gain of negative charges due to loss of positive charges.
4. Thus a vacancy or an interstitial impurity may produce the excess or the deficit of positive or negative charges.

Applications of point defects

1. Doped atoms or impurities in Si or Ge crystal increase its electrical conductivity.

2. The interstitial impurity carbon atoms in iron lattice increase the strength of iron.
3. Addition of copper atoms in gold increase the ductility of gold so that it can be drawn into wires
4. in copper lattice, the substitutional impurity atoms of tin increases the bearing properties of copper.

6.2.2 Line defects

1. Line defects are called dislocation. These are one-dimensional imperfections in the geometrical sense.
2. A dislocation may be defined as a disturbed region between two substantially perfect parts of a crystal. It is a line defect in a crystal structure whereby a partplane of atoms is displaced from its symmetrically stable positions in the array.
3. The dislocation is responsible for the phenomenon of slip by which most metals deform plastically.
4. One may conclude that dislocation is the region of localized lattice disturbance separating the slipped and unslipped regions of a crystal.
5. Burgers vector marks the magnitude and direction of the strain component of dislocation.
6. Dislocations arise in crystals as a result of
 - i. Growth accidents
 - ii. Thermal stresses
 - iii. External stresses causing plastic flow
 - iv. Phase transformations
 - v. Segregation of solute atoms causing mismatches, etc.

7. The two basic types of dislocations are:
 - a. Edge dislocation and
 - b. Screw dislocation

a. Edge dislocation

- ❖ An edge dislocation is created in the crystal by introducing an extra half plane or (any extra plane that does not extend up to the base of the crystal).
- ❖ The bond lengths have been compressed to smaller than the equilibrium value. Just below the edge of the extra plane the atoms are pulled apart and are in a state of tension.
- ❖ Here the bond lengths have been stretched to above the normal values.
- ❖ This distorted configuration extends all along the edge into the crystal. There is an extra energy due to the distortion in the region immediately surrounding the edge of the incomplete plane.
- ❖ As the region of the maximum distortion is centred around the edge of the incomplete plane, this distortion represents a line imperfection and is called an edge dislocation.
- ❖ The edge dislocation is said to be negative, denoted by T , when the insertion of the extra plane is from the bottom of the crystal.
- ❖ \perp denotes + ve edge dislocation in which the insertion of extra plane from the top of it.
- ❖ Let us see something about the Burgers circuit. Take a point P Starting from P, move x times the atomic distance in the positive x direction and then move ' y ' times the atomic distance in the positive y direction and then move x times the atomic distance in the negatively x direction and then move y times the y direction. After this movement

we can arrive at the original starting point 'P'. The circuit is a closed one and this type of circuit is called **Burgers circuit**.

- ❖ We draw the burgers circuit as explained above and if the circuit could not be completed then Immediately one can infer that there is a dislocation in the circuit.
- ❖ From the end point, if we want to arrive the starting point then we must move an extra distance 'b'. Therefore the vector b connecting the end point with the starting point is the **burgers vector of the dislocation**.

b. Screw dislocation

- ❖ Screw dislocation results from a displacement of the atoms in one part of a crystal relative to the rest of the crystal, forming a spiral ramp around the dislocation line.
- ❖ Figure 4.2 shows what happens when one part of the crystal is displaced relative to the rest of the crystal and the displacement terminals within the crystal. The row of atoms marking the termination of the displacement is the screw dislocation.
- ❖ By means of burgers vector as shown in the figure 4.2 one can determine the magnitude and direction of the screw dislocation.
- ❖ In the figure EF indicates the dislocation line.
- ❖ Normally the real dislocations which occur in the crystals are the mixtures of edge and screw dislocations.

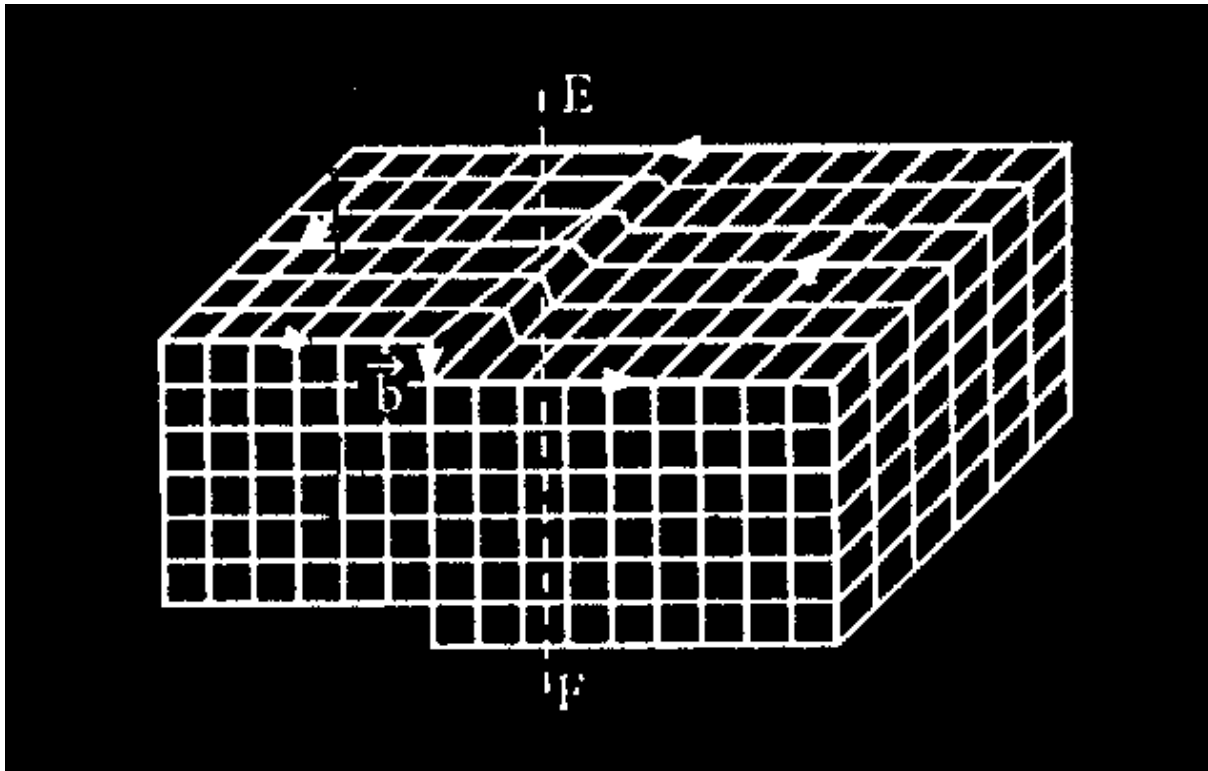


Fig. 6.2 Screw Dislocation

6.2.3 Surface Defects

- ❖ Surface imperfections which are two dimensional in the mathematical sense refer to regions of distortions that lie about a surface having a thickness of a few atomic diameters. These are also called plane defects.
 - ❖ We can classify these defects into two main types which are external surface imperfections and internal surface imperfections.
- a. **External surface imperfections.**
- ❖ The external surface of a crystal is an imperfection in itself, as the atomic bonds do not extend beyond the surface. Although we may visualize an external surface simply as a terminus of the crystal structure, the atoms on that surface cannot be compared with the atoms within the crystal.

- ❖ Because the external surface atoms have neighbours on one side only, while atoms inside the crystal have neighbors on either side of them. Since the external surface atoms are not entirely surrounded by others they possess higher energy than that of internal atoms.

b. Internal surface imperfections

- ❖ Internal surface imperfections arise from a change in the stacking of atomic planes across a boundary. The change may be one of the orientation or of the stacking sequence of the planes.
- ❖ Some important internal surface imperfections are given below:
 - i. Grain Boundaries
 - ii. Tilt boundaries and twist boundaries
 - iii. Twin boundaries
 - iv. Stacking faults and
 - v. Ferromagnetic domain walls

i. Grain boundaries

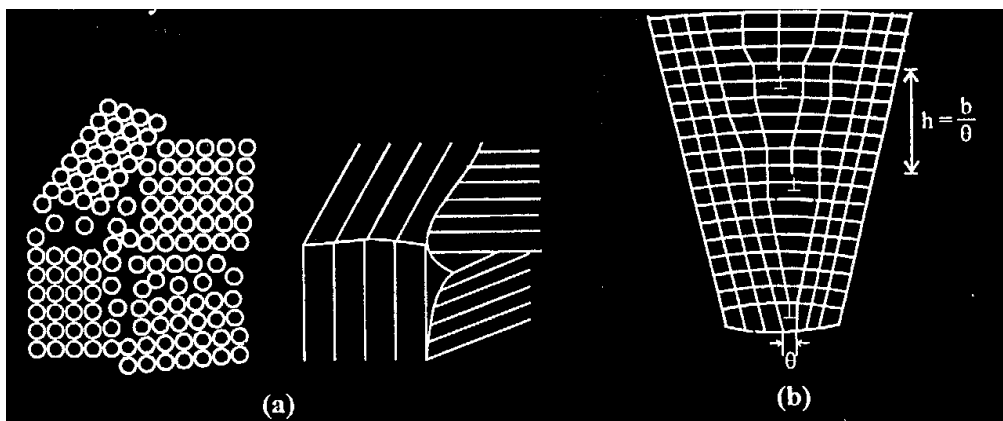
- ❖ The grain boundaries are those surface imperfections, which separate crystals of different orientations in a polycrystalline aggregate.
- ❖ During solidification or during recrystallization of polycrystalline crystals, new crystals are randomly oriented with respect to one another. They grow by the addition of atoms from the adjacent regions and eventually impinge on each other. When two crystals impinge in this manner, the atoms that are caught in between the two crystals are being pulled by each of the two crystals to join its own configuration.
- ❖ They can join neither crystal due to the opposing forces and therefore take up a compromise position. The thickness of this region is only a few atomic diameters, because the opposing forces from neighboring

crystals are felt by the intervening atoms only at such short distances. The boundary region is called a crystal boundary or a grain boundary.

- ❖ The crystal orientation changes sharply at the grain boundary, as shown in figure 4.3(a).
- ❖ It is obvious from this that the grain boundary forms a discontinuity in the periodicity of the lattice of crystallite or grain and is therefore a type of lattice imperfection called grain boundary.

ii. Tilt boundaries and twist boundaries

- ❖ Tilt boundary is another type of surface imperfection and it may be regarded as an array of edge dislocations (\perp)
- ❖ It is also a class of low angle boundaries
- ❖ By rotation of an axis in the boundary it is possible to bring the axis of two bordering grains into coincidence, i.e. a tilt boundary, (figure 4.3(b). In this figure 'h' is the distance between two neighbouring dislocations and ' θ ' is the angle of tilt, 'b' is the Burgers Vector.
- ❖ Twist boundaries are the second class of low angle boundaries result from the set of screw dislocations. In twist boundary the rotation is about an axis normal to the boundary.



6.3 (a) High angle grain boundaries (b) Tilt boundary

iii. Twin boundaries

- ❖ Surface imperfections which separate two orientations that are mirror images of one another are called twin boundaries
- ❖ Twin boundaries occur in pairs, such that the orientation change introduced by one boundary is restored by the other as shown in figure (4.4).

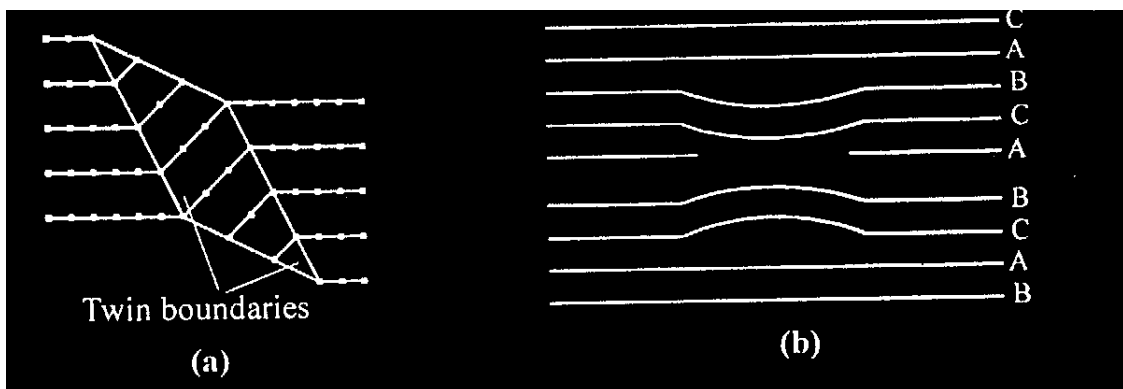


Fig. 6.4 (a) Twin Boundaries (b) Stacking fault

iv. Stacking faults

- ❖ A stacking fault is a surface imperfections that results from the stacking of one atomic plane out of sequence on another, while the lattice on either side of the fault is perfect. The stacking fault is a discrepancy in the packing sequence of the layers of atoms (although all the lattice sites are occupied).
- ❖ For example in the case of close packed FCC structure the stacking sequence can be written as ABC ABC ... In that sequence it is possible in one atom layer 'A' the atoms are not positioned properly in a small region and hence deviates from the sequence, relative to the atoms of the layers above and below giving a defect, since now there is a

sequence of ...BCBC... which belongs to HCP structure instead of ...ABC ABC...

- ❖ Figure 4.4(b) shows the stacking fault in a FCC metal. So one may conclude that stacking fault may arise when there is only small dissimilarity (electrostatically) between the stacking sequences of close-packed planes in FCC and HCP metals.
- ❖ Stacking faults are more frequently found in deformed metals than in annealed metals.

6.2 Volume defects

- ❖ Volume defects such as cracks may arise when there is only small electrostatic dissimilarity between the stacking of closed packed planes in metals.
- ❖ Further when clusters of atoms are missing, a large vacancy or void result which is also a volume imperfection.
- ❖ Foreign particle inclusions, large voids or non crystalline regions which have the dimensions of at least 10 to 30 Å are also called volume imperfections.

Effect of Crystal imperfections

1. The addition of impurities in the case of semiconductors increases the electrical conductivity; but in the case of metals, it decreases the electrical conductivity.
2. The impurity atoms in the lattice give characteristic colours to the crystals. These are called colour centers. If we take pure copper sulphate crystal it is colourless. but due to addition of water molecules, it turns out to be blue in colour. Similarly in the aluminium oxide lattice the addition of chromium atoms gives the red colour to it.

6.2.(b) Non-Stoichiometry

A defect like schottky defect, leaves the stoichiometry of the ionic crystal unaffected. For example there are equal number of Na^+ and Cl^- vacancies in NaCl. These are 2Cl^- vacancies per Ca^{+2} vacancy in CaCl_2 . But in certain transition metal compounds, especially oxides and sulphides, non-stoichiometric defect occurs. This is because of the ability of the metal to exist in more than one oxidation state. A well known case is "FeO" which consists of a 'CCP' array of oxide ions with all octahedral holes filled by Fe^{+2} ions. Actually some of these sites are vacant, while others— contain Fe^{+3} ions, sufficient to maintain electroneutrality. Thus the stoichiometry is commonly about $\text{Fe}_{0.95}\text{O}$. Ti_2O_3 can be obtained with compositions ranging from $\text{Ti}_{0.74}\text{O}$ to $\text{Ti}_{1.67}\text{O}$ depending on the pressure of oxygen gas while preparing the material.

CdO loses oxygen when heated to give yellow to black solids of composition Cd_{1+r}O similarly when NaCl is treated with sodium vapour, it absorbs sodium to give blue solid of composition Na_{1+r}Cl . An appropriate number (nr) of anion vacancies are created. These anion vacancies are occupied by electrons. These cavities are 'F' centers (fairbe).

Self Check Exercise – 1

1. What are point defects?
2. How are Frenkel and schottky defects created.

Please attempt (1) and (2) before you proceed further

Self Check Exercise – 2

1. Discuss the different types of dislocations please attempt (1) before you proceed further.

Self Check Exercise - 3

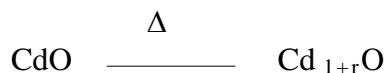
1. What are non stoichiometric defects? Does schottky defect lead to non-stoichiometry.

2. How are colour centers produced?

Model Answer:

Exercise – 3

2. Colour centers are produced due to anion vacancies and trapped electrons cdo



6.3 Let us Sum Up

Crystal imperfections such as i) point defects, ii) line defects, iii) surface defects and iv) volume defects are discussed in detail. Effect of crystal imperfections is indicated the different types of boundaries are discussed.

6.4 Points for Discussion

1. Transition metal oxides and sulphides can have non-stoichiometry, since these metals have variable oxidation states.
2. Anion vacancies can be created due to excess metal atoms.
3. ZnO, on heating loses oxygen creating oxide ion vacancies, thus ZnO is yellow when hot white when cold (F-centre formation).

6.5 References

1. Advanced Inorganic Chemistry – A comprehensive Text (3rd Ed). F.A.cotton and G.Wilkinson Wiley Eastern Limited- New Delhi (1972).
2. Inorganic chemistry (4th Ed) Re print – 2002 J.E. Huheey, E.A.Keitar and R.L.Keiter Pearson education – Asia.

UNIT – III

LESSON –7

CONTENTS

- 7.0. Aims and Objectives
- 7.1 Introduction
- 7.2 Electrical Properties of Solids
 - 7.2.1 Conductivity in metals
 - 7.2.2 Super conductors
- 7.3 Let us Sum Up
- 7.4 Points for Discussion
- 7.5 References

7.0 AIMS AND OBJECTIVES

The aim of this lesson is to understand the electrical conductivity or electrical properties of solids in general and electrical properties of metals in particular.

After going through this lesson you would be able to

- i) understand the electrical conductivity of metals and insulators
- ii) understand the super conducting behaviour of certain materials and the applications of super conducting materials

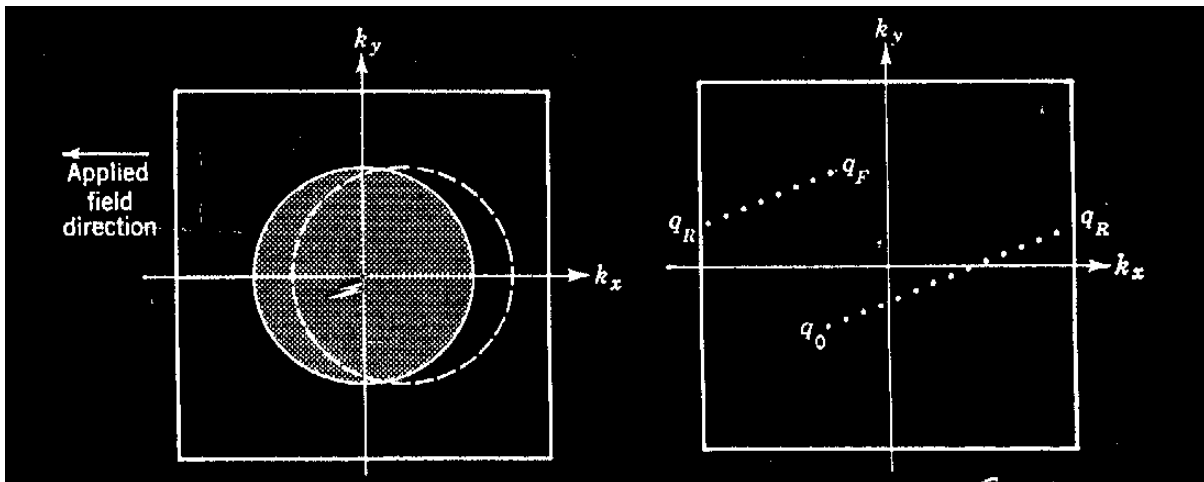
7.1 INTRODUCTION

The conductivity of metals can be explained on the basis of free electron theory. The quantum free electron theory successfully explains the conducting properties of metals and the decrease in electrical conductivity of metals with the increase in temperature can be explained on the basis of collisions of electrons with metal ions. Super conductors are zero resistivity materials. The superconductivity is explained by means of Cooper pair. The super conductivity depends on the critical temperature.

7.2. ELECTRICAL PROPERTIES

7.2.1 Conductors and nonconductors :

One of the successes of the zone theory is its ability to distinguish conductors of electricity from nonconductors. Consider a Brillouin zone that is only partly filled, as shown in Fig 1.1. In the absence of an external electric field, each electron moves with a velocity determined by its energy; however, no net movement occurs, since for each electron with an energy determined by k there is a symmetrically located electron at $-k$ moving in the opposite direction. When an external field is applied, the distribution can be displaced in the direction of the electric field by moving the electrons into adjacent quantum states in the same zone, as indicated in Fig 1.1 by the dashed circle. Obviously, only the electrons occupying energy levels lying near the Fermi surface can move into the higher energy states. Nevertheless, a net displacement of the electrons produces a net current, and a crystal with a partially filled zone is a conductor. As this process continues, it is possible that an electron ultimately occupies a quantum state on the Brillouin-zone boundary. At this point, it cannot move farther in the same direction without crossing the boundary, that is without a transition to a quantum state lying in the next zone. Such a transition is highly improbable so that the electron's velocity normal to the zone boundary is zero in this state. Physically, the electron can be pictured as being totally reflected by the crystallographic planes parallel to the zone boundary at this point. In terms of the zone model, the reflected electron "reappears" in the zone at a translation-equivalent point on the opposite zone boundary. Such a successive occupation of available quantum states in the Brillouin zone is shown schematically in Fig 1.2, where q_0 shows the initial quantum state of the electron, when an external field is applied; q_R is the quantum state of the electron when reflection occurs; and q_F is the final state when the external field is removed.



When the zone structure Fig 1.1 & 1.2 such that the energy values in two adjacent zones overlap, it is not possible to complete the filling of one zone without also occupying the lower-energy quantum states in the zone. This means, of course, that such a crystal must have at least one partially filled zone and that it is a conductor of electricity. An interesting situation arises when one of the zones is very nearly filled while the next zone is only partly occupied. The relative energy of the 4s states is slightly lower than that of the 3d states for the first transition series in the periodic table of elements. The partial occupation of these states by the outer electrons of transition metals means that the corresponding Brillouin zones are also partly filled. For example, it can be shown that the 3d zone of nickel is 94 percent filled, whereas the 4s zone is 70 percent empty. Furthermore, it is believed that conductivity in these metals takes place by transitions in the 4s zone. Now, when a 4s electron undergoes a transition from a quantum state on the zone boundary to an empty state it can be either "reflected back" into the same zone or "scattered" into the 3d zone because there are quantum states of equal energy present in both zones. Such scattering decreases the number of electrons contributing to the current and is believed to be responsible for the lower conductivity observed in the transition metals.

In case the Brillouin zones in a crystal are completely filled or completely empty and separated by a forbidden-energy region, the electrons cannot undergo transitions to adjacent quantum states and the crystal is an insulator. There are special cases of insulators in which one zone is very

nearly filled and the next zone almost but not quite empty. This situation occurs in semiconductors and also leads to conductivity. By comparison with metals, however, the currents in semiconductors are many orders of magnitude smaller.

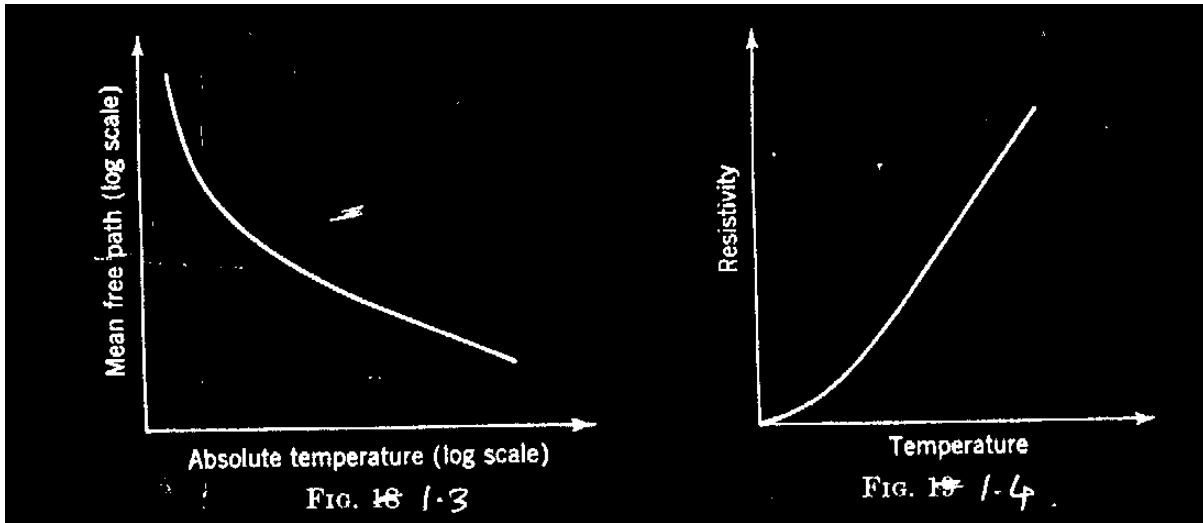
Conductivity in pure metals :

The conductivity of most metals can be explained without recourse to the zone theory. According to the free-electron theory, electrons can undergo transitions from one quantum state near the Fermi surface to another adjacent and unoccupied state under the influence of an external field. If this process were allowed to continue without end, the electrons would continue to occupy ever-increasing energy states, a situation that is contrary to the observed steady-state current, which is proportional to the applied field. The fact that the electrons cannot continuously increase their energy is explained by their collisions with the metal ions, which occupy most of the space in a metal. These collisions are elastic so that the electrons transfer both energy and momentum in the process. Because of the much larger mass of the ions, an electron loses most of its newly gained energy and momentum so that its velocity, averaged over a period of time, is altered only slightly. There is, nevertheless, a small but finite increase in the velocity component parallel to the applied field. Thus, even though the electron follows an erratic path, bouncing from atom to atom in all directions, it does undergo a net displacement in a direction determined by the applied field. The increase in its velocity component parallel to the applied field direction is called its *drift velocity*.

The average distance that an electron travels between collisions is called the mean free path l . The electron's acceleration due to the field is proportional to its charge e and inversely proportional to its mass m . The conductivity σ or its reciprocal, the resistivity ρ , is thus given by

$$\rho = \frac{1}{\sigma} = \frac{mv}{n_c e^2 l} \quad \dots (1)$$

where n_c is the number of *conduction electrons* and v is the average velocity as determined by their average kinetic energy E_v .



The vibration of the crystal increases with increasing temperature. This has the effect of increasing the probability of an electron collision or of decreasing the mean free path. Conversely, as the temperature decreases, the mean free path should increase. This is actually the case, as is shown in Fig 1.3. Note that the mean free path tends to infinity as the temperature approaches zero. According to (1) this implies that the resistivity of a metal should tend toward zero as the temperature approaches zero. This conclusion is borne out by experiment, as shown by the curve of resistivity plotted as a function of temperature in Fig 1.4. Note that for all temperature above a certain low temperature the resistivity is directly proportional to the temperature.

Quantitative calculations of the mean free path have been made for certain metals, using quantum mechanics. These calculations have led to results that are in good agreement with experimental values, particularly for the simpler metals such as the alkalis. The conductivities (expressed in millions of mhos per meter) of several metals at 20°C are compared with calculated values below.

	Fe	Na	Al	Cu	
Observed σ	10	22	35	59	$\times 10^6$ mhos/m
Calculated σ	..	22	..	161	$\times 10^6$ mhos/m

In crystals belonging to the cubic system, the conductivity is independent of direction. The conductivity (or its reciprocal, the resistivity) does depend on direction in crystals of lower symmetry. In the case of crystals possessing one unique axis, that is in the hexagonal and tetragonal systems, the resistivity is different for current flow parallel to the unique axis and normal to it.

Conductivity in alloys :

The mean free path of an electron decreases in an alloy for two reasons. The first is an increase in the number of scattering centers caused by local inhomogeneities in the crystal structure produced by the difference in the sizes of the different atoms. This effect is particularly noticeable in the case of solid-solution alloys. In the unannealed or random solid solution, the resistivity reaches a maximum at the 50-50 composition, since this corresponds to the maximum possible distortion of the structure, and drops rapidly at both ends as the pure metals are approached. The increase in the resistivity is due to a discontinuity in the periodic potential encountered by the electrons in the vicinity of the solute atoms. At the compositions of the ordered alloys Cu_3Au and CuAu , the curve exhibits definite minima, corresponding to the increased mean free path of the electrons due to ordering, which restores a periodicity to the alloy. In practice, it turns out that annealing serves to decrease the resistivity also because it removes other imperfections present which may also act as scattering centers for electrons.

In a solid solution, the increased resistivity, due to the introduction of solute atoms, does not disappear at the absolute zero. The resistance that remains is usually called the residual resistance. The residual resistance is independent of temperature in dilute alloys but varies with changes in the composition of an alloy. According to Matthiessen's rule, the resistivity of

an ideal alloy can be expressed as the sum of the residual resistance and a resistivity term which varies with temperature in the same linear manner as the resistivity of a pure metal.

Self check exercise –1

1. If kinetic energies and mean free paths are assumed to be equal for Na and Al, what would be the ratio of the free electrons $n_{\text{Na}} \div n_{\text{Al}}$?
2. Discuss the variation of resistivity with the compositions of Cu-Au alloy.

Please answer the above before you proceed further. The space below is for your answer.

7.2.2 Zero resistivity materials (Superconductors)

The ability of certain ultra cold substances to conduct electricity without resistance is called superconductivity. Substances having this property are called superconductors.

Thus a superconductor is a conductor having almost zero resistivity and also behaves as diamagnetic below its superconducting transition temperature.

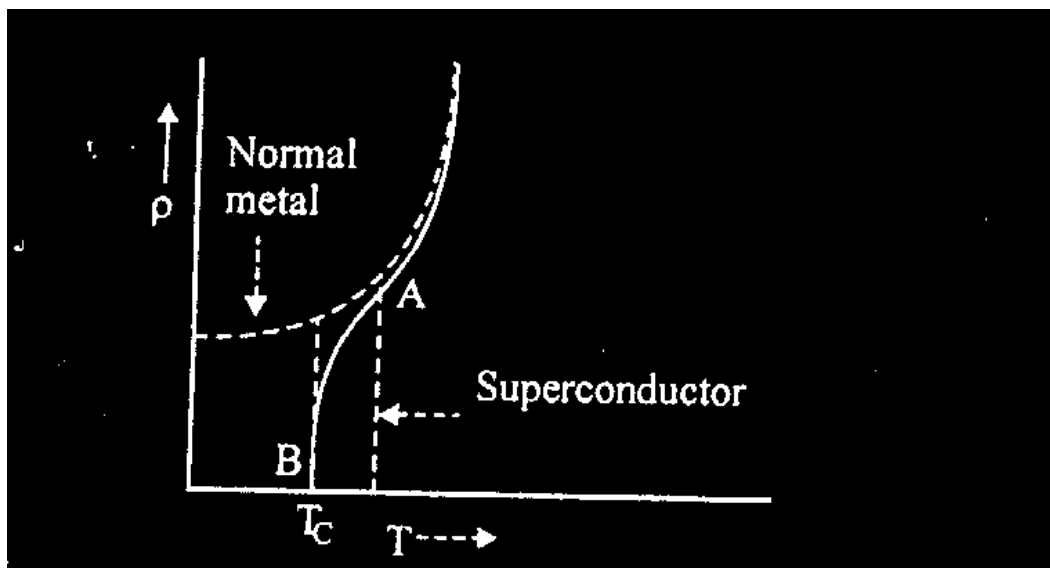


Fig 7.5

The superconducting transition temperature ' T_c ' of a material is defined as a critical temperature at which the resistivity of the material is suddenly changed to zero as shown in fig. 7.5. Thus at that temperature a material is changed from normal material to superconductor. In the figure the transition region is of finite width AB and depends upon the presence of impurities and internal stresses in the sample. In chemically pure crystal which is also free from lattice defects, the width of the transition region is very very narrow. The temperature ' T_c ' of pure metals range from 0.35 K (Hafnium) to 9.22 K (Niobium) and of semiconductors from 0.3K (Ge Te) to 1.25 K (NbO). Commonly alloys have higher transition temperatures. Particularly Niobium compounds such as $Nb_3 Sn$ ($T_c = 1.81$ K) and $Nb_3 Ge$ ($T_c = 22.65$ K) have higher transition temperatures and so they are technically important superconductors.

At the transition temperature, the following physical changes are observed.

1. The electrical resistivity drops to zero
2. The magnetic flux lines are excluded from the material
3. There is a discontinuous change in specific heat.
4. Further there are also small changes in thermal conductivity and the volume of the material.

Explanations for the occurrence of superconductivity

1. At the extremely low temperatures, vibrations of the nuclei of certain atoms slow down so much and they synchronise with passing waves of electrons in a flow of electric current. When this happens resistance to electric current disappears.

2. BARDEEN COOPER AND SCHRIEFFER THEORY

According to that, superconductivity occurs when there is a formation of cooper pair of electrons (or) bound electron pair. These two electrons with opposite spins and momenta form a pair through electron – electron interaction via the lattice deformation or phonon field. This type of interaction can occur only at very low temperatures. Thus during the transition from normal state to super conducting state electrons of opposite spin couple with each other via the vibrations of the lattice that the material's atoms form. One electron in the communicating pair distorts the lattice which can then take up energy from the second electron and immediately they form a bound electron pair or Cooper pair.



Fig 7.6

As shown in figure 1.6, one electron with wave vector k distorts the lattice emitting a phonon of wave vector q . The other electron with wave vector k takes up the energy down the lattice and its wave vector changes into $k + q$. Thus these two electrons with wave vectors $k - q$ and $k + q$ form a cooper pair and superconductivity occurs.

3. RVB Theory :

The conventional BCS theory accounts for superconductivity only at low temperatures. At higher temperatures thermal degradation breaks the cooper pairs leading to ordinary electrical conductivity. Thus it is unable to explain the formation of high temperature superconductivity having high T_c (≈ 80 K)

Many theories have been suggested, but none is satisfactory. One of the promising one is the Resonating Valence Bond (RVB) state theory initiated by P.W. Anderson and the Princeton university group. According to that intense electron pairing needed to explain high superconductivity may be brought about through an attractive correlation quite similar to that responsible for bonding hydrogen atoms in a molecule. Further it is based on the idea that it is the short range repulsion between electrons in a narrow band which gives rise to superconductivity.

A key element of RVB theory is that electron pairs can exist in a material that is not superconducting. Superconductivity occurs when the material is doped to create holes in it. The holes then form pairs and undergo Bose Condensation, making superconductivity possible. These high temperature superconductors are normally called p type superconductors since the charge carriers are holes.

Recently 'n' type superconductors ($\text{Ln}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$) where Ln = Pr, Nd and Sm have been prepared but the transition temperature for this system are very low ($\approx 20\text{K}$).

General properties of superconductors

1. Electrical resistance

The electrical resistivity drops to zero at the transition temperature. One can conclude that superconductors have virtually zero electrical resistance and they can conduct electricity without resistance.

2. Diamagnetic property

The superconductor is a perfect diamagnet. As the material which is placed in an uniform magnetic field (whose value is smaller than the critical magnetic field H_c), is cooled below ' T_c ' the magnetic flux inside the

material is excluded from the material (fig 1.7). This is called MEISSNER EFFECT.

Thus a material can behave as a superconductor only when

- i) the resistivity of the material should be zero and
- ii) the magnetic induction in the material should be zero when it is placed in an uniform magnetic field.

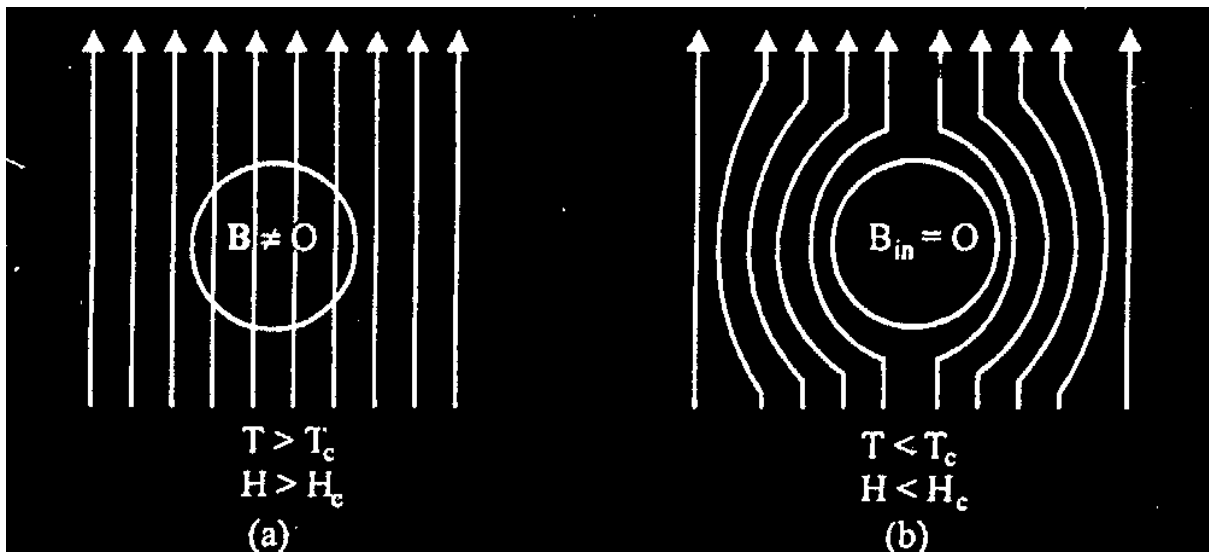


Fig 7.7

Both the conditions are independent to each other and to get superconducting state, these two conditions should simultaneously exist in the material.

3. Effect of magnetic field

Below T_c superconductivity can be destroyed by the application of strong magnetic field. At any temperature, the minimum field required to destroy superconductivity is called critical field (H_c) of the material. Thus the value of the critical field depends upon the temperature of the superconducting material.

$$H_c = H_0 \left[1 - \frac{T^2}{T_c^2} \right]$$

Where H_0 = critical field 0 K.

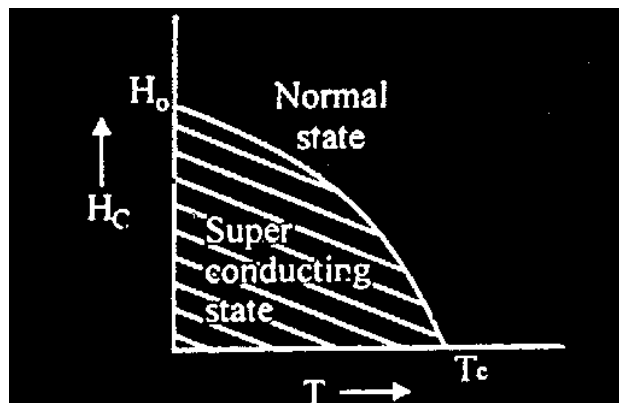


Fig 7.8

From the fig. 7.8 one can know that when the temperature of the material increases, the value of the critical magnetic field decreases correspondingly. The value of the field will be different for different materials.

Table 1.1 SUPERCONDUCTORS AND THEIR CRITICAL FIELD

Material	H _o ampere/metre X 10 ³	Material	H _o ampere/metre X 10 ³
Al	7.9	Sn	24.5
Co	2.4	Ba Bi ₃	59.0
Hg	33.0	Ca Si ₂	1.4
Pb	64.0	Nb ₃ Sn	18.1

4. Effect of heavy current

The super conductive properties of conductors disappear when a sufficiently heavy current is passed through them. Since when current flows through a conductor it will set up the magnetic field which destroys the superconducting state. According to Silsbee's rule, for a superconducting wire.

$$I_c = 2\pi rH_c$$

Where I_c is the critical current and 'r' is the radius of the wire.

5. Effect of pressure

By applying very high pressure, we can bring T_c of a material nearer to room temperature i.e. if we increase the pressure on the material, T_c also increases. T_c is directly proportional to pressure at very high pressures. Researches are going on to get superconducting state at room temperatures by applying very high pressures.

6. Isotope effect

Maxwell found that the transition temperatures are inversely proportional to the square roots of the atomic weights of the isotopes of a single superconductor. Thus,

$$M^\alpha T_c = \text{a constant}$$

Where α is a constant and it is approximately equal to 0.5. For example the atomic weights of isotopes of mercury are from 199.5 to 203.4 atomic mass units. Therefore their transition temperatures are also from 4.185 K to 4.146 K respectively.

Types of superconductors

Based on the value of superconducting transition temperature we have

1. High temperature superconductors
2. Low temperature superconductors

	High Temperature superconductors		Low Temperature superconductors
1	It has high super conducting transition temperature ($> 100\text{K}$)	1	It has low superconducting transition temperature ($< 20\text{K}$)
2	Super conductivity is obtained by the hole states. Dislocations also increase the value of transition temperature.	2	Superconductivity is obtained by the formation of cooper pair having two electrons with equal and opposite spins and momenta.
3	It does not obey B.C.S. theory. High temperature superconductivity can be explained from resonance valence bond (RVB) theory only.	3	It can be explained only from BCS theory.
4	It is very useful for commercial and other applications because these have high superconducting transition temperatures and are hard super conductors which can produce strong magnetic fields.	4	It is not so useful, due to maintaining of ultra low temperature (20 K)
5	It is called p-type super conductor due to the formation of superconductivity from holes.	5	It is called n-type superconductor due to the formation of superconductivity from cooper pairs or electron pairs.

Based on critical magnetic field, there are two types of superconductors

- i. Type I (soft) superconductors

ii. Type II (hard) superconductors

Type I Superconductors

1. Type I superconductor is the one which exhibits a complete Meissner effect or perfect diamagnetism. i.e., above the critical field H_c , the specimen is a normal conductor. Below the critical field, the specimen excludes all the magnetic lines of force inside the specimen or it will become a diamagnetic material

2. These are also called soft superconductors
3. The values of H_c , are always too low for these materials.
4. Example: Al, Zn, Ga.

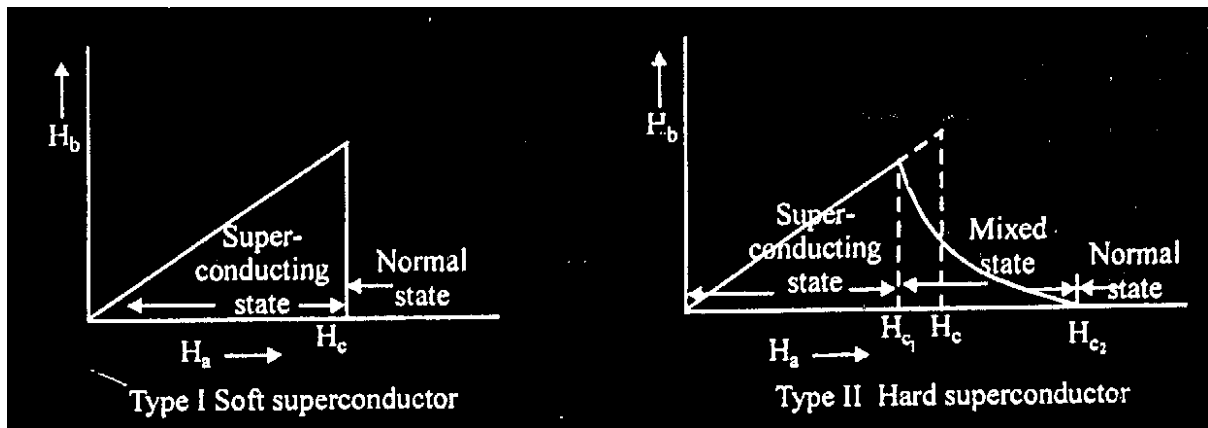


Fig 7.9 (a) & (b)

In the Figure 1.9 H_a - applied external magnetic field and
 H_b - Magnetic field produced by the induced superconducting currents when an external field is applied.

Type II Superconductors

1. Type II Superconductors are the superconductors in which the magnetic flux starts to penetrate the specimen at a field H_{c1} which is lower than critical field H_c . The specimen is in a mixed state between H_{c1} and H_{c2} and it has superconducting electrical properties upto H_{c2} . Above H_{c2} the specimen is a normal conductor (figure 1.9 (b)).
2. Type II superconductors are called hard superconductors which have a large amount of magnetic hysteresis induced by mechanical treatment. Solenoids wound with wire of a hard superconductors can produce field over 100 kilo tesla.
3. So type II superconductors can carry high super current densities in high magnetic fields and are of great commercial importance.
4. Incomplete Meissner effect occurs in the region between H_{c1} and H_{c2} and this region is called **vortex region**. In this region the magnetic flux lines gradually penetrate the specimen as the magnetic field is increased beyond H_{c1} .
5. Heavy cold-worked and recovery annealed materials having high dislocation density and fine grains are used for making type II superconductors.
6. Examples : Zr, Nb, 60% Nb – 40 % Ti alloy.

High Temperature superconductors

Sodium tungsten bronzes and barium lead bismuth oxides are important intermetallic compounds with high superconducting transition temperatures (20K). In Bell Laboratory, during the end of 1986, it was detected that a crystalline complex of lanthanum, strontinum and copper grown in an atmosphere of oxygen has the highest superconducting transition temperature, 37K. Following the Bell Laboratory discovery , the Chinese group of

scientists has found a superconducting state in an octahedral crystalline complex of lead, lanthanum, copper and oxygen at 77K.

After that C.W. Chu and his collaborators of university of Houston, U.S.A. found stable superconductivity at 90K in yttrium barium-copper oxide compounds. Detection of super conductivity especially in yttrium complexes at operating temperature much above 130 K has been performed recently. Now the stable and reproducing superconducting state is observed at a high transition temperature around 165K. Researches are going on to get the superconducting state at room temperature conditions.

Some of the high temperature ($T_c > 100K$) superconductors are given below:

$Tl_2Ba_2Ca_2Cu_3O_y$, $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{7-y}$ and $Bi_2(CaSr)_3Cu_2O_y$. Here the value of x is less than 0.2. Further the value of y is a variable one and depends upon the stability of the system. The rare earth oxide systems, like La-Sr-Cu-O and Y-Ba-Cu-O have so far been found to have stable superconducting transition temperatures in the range 80-100K range.

Recently T. Ogushi and his associates from Japan have reported in La-Sr-Nb-O system (without copper) that shows superconductivity upto 255K. Some scientists believe that this copperless Y-Sr-Nb-O or La-Sr-Nb-O system may lead to the real room temperature superconductors.

New oxide superconductors having $T_c > 90K$ without rare earth element

New oxide superconductors with above 90K transition temperatures have been discovered in 1998. The newer compounds are still layered copper oxide materials, but they do not contain rare earth elements. In place of yttrium or other rare earths, the compounds contain metals like bismuth or thallium. Thus they contain four metallic elements instead of three. For

example, thallium-barium-calcium-copper oxide superconductor contains three copper oxygen layers and it becomes superconductor at 120K.

Similarly bismuth-strontium – calcium- copper oxide has the superconducting transition temperature around 120K.

Preparation and characteristic of high temperature ceramics superconductors

The new ceramic oxide superconductors like yttrium barium copper oxide, Lanthanum barium copper oxide, Neodymium barium copper oxide and Thallium barium copper oxide are all types II superconductors which have higher critical fields and hence are used to manufacture superconducting magnets having higher strengths.

Let us see the preparation of yttrium barium copper oxide superconductors by the 'Shake and Bake' method. This method involves a four step process: 1.Mixing the chemicals 2. Calcination (initial firing) 3. The intermediate firing (oxygen annealing) and 4. The final oxygen annealing.

1. Mixing the Chemicals

The powders of yttrium oxide, barium carbonate and cupric oxide are taken such that 11.29 gram of Y_2O_3 , 39.47 gram of $BaCO_3$ and 28.86 gram CuO so that the atomic ratios of yttrium, barium and copper are 1:2:3. A mortar with pestle is used to grind down any lumps or large particles in the powders. Then the powder mixture is shaken vigorously in a capped jar or stoppered flask for several minutes.

2. Calcination

After the powders are thoroughly mixed, they are kept in an alumina crucible and heated in a furnace of about 950°C for about 18 hours. The following chemical reaction takes place.



This initial heat treatment is called calcinations and results in a porous dark gray or black clump and the basic crystal structure is developed. The material formed will be shrunk and becomes much denser than the original powder mix.

3. Intermediate Firing

The porous black clump is ground into a fine powder and placed in the furnace. After the furnace temperature reaches about 500°C, a slow flow of oxygen into the furnace is maintained. This heat treatment under oxygen flow is called oxygen annealing. The oxygen flow should be maintained in a constant rate for 18 hours at 950°C. The maximum temperature of 950°C should be reached in an hour. After this firing, the cooling rate must be no more than 100°C per hour upto 400°C and the oxygen flow is also maintained. By this manner the oxygen content of each crystal unit is increased from 6.5 atoms to 7 atoms and the chemical formula for the material becomes YBa₂Cu₃O₇. At 400°C, the supply of oxygen is cutoff and the rate of cooling can be increased to 200°C per hour. Once again the material should be thoroughly re-ground in a mortar and pestle.

4. The final oxygen annealing

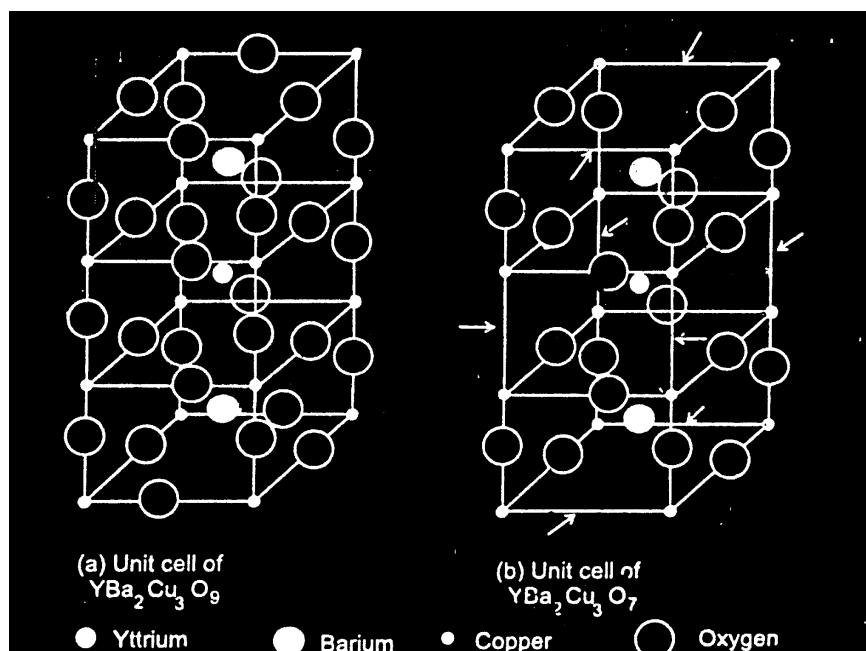
The reground black powder is placed back in the alumina crucible. The powder should be as finely ground and as densely evenly packed. Now heat the sample between 950°C and 1000°C for about 18 hours. The cooling takes place in a very slow manner with adequate oxygen flow. The rate of cooling must be less than 100°C per hour upto 400°C. After that the rate of cooling can be increased.

Pervoskite superconductivity

It is found that ceramic superconductors have the unit cell such that one atom of a rare earth metal, two barium atoms, three copper atoms and seven oxygen atoms. In the superconductors the metallic atoms are in the ratio 1:2:3. Thus these new kind of superconductors are called 1-2-3 superconductors. The electrical conductivity of 1-2-3 superconductors is based on the presence of oxygen atoms in their unit cell. The oxygen atoms have more vacancies and so they can accommodate electrons from other atoms. It is found that electricity flows through the material by allowing these holes to move from atom to atom in the crystal.

The unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_9$ is a stack of alternating cubic perovskite structures (figures 1.11 (a) $(\text{BaCuO}_3) : (\text{Y Cu O}_3) : (\text{Ba Cu O}_3)$). But is not a superconductor. The unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$ which is superconductor when $T_a = 90\text{K}$ is a stack of alternating oxygen deficient (or defect) cubic perovskite structures in the idealized sequence noted, arrows. The chains of alternating Ba:Y: Ba atoms which characterize the $\text{Y Ba}_2\text{Cu}_3\text{O}_7$ lattice are perpendicular to Cu-O planes with alternating oxygen defects (Vacancies) as shown in figure 1.11(b).

So the oxygen defects induce superconductivity in the perovskite structures.



Applications of superconductors

1. Electric generators

Superconducting generators are smaller in size and weight when we compare with conventional generators. These generators consume very low energy and so we can save more energy. The superconducting d.c. generators are available which have electrical power of 2500kW having very high current and very low voltage. These are in small size with superconducting windings. The low loss superconducting coil is rotated in an extremely strong magnetic field. Similarly there are d.c. superconducting motors which are used in ship propulsion and large mills where very high torques are necessary even at low speeds.

2. Electric Power Transmission lines

Electric power companies look forward to superconducting transmission systems that would save most of the energy now being lost from conventional power lines in the form of useless radiation and heat ($I^2 R$ Joule heat losses). The electric cables are designed with superconducting wires. Portable superconducting transformers with low loss are available for step up or step down a.c. voltages.

3. Magnetic Levitation

In Japan, superconducting magnets have been used to levitate an experimental train above its rails and drive it at great speed with minimal expenditure of energy. A similar magnetic propulsion system may be used to launch satellites in to orbit directly from the earth without the use of rockets.

Principal of Magnetic levitation

The diamagnetic property of a superconductor is the basis of magnetic levitation. A sheet of superconductors in the superconducting state is kept below the horizontal bar magnet suspended from a flexible chain and then

lowered over the superconductor. As the magnet approaches the superconductor, the supporting chain becomes limp and eventually dropped down in a loop below the magnet which floats horizontally above the superconductor. The magnetic field due to the approaching magnet induces current in the surface of the superconductor. Since the resistance of the superconductor is zero, the current persists in the superconductor and a magnetic field due to this induced current repels that the bar magnet. When a superconductor levitates a magnet, a magnetic mirror image is formed in the superconductor such that there is always a north pole induced in the superconductor directly below the north pole of the levitating magnet and a south pole is induced in the superconductor directly below the south pole of the levitating magnet. The mirror image moves with the magnet as the magnet moves so that the disk magnet can be given a rapid spin without affecting its levitation. In fact the magnet may continue to spin for quite a long time because its spinning encounters no friction other than the friction of air resistance. When the surrounding air pressure is reduced, the levitating magnet rises higher.

Instead of a permanent magnet, the supporting field is provided by superconducting solenoid carrying a current. The repulsion between the supporting magnetic field and superconducting surface having persistent current is the basis for magnetic levitation of trains and other machines.

4. Ore Separation

High efficiency ore-separating machines may be built using superconducting magnets which are also used to separate tumour cells from healthy cells by high Gradient Magnetic separation method.

Self Check Exercise – 2

1. Explain the BSC theory and RVB Theory
2. What are type I and type II superconductors
3. Explain the term meissner effect
4. Give a few applications of superconductors

Source : 1) Introduction to solids – Azaraff
TMH – EdN - New Delhi – 1960.

Model Answers

Self check Exercise – 2

2. Type I super conductors exhibits a complete meissner effect or perfect diamagnetism H_c (Critical field is too low)

(eg) Al, Zn, Ga

Type II Can carry high super current densities in high magnetic fields.

(eg.Zr, Nb etc.)

7.3 Let us Sum Up

Conductivity in metals and alloys is discussed on the basis of zone theory. Different types of super conductors, their synthesis and theories of super conductors such as BCS theory and RVB are discussed in detail Magnetic levitation is explained.

7.4 Points for Discussions

i) The variation of electrical conductivity with 'T' in the case of metals and semiconductors are different

ii) Resistivity of a metal at a given temperature is $\propto \frac{1}{\text{Carrier concentration}}$

iii) Cooper Pair concept explains the low temperature super conductivity

7.5 References

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LESSON – 8**CONTENTS**

8.0 AIMS AND OBJECTIVES

8.1 INTRODUCTION

8.2 MAGNETIC PROPERTIES

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8.0. AIMS AND OBJECTIVES

The aim of the lesson is to study in detail, the magnetic properties of materials. After going through this lesson you would understand the fundamental theories of magnetism. The knowledge of the theories of magnetic properties is important for selecting different types of magnetic materials for various applications.

8.1 INTRODUCTION

When a substance is placed in an inhomogeneous magnetic field, it is either attracted toward the strong part of the field or repelled toward the weaker part. If it is attracted by the field, it is said to be paramagnetic, if repelled it is said to be diamagnetic. A Ferromagnetic solid is one that can have a permanent magnetization, after the magnetic field is removed.

8.2.1 MAGNETIC PROPERTIES

Diamagnetism: when a substance is placed in an inhomogeneous magnetic field, it is either attracted toward the strong part of the field or repelled toward the weaker part. If it is attracted by the field, it is said to be paramagnetic, if repelled, it is said to be diamagnetic. The force F with

which a diamagnetic substance is repelled when placed in a field of strength H and gradient dH/dx is determined by

$$F = x V H \frac{dH}{dx}$$

Where x is called the magnetic susceptibility and V is the volume of the substance. The magnetic susceptibility is a measure of the change in the magnetic moment of the atoms caused by an applied field. It is usual to speak of the atomic susceptibility x_A which is determined according to Langevin's equation.

$$\begin{aligned} x_A &= \frac{N_0 e^2}{6 m c^2} \bar{r}^2 \\ &= - 2.83 \times 10^{10} \bar{r}^2 \end{aligned} \quad \dots(2)$$

where N_0 is Avogadro's number; e , m , c have their usual meaning for an electron; and \bar{r} is the average radius of the orbits of the electrons. Note that the right side of (2) is negative, which indicates that the force in (1) is negative. This is in agreement with Lenz's law that the magnetic flux produced by an induced current opposes the change in the magnetic field which produces it.

In quantum mechanics, The Langevin equation is valid provided that the electron distribution is spherically symmetrical. Thus it is quite useful when dealing with inert gases, ions, and neutral atoms. The value of \bar{r} is determined by the wave function, and since the susceptibility is proportional to \bar{r}^2 , it follows that the outer electrons make the largest contribution. The value of x_A , calculated using quantum mechanics, is in good agreement with the values found experimentally. For most elements, including Cu, Zn, Ga, Ge, As, Se, Br, Ag, Cd, Te, and the inert gases, the magnitude of the atomic susceptibility lies in the range 10^{-6} to 10^{-5} , whereas for Sb, Au, Hg, Tl, Pb, and Bi it is greater than 10^{-5} . Bismuth is exceptional in this regard; $x_A = - 1.35 \times 10^{-4}$ in MKS units.

Paramagnetism: It is possible for an atom to have a net magnetic moment resulting from a particular combination of the orbital magnetic moments and the spin magnetic moments of its electron. The unit for measuring the spin magnetic moment of an electron is the Bohr magneton.

$$= \frac{eh}{4\pi mc} = 9.27 \times 10^{-21} \text{ erg/gauss.} \quad \dots(3)$$

If an external magnetic field is applied, the spin moments can line up either parallel to the field or antiparallel to the field.

The magnetic properties of many materials were first studied systematically by P.Curie before the end of the nineteenth century. He found that the paramagnetic susceptibility x_p was inversely proportional to the absolute temperature.

$$x_p = \frac{C}{T} \quad \dots(4)$$

Where C is the Curie constant and is characteristics of the material Langevin later applied classical mechanics to paramagnetism in gases and found that the Curie constant could be expressed theoretically

$$C = \frac{N_0 \mu^2}{3k} \quad \dots(5)$$

where N_0 is Avogadro's number

k is Boltzmann's constant

μ is a average magnetic moment per molecule

It also follows from classical mechanics that, for free electrons in a metal, the Curie constant can be written

$$C = \frac{n^2}{k} \quad \dots(6)$$

where n is the number of free electrons per unit volume. By substituting (6) in (4) it is possible to calculate the paramagnetic susceptibility of any metal. The value obtained in this way is approximately 100 times larger than the values obtained experimentally. This is one of the properties of metals, therefore, that the classical free-electron theory cannot explain correctly.

The total magnetization M is defined as the magnetic moment per unit volume and is given by

$$M = X_p H$$

$$M = \frac{n^2}{kT} H.$$

Now, according to the Curie law (4), the susceptibility and, hence, the magnetization should vary with the temperature. Again, this is not the

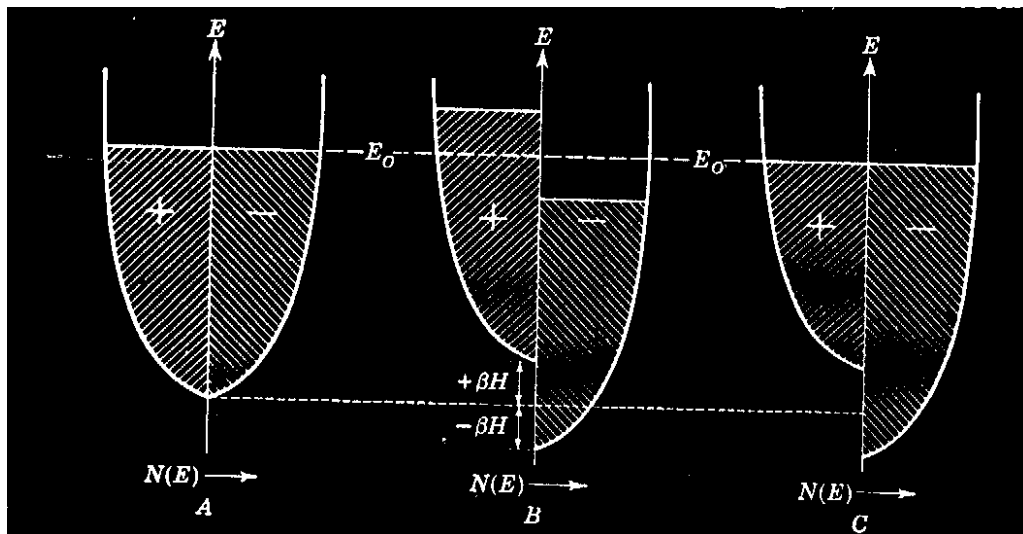


Fig 8.1

case for many metals. The observed weak and temperature-independent paramagnetism can be explained by applying Fermi-Dirac statistics to this problem.

The distribution of electrons in a metal at the absolute zero of temperature is shown in Fig.2.1 by plotting the parabola-shaped function representing the density of states as a function of energy. In the absence of an external magnetic field, the electrons occupy all the available states having energies less than the Fermi energy E_0 . They are shown divided into two groups, in Fig.2.1A, accordingly as their spins are plus or minus. When an external field is applied, the magnetic moments due to the spins line up either parallel or antiparallel to the field. Assuming that a plus denotes electrons which have antiparallel moments, these electrons undergo a shift in energy $+H$, as shown in Fig. 2.1. This situation is not stable, and at equilibrium, some of the electrons in the antiparallel states undergo transitions to the lower energy parallel states. This leads to the situation shown in Fig.2.1C. The magnitude of the energy shift, even due to a fairly strong field, $H = 10^5$ gauss, is very small, $H \sim 10^{-3} \text{ eV}$, so that, at room temperature, the thermal energy, $kT \sim 0.03 \text{ eV}$, is sufficiently greater to keep the number of electrons having parallel and antiparallel moments very nearly equal. Not only does this explain the very small value of the observed susceptibility but also why the susceptibility is virtually independent of reasonable changes in temperatures.

8.2.1 Ferromagnetism. It has been assumed, in the above discussion, that the magnetic moment of the atoms was due entirely to the electron spin. This is a fairly accurate picture for such metals as Li, Na, Mg, Al, and K. In these metals, the valence electrons are quite free to migrate through the crystals so that they contribute primarily spin moments, whereas the inner shells are filled and contribute only weak diamagnetism. On the other hand, if an atom has incomplete inner shells, then it is possible that not only the spin moments but also the orbital moments can contribute to the magnetic moment of the atom. This normally leads to large paramagnetic susceptibility in accord with the Curie law. Such relatively large susceptibilities are found among the rare earths and the platinum and palladium-group metals. An anomalous behaviour is encountered in the case of Fe, Co, and Ni, which are paramagnetic at elevated temperatures but become ferromagnetic below a transition temperature called the Curie point. A ferromagnetic solid is one that can

have a permanent magnetization after the external magnetic field is removed. This permanent magnetization was first explained by P.J. Weiss in 1907 as being due to a parallel orientation of the permanent magnetic moments of the constituent atoms. The paramagnetic — ferromagnetic transition can be likened, therefore, to the disorder — order transition. Above the Curie temperature, thermal agitation is responsible for keeping the magnetic moments randomly oriented, whereas below the Curie point the energy favours an ordered arrangement in which more magnetic moments are aligned in one direction than in another. In order to explain why an excess of magnetic moments along one direction is more stable than a uniform, distribution, Weiss proposed that a molecular field exists in the crystal and favors such an alignment.

Heisenberg was the first to propose an explanation of this molecular field based on the principals of quantum mechanics. He treated the problem similarly to the Heitler-London treatment of the hydrogen molecule. In this treatment, an exchange interaction between electrons in different quantum states is shown to lead to a lower energy for a molecule than that obtained by a mere superposition of the wave functions of each atom. Experiments have proven that the magnetic moment, due to the electron spins rather than the orbital moments, contributes to the permanent magnetic moment of the iron-group atoms. The exchange forces, therefore, are necessary in order to explain why, in certain metals, the atoms have electrons with parallel magnetic moments. It is reasonable to expect that such exchange forces are negligible unless the atoms are brought closely together. It can be shown that, as two atoms approach each other, the electron spins of unpaired electrons in each atom assume parallel orientations. As they are brought closer together, the spin moments are maintained parallel by increasing forces. As the interatomic distance is decreased still further, however, these exchange forces decrease until finally they pass through zero and an antiparallel spin orientation is favored. It has been shown by Bethe that, for the iron group, the conditions favoring parallel orientations occur when the ratio between one-half the interatomic distance in a crystal and the average

radius of the 3d shell is greater than 1.5. Some typical values of this ratio for these metals are

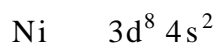
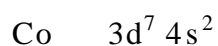
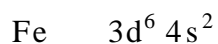
	Mn	Fe	Co	Ni
Ratio	1.47	1.63	1.82	1.98

As can be seen, the ratio for manganese is slightly less than 1.5, which explains why manganese crystals are not ferromagnetic whereas compounds containing manganese atoms spaced farther apart are. Notable examples are the Heusler alloys Cu_2MnSn and Cu_2MnAl . (Note that these ferromagnetic alloys contain neither Fe, Co, or Ni)

According to the zone theory, two factors determine the energy of a crystal. The first is the Fermi energy, which makes a positive contribution to the total energy, and the second comes from the exchange integral and makes a negative contribution. A crystal then is ferromagnetic when the negative energy due to the exchange integral is greater than the positive energy term due to the kinetic (Fermi) energy of the electrons, which tends to randomize the spin directions. The exchange integral used in this calculation is somewhat different from the one proposed by Heisenberg in that it is based on the electrostatic interaction between one electron and the electrons in an identical fictitious crystal having a hole in place of this electron. It turns out that this exchange integral is independent of interatomic distance and does not vary too much from atom to atom in the metal. In order to explain ferromagnetism, therefore, it is necessary to compare the Fermi energies of different metals. Although only nickel has been examined in detail, the results can be extended to show that the Fermi energy is smaller than the exchange energy in Fe, Co, and Ni. As expected, it is somewhat greater in the case of Mn. It should be noted that a small Fermi energy denotes a narrow energy zone, that is, a larger number of electrons having very closely spaced energies. Thus this calculation supports the earlier conclusions that narrow, partially filled d zones, which do not overlap in neighboring atoms to any appreciable extent, are necessary and sufficient for ferromagnetism to occur.

More recently, Zener has proposed a different explanation for the occurrence of ferromagnetism. The exchange integral, as calculated in the Heitler-London model for the bonding of two atoms, is negative. Heisenberg, therefore, was forced to postulate that the exchange integral was negative only when the atoms were brought very closely together and became positive when the unfilled d shells did not overlap appreciably. It has never been proven, however, that such a reversal in the sign of the exchange integral actually occurs. Zener has suggested that the exchange integral always remains negative and that ferromagnetism is due to an interaction between electrons occupying quantum states in the partially filled d and s zones. The proposed interaction, which accounts for the excess of parallel spin moments of one kind, similar to the interaction (Hund's rule) that causes unpaired electrons in different orbitals to have parallel spins. According to this model, an over-all decrease in the energy is obtained when the electrons occupying states in the d zones have parallel spin moments and the s-zone electrons contribute a small moment in the same direction. Because of the approximate nature of the calculations used to support the above stated competing theories, it is not possible to decide, at present which one describes most correctly the interactions responsible for ferromagnetism.

On an atomic scale, the reason for the permanent magnetic moment of Fe, Co, and Ni atoms is best understood by considering their electronic structures. Each atom has two 4s electrons and an incomplete 3d shell.



The atomic moments of these metals should be, respectively, four, three and two Bohr magnetons. The actual values turn out to be

	Fe	Co	Ni	
Atomic moment	2.22	1.70	0.61	Bohr magnetons

The no integral number of electron spins per atom determined from saturation magnetization measurements given above is explained by making use of the zone theory as follows: The 3d 4s zones of these metals overlap, as shown for the case of nickel in Fig.2.2. Since the relative occupation of these two zones is determined by the Fermi energy E_0 , it is assumed that 0.6 electron occupies states in the 4s zone and 9.4 electrons in the 3d zone. Of these, five must have one kind of spin and 4.4 the other, leaving 0.6 spin of the same kind per atom. The accuracy of this model can be readily checked by alloying nickel with copper or zinc. The substitution of a copper atom for a nickel atom introduces one additional electron in the crystal, whereas zinc introduces.

Two additional electrons. It is reasonable to expect that these electrons will prefer the lower-lying 3d states of nickel and therefore, as more copper (or zinc) is added, the magnetic susceptibility should decrease. It has been shown from saturation magnetization measurements that this is indeed the case; the magnetization becomes virtually zero when 60 per cent Cu or 30 per cent Zn is added, that is, when enough electrons are added to fill completely the 3d zone of nickel.

8.2.2 Domain Structure. The above discussion has explained why iron, cobalt, and nickel are ferromagnetic, but it has not accounted for such physical properties of magnets as, for example, the well-known hysteresis loop, relating the amount of magnetization to the strength of the applied field. Even before the atomic mechanism of ferromagnetism was clearly understood, Weiss assumed that a single crystal of iron consists of small regions or domains, within each of which the electrons have all their spins parallel, but that the spins of neighboring domains are not parallel.

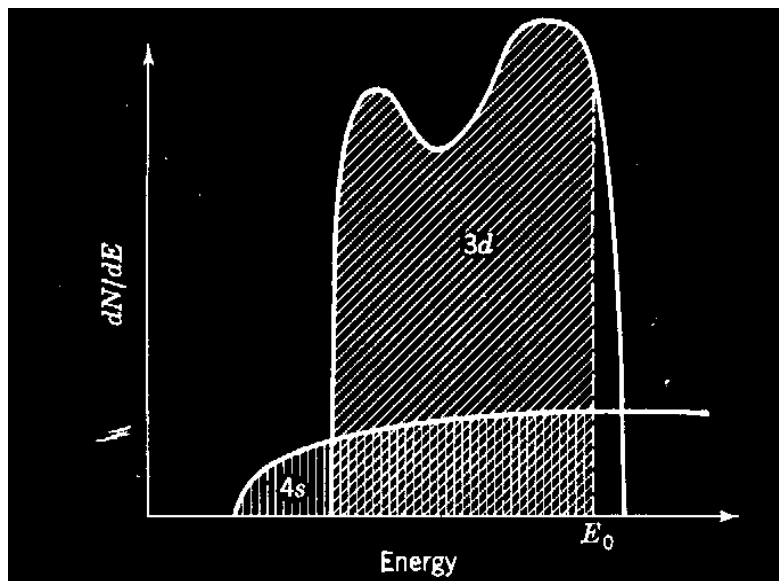


Fig. 8.2

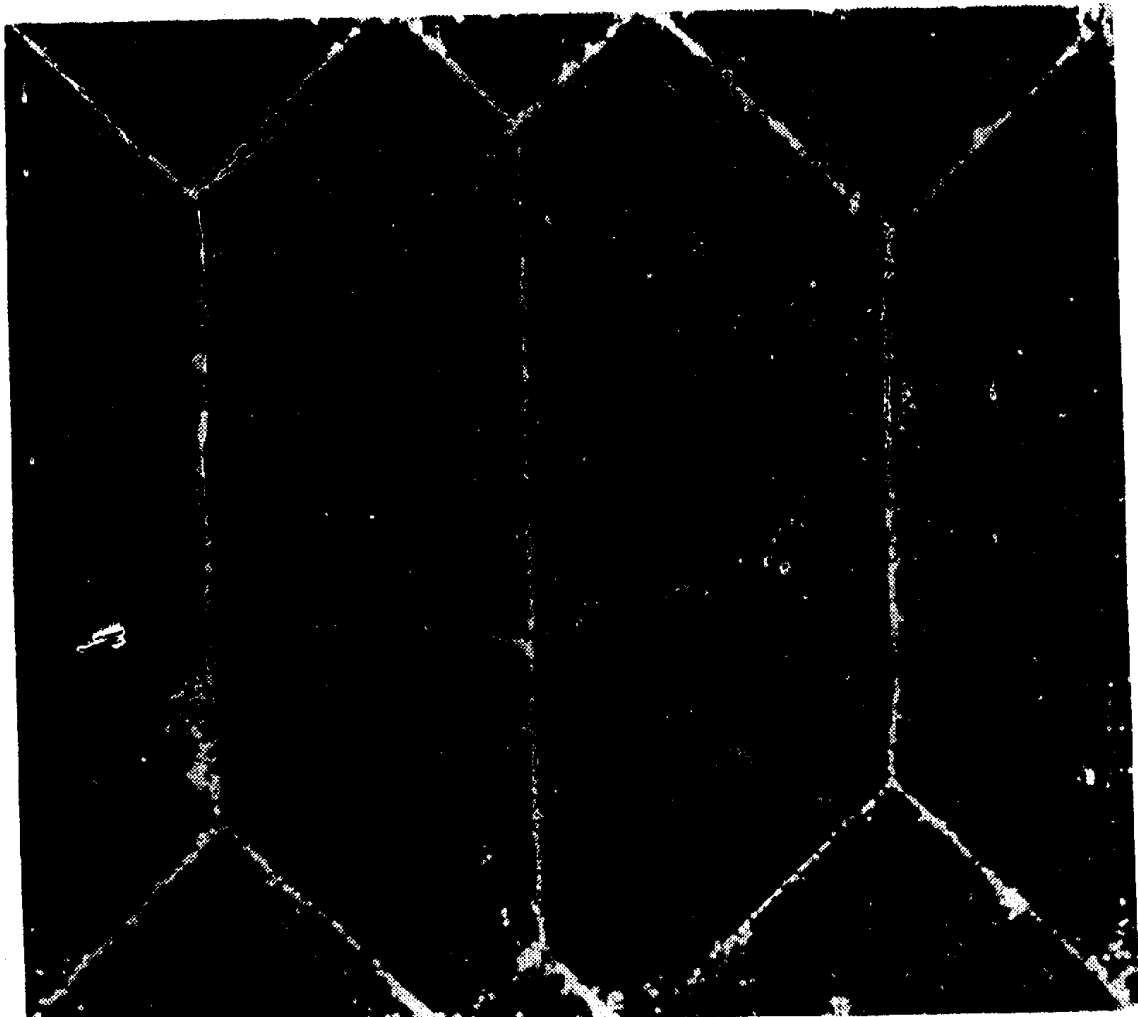
Fig. 8.2 Schematic representation of overlapping 3d and 4s states of nickel. On an average, 9.4 of the 10 available 3d states and 0.6 of the 2 available 4s states are occupied (After Slater).

When an external field is applied, the domains that have net moments parallel to the directions of the field have their energy reduced, whereas those domains that do not have their energy increased. The crystal's energy, obviously, can be lowered if all the domains align themselves parallel to the field. This can be accomplished in either of two ways. Either the direction of magnetization of an entire domain changes at once, or a domain that is favorably oriented grows in size at the expense of a less favorably oriented domain. When the external field is reversed in direction, all the domains must be reoriented, and, owing to several causes discussed below, this requires an additional field to overcome the factors opposing such reorientation so that a hysteresis loop results.

It turns out that magnetization is an anisotropic property in crystals. For example, it is easier to magnetize iron (body-centered cubic) along (100) than along any other directions, and most difficult along (111). It is common

practise to refer to these as easy and hard directions of magnetization, respectively. To show that this is a structure-sensitive property, the easy directions in nickel are (111) (normal to the closest packed layers) and the hard directions are (100). Similarly, the easy direction in the hexagonal closest packing of cobalt is normal to the hexagonal closest-packed layers. The magnetization of single crystals along certain directions is invariably accompanied by changes in their physical dimensions. For example, iron crystals expand along the direction of magnetization and contract at right angles to it so that the total volume tends to remain the same. In a nickel crystal, the dimensional changes are reversed; it contracts along the magnetization direction and expands in directions normal to it. Thus the magnetization of ferromagnetic crystals depends on the way that the structure is strained, a phenomenon called magnetostriction. As might be expected, magnetostriction is related to the elastic properties of the crystal and can be used to explain the formation of magnetic domains in crystals. With six (100) directions equally easy, it is natural that a single crystal of iron has domains containing magnetic moments aligned parallel to each of these six directions. Obviously, the domains must be separated by boundaries in which the magnetic moments undergo a gradual transformation from one orientation to the other. The exchange energy favoring parallel alignment of all moments prefers thick boundaries. It is opposed by the magnetic anisotropy, which favors a minimum deviation from the easy directions of magnetization. A compromise between these opposing forces is reached, and it turns out that the boundaries have thicknesses of the order of hundreds of atoms in actual crystals. The domains themselves can have various sizes, determined primarily by the free energy of the boundaries, whose contribution to the crystal's energy decreases with increasing domain size, since the ratio of boundary area to domain volume decreases. Lest it be deduced from this that a single crystal consisting of a single domain has the lowest possible energy, it should be realized that such a crystal is a permanent magnet whose magnetic field contains magnetic energy. Thus the domain structure proposed by Weiss serves to lower the over-all energy, thereby neutralizing the individual permanent magnets.

When a weak magnetic field is applied parallel to an easy direction of a crystal, the domains having lower energies, because of their more favorable orientation, grow in size owing to the reorientation of the moments in the boundaries. The resulting movement of boundaries can actually be observed by sprinkling a fine powder of Fe_2O_3 on a polished crystal surface. The powder particles align themselves along the domain boundaries and a so-called bitter pattern is obtained. Several domains can be seen in the Bitter pattern of a single crystal of iron shown in Fig.2.3. It has been observed that the movement of domain boundaries is impeded by imperfections and proceeds in jumps. These jumps can be made audible by surrounding the crystal with an induction coil connected to an amplifier. This so-called Barkhausen effect is even more noticeable if the domains change their magnetization directions by rotation. The latter effect becomes more



prominent when the strength of the field is increased.

Fig 8.3

In a polycrystalline material, magnetization is impeded by the random orientation of the grains. Consequently only some of the grains have their easy directions parallel to the direction of the applied field. Moreover magnetostriction in these crystallites produces strains in their neighbors which, in turn, affect the ease of magnetization in a more complicated way. Thus, if a material that is easily magnetized is desired say, for transformers, it is necessary to find one having little magnetic anisotropy or magnetostriction. Such a material does not necessarily have higher saturation magnetization, it simply reaches saturation more rapidly. On the other hand, if a permanent magnet is desired, the strong magnetostriction is an asset. This is so because, once such a material is magnetized along a given direction, it is more difficult to change its magnetization direction.

Self Check Exercise - 1

1. Using Langevin's equation, calculate the value of the constant in the equation.
2. Calculate β from $\beta = eh/4\pi mc$
3. If $x_p = 1.732$, calculate, Curie constant at 300 K.

Self Check Exercise 2

1. Discuss the ferromagnetism of Fe, Co, Ni
2. Write a note on domain theory

Model Answer

Exercise – I

$$2. \quad \beta = \frac{e \times h}{4\pi \times m \times c} = \frac{4.8 \times 10^{-10} \times 6.627 \times 10^{-27}}{4 \times 3.14 \times 9.1 \times 10^{-28} \times 3 \times 10^{10}}$$

$$= 9.27 \times 10^{-21} \text{ erg/gauss}$$

$$3. \quad x_p = \frac{C}{T}$$

$$C = x_p \times T$$

$$= 1.732 \times 300$$

$$= 5.19 \times 10^2$$

$$= 5.19 \times 10^2$$

8.3 Let us Sum Up

Langevin equation is discussed paramagnetism and Curie's law are explained. Theories of ferromagnetism (for e.g., Zener's theory are discussed in detail).

8.4 Point for Discussion

1. The Curie constant is characteristic of the material.
2. The Paramagnetic susceptibility is $\propto 1/T$
3. Zener's theory to explain ferromagnetism the exchange integral is always negative and that ferromagnetism is due to an interaction between electrons occupying quantum states in the partially filled 'd' and 's' zones.

8.5 Reference:

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LESSON – 9

CONTENTS

9.0 AIMS AND OBJECTIVES

9.1 INTRODUCTION

9.2 THERMOELECTRIC PROPERTIES

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9.0 AIMS AND OBJECTIVES

The aim of this lesson is to study the phenomenon of thermoelectricity and to learn the several applications of thermoelectric materials, such as thermoelectric generations and thermo electric refrigeration. After studying this lesson you would be able to

- i) Understand the Phenomena of Thermoelectricity
- ii) Know about the synthesis and applications of thermoelectric materials like lead telluride, bismuth telluride.

9.1 INTRODUCTION

In Several space crafts the source of electric power, is the thermoelectric material like RTG (Radio Isotope thermoelectric generator).

The thermoelectric material uses the Seebeck effect and the reverse phenomenon, the Peltier effect. The Seebeck effect converts the heat from a radioactive heat source directly into electrical energy. The Seebeck effect and the Peltier effect are the principal elements of thermoelectrics the science and technology associated with thermoelectric generation and refrigeration.

9.2.1 GENERAL PRINCIPLES AND THEORETICAL CONSIDERATION

An electric potential (Voltage) is generated with any isolated conducting material that is subject a temperature gradient, this is the absolute Seebeck effect, (ASE). The absolute Seebeck coefficient (ASC) is defined as the instantaneous rate of changes of the ASE with respect to temperature at a

given temperature.
$$ASC = \left(\frac{d(ASE)}{dT} \right)_T$$

The simple example of the way in which this phenomenon is used is to form a thermocouple composed of two dissimilar conductors, or thermoelements, by electrically joining one set of their ends. The application of a temperature difference or gradient, between the ends of the device will produce a voltage across its unpaired terminals that is a function of the temperature distribution. The resulting voltage is the relative seebeck emf, 'RSE'/. It results only from the difference between the internal potentials or ASE, within the individual conductors of which it is composed. Relative seebeck coefficient is the variation of relative seebwck emf with temperature, i.e.

$RSC = [d(RSE)/dT]_T$. The seebeck effect is not affected by Thomson or Peltier effects. Thomson and Peltier effects are present only when current flows in a thermoelectric circuit. But seebeck effect exists as long as temperature gradient is maintained, regardless of whether current flows in the circuit or not . The greatest application of the seebeck effect is in thermal electric thermometry. This results from the fact that thermoelectric circuits convert thermal energy into electrical energy. The open circuit emf obtained this means is the RSE, which can be used to measure temperature. Thermocouples composed of standardized metallic conductors are widely used for the accurate sensitive, and reliable instrument and /or control of temperature.

Peltier showed that heat is liberated or absorbed when a current crosses an interface between two different conductors. The peltier coefficient, π_{AB} is the change in the reversible heat content at the junction of conductors A and B when unit current flows across it in unit time.

$\pi_{AB} = \pi_A + \pi_B$. π_A and π_B are the absolute Peltier coefficients of the conductors. The direction in which current flows across a junction and the values π_A and π_B determine whether heat is liberated or absorbed. The peltier effect is a result of the change in the entropy of the electrical charge carriers as they cross the junction. It is not an emf in spite of the fact that π_{AB} can be expressed in energy units involving volts.

For a constant current the peltier effect is proportional to RSC, and at any fixed junction temperature, it is proportional to the current. These reversible effects are independent of the shape or dimensions of the junction. This is different from joule heating which is a function of dimensions, does not require a junction and is irreversible.

The Thomson effect is the reversible change of heat content within any single homogeneous conductor in a temperature gradient when an electrical current passes through it.

This may occur in any non-isothermal segment of a conductor. The Thomson coefficient is the reversible change of heat content within a single conductor per unit temperature gradient per unit current flow. Thomson termed it the "Specific heat of Electricity".

The Thomson effect is not a voltage. But it can be expressed in energy unit involving volts. Let the relative Seebeck emf generated by the temperature difference be E_{AB} . For a unit current flow in a thermoelectric circuit.

$$E_{AB} = \frac{d E_{AB}}{dT} T \quad (1)$$

The other energy factors in a closed thermoelectric circuit are Peltier effects and Thomson effects.

Peltier effect at the junctions. Heat absorbed at the hotter junction

$$= \pi_{AB} (T_+ - T_-)$$

Heat liberated at the colder junction

$$= -\pi_{AB} (T_+ - T_-)$$

Thomson effect within the conductors; Heat absorbed in conductor

$$Q_B = \tau_B (T_+ - T_-)$$

Heat liberated in conductor A = $Q_A = \tau_A (T_+ - T_-)$

π and τ are peltier and Thomson coefficient, respectively. It is possible to show that for a unit current flow:

$$\frac{dE_{AB}}{dT} = \frac{d\pi_{AB}}{dT} + (\tau_B - \tau_A) \quad \dots(2)$$

This is the fundamental thermodynamics theorem for closed thermoelectric circuits. It shows the relation between electrical seebeck effect and the thermal Peltier and Thomson effects.

By a rigorous analysis it is possible to show that $\pi_{AB} \sim \frac{dE_{AB}}{dT} T$... (3)

This equation is helpful in understanding the operation of peltier devices. This shows why combination of thermoelements with large peltier effects must be used for power generation or refrigeration.

9.2.2 MATERIAL PREPARATION AND THERMOELECTRIC MATERIALS

Compounds like, Bimuth Telluride, antimony telluride, lead Telluride and alloys have been synthesized and studied for their thermoelectric properties. The deviation in stoichiometry of the compound bismuth Telluride

accounts for its usefulness as a thermoelectric device. Bismuth telluride has a hexagonal cell, which is formed by the stacking of layers as;



The $\text{Te}^{(1)} - \text{Te}^{(1)}$ bonds are of vanderwaals type while $\text{Te}^{(1)} - \text{Bi}$ and $\text{Bi} - \text{Te}^{(2)}$ bonds are of ionic - covalent type. The energy gap for Bi_2Te_3 was found to be 0.16eV at 300k and 0.18eV at Ok. For example binary compounds of Bi_2Te_3 and Sb_2T_3 have been obtained by travelling heater method. In this method a molten zone passes through a polycrystalline ingot (source ingot) in a quartz ampoule sealed under high vacuum. The source ingot is prepared by the synthesis of high purity components with the stoichiometric composition of the compound to be prepared (Bi_2Te_3 , Sb_2Te_3). This method allows single crystals to be prepared at a temperature lower than the melting temperature and consequently of high quality. The transfer of the zone through the source ingot improves the purity of the material by a zone melting process. Single crystals of n and p type were grown by the traveling heater method, at different temperatures. In this preparation, the carrier concentrations on the p-type ($\sim 10^{20} / \text{cm}^3$) are greater than the n-type. It is found that the change in type occurs at about 583°C. The concentration of charge carriers is directly related to the concentration of inherent defects. These defects are responsible for deviation from stoichiometry. Sb_2Te_3 prepared by the above method shows p-type conduction. Bi_2Te_3 is a more useful than Sb_2T_3 as a thermoelectric material. Thermoelectric figure of merit is given by the relation.

$Z = \alpha^2 / (\lambda p)$, where ' α ' is the seeback coefficient λ = thermal conductivity and P = electrical resistivity.

Z is a common measure of the effectiveness of a material to function in a thermoelectric couple for heating or cooling applications various types of 'Z' meters have been developed for the measurement of figure of merit of thermoelectric materials. By measuring α , λ and P , one can calculate 'Z' for any material. For example Bi_2Te_3 (P-type) has a 'Z' value of $Z \cdot 10^{-3} = 2.2$ at

582°C. 'Z' has been found to be anisotropic. Along the 'C' axis Sb_2Te_3 has a Z value of $1.6 \times 10^{-3} \text{ K}^{-1}$.

At present solid solutions of the compounds Bi_2Te_3 , Sb_2Te_3 and Bi_2Se_3 have the highest thermoelectric figures of merit in the temperature range around room temperature. Lead telluride and alloys of Pb-Sn-Te have also been studied for thermoelectric characteristics.

9.2.3 APPLICATIONS

1. THERMOELECTRIC POWER GENERATION

Thermoelectric power generations have been employed for generating power from milli-microwatts generated in miniature thermocouple arrays integrated into a semiconductor microelectronic chip) to the multikilowatt nuclear reactor powered generators.

As detectors and sensors miniature thermocouple arrays (thermopiles) have found wide applications as pyrometers and as sensor elements used in the measurement of magnetic, radiation, chemical and mechanical signals.

Thermoelectric generator consists of a large number of thermocouples connected electrically in series to form a module the module is the basic building block of the generator.

Heat from a variety of sources is applied to one surface of the module (referred to as the hot side) and rejected at a lower temperature from the opposite surface (Cold side/Heat sink). Provided a temperature difference is maintained across the module, electrical power would be delivered to an external load. The power output from a thermocouple is approximately proportional to area and inversely proportional to the length.

The best known medical application of a miniature thermoelectric batteries is in the cardiac pacemaker thin film thermo elements, deposited on glass slides ($\text{Bi}_2\text{Te}_3 + \text{Bi}_2\text{Se}_3$ and $\text{Bi}_2\text{Te}_3 + \text{Sb}_2\text{Te}_3$) have been employed for power generation.

All of the currently available generators that operate on gaseous fuels (Propane or natural gas) are intended for stationary out door application. The output of these generators is fixed. The generators produce a constant amount of power. The thermoelectric converters used in commercial thermo electric generators use either lead telluride or bismuth telluride.

The heat sinks are usually a series of aluminium fins. The most important applications of thermoelectric generators are cathodic protection, data gathering and telecommunication. The generators usually used for cathodic protection have out puts of 60W are higher. Thermoelectric refrigerators (Peltier Cooling) are silent and have neither moving parts nor, gases to leak away. Thermoelectric refrigerators do not pollute the atmosphere as conventional refrigerator. If the thermoelectric generator is operated under conditions of maximum cooling power, the coefficient of performance is high.

Self Check Exercise -1

1. Explain Seebeck effect
2. How are Peltier and Thomson effects are different from Seebeck effect?

Self Check Exercise -2

1. Give the fundamental thermodynamic theorem for closed thermoelectric circuits?
2. Explain the term 'Z'? How can it increase?

9.3 Let us Sum Up

Seebeck, Peltier and Thomson effects are explained. Thermoelectric material synthesis is indicated. Thermoelectric figure of merit 'Z' is defined. Applications of thermoelectric materials are indicated.

Model Answers:

Self Check Exercise -1

- 2) The seebeck effect is not affected by Thomson or peltier effects. The latter are present only when current flows in a thermoelectric circuit. But seebeck effect exists as long as temperature gradient is maintained, regardless of whether current flows in the circuit or not.

9.4 Points for Discussion

- i) Absolute seebeck coefficient, thermal conductivity and electrical resistivity would decide the figure of merit of a thermoelectric material.
- ii) The utility of thermoelectric materials in power generation and applications have to be discussed.

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UNIT – IV
LESSON – 10

CONTENTS

- 10.0 AIMS AND OBJECTIVES
- 10.1 INTRODUCTION
- 10.2 N-P-RATIOS DIFFERENT TYPES OF NUCLEAR FORCES
 - 10.2.1 NEUTRON PROTON RATIO
 - 10.2.2 NUCLEAR FORCES
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10.0 AIMS AND OBJECTIVES

To learn, how neutron/proton ratio helps in the understanding of nuclear stability and to understand the basic nature of the forces that bind nucleons together

10.1 INTRODUCTION:

The packing fraction is an important concept in understanding the stabilities of nuclei. A negative packing fraction implies exceptional stability of the nucleus and a positive packing fraction suggests that the nucleus is somewhat less stable. This chapter describes the other important concepts like n/p ratio and binding energy, in understanding nuclear stability.

10.2.1 NEUTRON PROTON RATIO

A review of the nuclear compositions and masses of various nuclides has revealed a number of general rules concerning the stability or instability

of atomic nuclei. Consider the variation with increase in mass number, the ratio of neutrons to protons in the stable nuclides. The results are plotted with the number of protons (Z) on the x-axis and the number of neutrons ($A - Z$) on the Y-axis. A line is drawn at an angle of 45° , so that points lying on this line represent nuclei containing equal numbers of protons and neutrons. For elements of low mass numbers the neutron-to-proton ratio is equal to unity for stable nuclei of the 18 nuclides with mass numbers through 20, there are equal numbers of neutrons and protons in eight and a difference of only one in nine others. This exact equality is to be expected from the similarity of (P-P), (n-n) and (n-p) forces. To maintain stability the number of neutrons must exceed the number of protons. For the heaviest stable

nuclides, such as $\begin{matrix} 206 \\ 82 \end{matrix}$ Pb and $\begin{matrix} 209 \\ 83 \end{matrix}$ Bi, the ratio of neutron to proton is slightly

greater than 1.5. Each proton repels and is repelled by, all others present in the nucleus. As a result the electrostatic repulsive force grows rapidly with increase in atomic number. The total repulsive energy in a nucleus is roughly proportional to Z^2/R , Z is the number of protons and R is the radius of the nucleus. R varies as $A^{1/3}$ (A =mass number). Hence electrostatic repulsion is determined by $(Z^2/A^{1/3})$. For e.g., the repulsion energy of protons in

$\begin{matrix} 209 \\ 83 \end{matrix}$

Bi, is about ten times as great as that of ^{40}Ca ($N/P = 1$).

$\begin{matrix} 83 \\ 83 \end{matrix}$

To attain stability, the heavier elements should contain larger proportion of neutrons. The additional (n-n) and (n-p) attractive forces then compensate for the growing p-p repulsion.

Nuclei containing even numbers of both protons and neutrons are much more common than any others. Nuclei containing odd number of protons and even number of neutrons and vice versa are equally common. But those containing odd numbers of both protons and neutrons are rare. Stable nuclei contain even numbers of both neutrons and protons. Those containing both odd numbers are very unstable. Thus six nuclides ^{16}O , ^{24}Mg , ^{28}Mg , ^{28}Si , ^{40}Ca , ^{48}Ti , ^{56}Fe , constitute about 80% of the earth's crust. Thus a pair of neutrons and of protons may be regarded as constituting a sub-shell, leading to

greater stability than would be the case for incomplete sub-shell i.e., with odd numbers of nucleons.

${}^4_2\text{He}$ is highly stable (2P and 2n). But ${}^5_2\text{He}$ and ${}^5_3\text{Li}$ which contain one neutron and one proton more than ${}^4_2\text{He}$ respectively, almost instantaneously expel the extra nucleon. ${}^9_4\text{Be}$, ${}^{13}_6\text{C}$ and ${}^{17}_8\text{O}$, with one excess neutron are stable nuclides. But ${}^9_5\text{B}$, ${}^{13}_7\text{N}$ and ${}^{17}_9\text{F}$ with one excess proton are not. There are only four nuclides of the odd-odd type =

${}^2_1\text{D}$, ${}^6_3\text{Li}$, ${}^{10}_5\text{B}$ and ${}^{14}_7\text{N}$. The stability of ${}^2_1\text{D}$, has been attributed to the attraction of neutron and proton, having the same spacial co-ordinates and parallel spins. In the other three stable odd-odd nuclides, the numbers of neutrons and protons are equal, so that the extra, unpaired neutron and proton probably have the same spatial coordinates. In

${}^{19}_9\text{F}$, ${}^{23}_{11}\text{Na}$, ${}^{27}_{13}\text{Al}$, the one extra neutron, causes stability in these nuclides. Sn(Z=50) is the only element with stable isotopes (115, 117 and 119).

If the atomic number is odd, the element has few stable isotopes, never more than two. In general regardless of its atomic number no element (with exception of Sn), has more than two stable isotopes of odd mass number.

Isobars and β -decay

If there are two isobars of adjacent elements, with atomic masses which differ by a small amount, the one with the larger atomic mass will tend to disintegrate by β -decay consider ${}^3_1\text{T}$ and ${}^3_2\text{He}$. The atomic masses are 3.016049 and 3.016029 amu, respectively; the mass difference is thus only 0.00002 amu, equivalent to 0.018MeV. But tritium is radioactive, since it has the higher atomic mass, decaying to form ${}^3_2\text{He}$, with the emission of β -particle, having a maximum energy of 0.018MeV. Consider for e.g., Cd-113

and In – 113 and Sb-123 and Te-123. These pairs differ by 1 unit of atomic number. These pairs appear to be quite stable. The reason given for the stability is probably that the beta transitions are highly forbidden because of the large differences of nuclear spins. For e.g., the nuclear spin of Cd-113 in the ground state is $\frac{1}{2}$, Whereas that of ^{113}In is $\frac{9}{2}$ and the energy difference is small. It may be noted, however the negative β -decay of a 'metastable' (isomeric state) of ^{113}Cd with an estimated nuclear spin of $\frac{7}{2}$, has been observed to the ground state of In-113. It would appear therefore that Cd-113 is beta active. In the pair Sb-123 and Te-123 also a similar situation exists. Te-123 decays by orbital electron capture with a half-life of 1.2×10^{13} years.

10.2.2 NUCLEAR FORCES

i) Packing Fraction:

It is defined as :

$$\text{Packing fraction} = \frac{\text{Atomic mass} - \text{mass number} \times 10^4}{\text{Mass number}}$$

The following observation can be made when packing fraction is plotted against mass number. The packing fraction is high for elements of low mass number, apart from (He-4), C-12 and O-16), but it decreases rapidly with mass number. Then after passing through a flat minimum, the packing fraction begins to increase slowly but steadily. Negative packing fraction implies exceptional nuclear stability. On the other hand a positive packing fraction suggests that the nucleus is somewhat less stable. Nuclides He-4, C-12 and O-16 are very stable. Elements of high mass numbers having positive packing fractions are unstable and radioactive.

Determination of Binding Energies

Binding energy is a more important concept in understanding nuclear stabilities. True mass defect is obtained as follows:

$$\text{True Mass defect} = (Zm_H + (A-Z)m_n) - M$$

Zm_H is the mass of the protons and $(A-Z)m_n$ gives the mass of neutrons. M is the experimentally determined atomic mass. The mass defect may be regarded as the loss of mass or more correctly the mass which would be converted into energy, if a particular atom were to be assembled from a given numbers of electrons, protons and neutrons. The same amount of energy would be required to break up the atom into its constituent particles. Therefore the energy equivalent of true mass defect is taken as a measure of 'binding energy'.

Hence binding energy in MeV, is given by=

$$\text{Binding energy} = 931.4[Zm_H + (A-Z)m_n - M] - \text{MeV}.$$

The masses of the proton and of the neutron are respectively 1.007825 and 1.008665, amu. the atomic mass of

$$\begin{aligned} & \text{Ne, is } 19.992440 \text{ amu. } A \text{ is } 20 \text{ and } Z=10. \text{ Therefore the binding} \\ & \text{energy is } = 931.4[(10 \times 1.007825) + (10 \times 1.008665) - 19.992440] \\ & = 160.6 \text{ MeV} . 160.6/20 = 8.0 \text{ (B.E per nucleon)} \end{aligned}$$

Self Check Exercise - 1

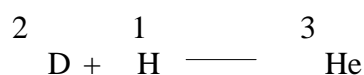
Calculate the binding energy for ${}_{83}^{209}\text{Bi}$, using the same values of masses for protons and neutrons. The atomic mass of this isotope is 208.9804 and also the B.E per nucleon.

The binding energies of some of the lighter nuclides such as ^2D and ^3He are very low, but over a very considerable range of mass numbers, the binding energy per nucleon is close to 8MeV. As mass number increases, the binding energy decreases to 7.6MeV per nucleon (say for Uranium). It is this diminution in binding energy which is the fundamental cause of the release of energy in the fission of nuclei of high mass number. Calculation of mean binding energy per nucleon indicate that α -decay is common among elements with mass numbers exceeding 210.

Nucleon – Nucleon Forces:

We have to understand the nature of forces which bind together the protons and neutrons in the nucleus. These forces are fundamentally different from the more familiar gravitational and electrostatic forces of attraction as well as from weak interactions involved in beta decay. The nucleon forces are known as short range forces, operating over very short distances only, of the order of 10^{-13}cm . The binding energy is approximately proportional to the number of nucleons. This is attributed to the saturation character of the forces between nucleons that is to say each nucleon attracts those in its immediate neighbourhood, but is relatively indifferent to the others. Thus the nucleus may be compared to a liquid drop.

Each molecule in the drop attracts those with which it is in contact but has no influence on the more distant molecules. As a result, the total energy and volume of a liquid drop are proportional to the number of molecules it contains. The same is true of atomic nuclei; the binding energy and volume are related to the mass number, i.e., the number of nucleons in the nucleus. The existence of (p-n), (p-p) and (n-n) forces of attraction can be proved by consideration of a few simple nuclei. The relative stability of the deuteron made up of one proton and one neutron shows that the (p-n) force has appreciable magnitude. Tritium contains an extra neutron. Its binding energy increases partly due to (n-n) forces. He-3 contains



contains an ${}^1_1\text{T}$ extra proton and its binding energy increases due to (p-p) forces. The binding energy of ${}^3_1\text{T}$ is greater than that of ${}^3_2\text{He}$. It would appear that (n-n) forces are larger than (p-p) forces. The interaction between two protons always involves a force of electrostatics repulsion. It looks as though that the attractive nuclear forces between two neutrons and two protons is essentially, identical. This result is referred to as the charge symmetry of the inter nucleon forces. The scattering of protons and neutrons by protons is studied with targets of hydrogenous materials. Such scattering studies indicate that (n-p), (p-p) and (n-n) forces are equal.

This principle is known as the 'charge independence' of the nucleon force. Comparison of binding energies of certain isobaric nuclides e.g., Be-10, B-10 and C-10 confirms that nuclear forces are charge independent. In B-10 however, the number of (n-p) forces is different from that in other two nuclides. Theoretical considerations indicate that if the nucleon forces are charge independent, there should be an excited state of B-10 with the same binding energy, apart from electrostatic effects, as the other nuclei in their ground states. There is evidence that such an excited state of ${}^{10}\text{B}$ exists. The remarkable constancy of nuclear densities is also in agreement with charge independent principle.

Characteristics of Nucleon Forces:

There is undoubtedly an attractive central force between nucleons. There is a force of attraction acting along the line joining the nucleons, that depends on their distance apart. This force is independent of charge, on the nucleons and is the same for all three types of nucleon pairs, namely (n-n), (n-p) and (p-p). It is a short range force that decreases sharply at distances greater than 10^{-13}cm . Its magnitude depends on the directions of the spins of nucleons. Deuteron having a nuclear spin of 'One' ($I=1$) i.e., the proton and neutron have parallel spins, is stable.

But diproton and dineutron, in which, the nucleons would have anti-parallel spins do not exist.

The magnetic properties of the deuteron can be accounted for only by postulating the existence of a 'tensor force' between the proton and neutron. The magnitude of this force depends on the directions of spin axes of the nucleons with respects to the line joining the particles; but unlike the central force, it does not necessarily act along this line.

Another type of inter-nucleon force to be considered results from the interaction of the spin and orbital angular moments. Evidence for the spin-orbit force comes from the scattering of protons by protons. The possibility of spin-orbit interaction is also indicated by the success achieved in arranging the nucleons in various groups or shells, in a nuclei. Nucleon-Nucleon repulsive force also has to be taken into account. If the forces between the nucleons were only attractive, with no repulsive forces, neither the binding energy nor the nuclear volume would be proportional to the number of nucleons. If the nucleus were to be stable, then there should be a repulsive force operating over a shorter range than the attractive force.

The Meson Field Theory of Nucleon Forces:

H. Yukawa proposed a theory of nucleon forces, based on an analogy with electromagnetic forces. The photon is referred to as the field particle of the electromagnetic field. Yukawa proposed that the (Strong) interaction between nucleons might be accounted for in a similar manner by postulating an appropriate 'field particle'. He showed that the field particle could have a mass roughly 200 times the mass of an electron. Such a particle was discovered in cosmic rays and is known as muon. But another particle heavier than muon was discovered in cosmic rays. This particle is known as pion and it is now called pi-meson.

The pion occurs in positive, negative and neutral forms and has a mass about 270 times the electron. It has properties like spin and parity which

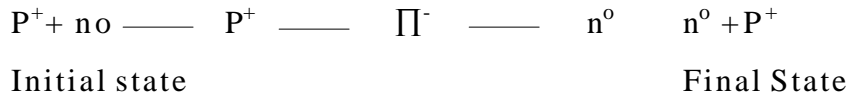
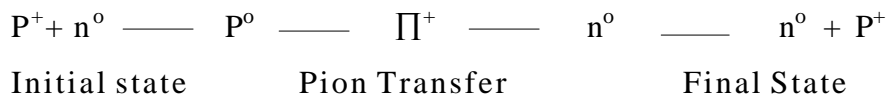
qualify to be the field particle. The theory of nucleon forces based on π meson may be stated as follows. Every nucleon is surrounded by a meson field through which it interacts with other nucleons, just as a charged body interacts with other charged bodies through an electro magnetic field. The pion then serves the same function in the meson field as the photon does in the electro magnetic field.

Interaction between the two nucleons occurs by the transfer of a pion from one particle to the other. In order to account for the existence of the meson field, it is postulated that neutrons and protons are continuously emitting and absorbing, positive, negative and neutral pions. These mesons remain free for such an extremely short time that they are undetectable and these mesons are called 'Virtual Mesons'. The meson has a mass of about 270Me. The uncertainty in energy corresponding to this is about 2.22×10^{-14} erg. Hence the time interval in which a virtual meson can exist without being detected is about 5×10^{-24} sec.

$$\begin{aligned} E \times t &= h/2\pi; & t &= \frac{h}{2\pi \times E} \\ & & &= \frac{6.63 \times 10^{-27}}{2 \times 3.14 \times 2.22 \times 10^{-4}} \\ & & &\approx 5 \times 10^{-24} \text{ sec} \end{aligned}$$

The distance a meson can travel and get remain undetected is $5 \times 10^{-24} \times 3 \times 10^{10}$ cm/s = 1.5×10^{-13} cm (3×10^{10} cm is the maximum speed of meson) This distance is close to the range of nucleon forces; hence the concept of virtual emission of mesons appears justified.

The force between a proton and a neutron could result alternatively from the transfer of a positive pion from the proton to the neutron and the transfer of a negative pion from neutron to proton.



i.e., the positive proton is converted into a (neutral) neutron and vice versa, leaving the combination unchanged. In such a change from one nucleon to the other, the spin angular momentum is conserved. Experimentally it is known that the spin of Pi-meson is zero. (Neutron and proton each have a spin of $\frac{1}{2}$). The interaction of a Pi-meson field is called strong interaction. Coupling constant calculations shows that for the pion-nucleon field, the value of the coupling constant is about 15. It is about 2000 times greater than the coupling constant of an electromagnetic field.

Repulsion has been accounted for by the transfer of two or three pions between nucleons.

Self Check Exercise 2

i) Discuss the concepts of

- 1) N/P ratio and
- 2) Binding energy

ii) Discuss in detail the different types of nuclear- nucleon forces.

10.3 Let us Sum Up

Packing fraction and binding energy calculations are explained. N/p ratio and like different types of nucleon forces are discussed. Meson theory is also discussed.

10.4 Points for Discussion

- i) Packing fraction and binding energy curves.
- ii) N/P ratio and the stabilities of nuclei
- iii) Nucleon – Nucleon forces-strong interaction pions and heavier mesons.

10.5 References

- 1) Atomic physics – J.B.Rajan. S.Chand & Co, New Delhi.
- 2) Source book on atomic energy – Glass tone
East-West press, New Delhi.

LESSON – 11

CONTENTS

11.0 AIMS AND OBJECTIVES

11.1 INTRODUCTION

11.2 NUCLEAR STRUCTURE

11.2.1 LIQUID DROP MODEL

11.2.2 SHELL MODEL

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11.0 AIMS AND OBJECTIVES

To study and understand the behaviour of nucleus on the basis of different types of models proposed for the nucleus.

11.1 INTRODUCTION

The forces between the nucleons could not be explained quantitatively and hence several models have been proposed for the nuclear structure. The liquid drop is discussed first and then the shell model, representing a diametrically opposed point of view, can be discussed. The collective and unified models. Combine certain features of the other two models.

11.2.1 LIQUID DROP MODEL

Since the binding energies and volumes of nuclei are approximately proportional to the number of constituent nucleons, (indicating saturation character) the nucleus has been compared to a drop of liquid. N.Bohr proposed the liquid drop model of the nucleus to explain nuclear reactions on the basis of compound nucleus theory. According to this model, each nucleon

in a nucleus interacts with adjacent nucleons, in the same manner as molecules in a liquid. Hence any excess energy of a given nucleon would be very rapidly shared among the other nucleons. The energy levels of the nucleons are thus regarded as quantum states of the nucleus (or liquid drop) as a whole, rather than of a single nucleon. The application of the liquid drop model in nuclear fission has already been considered. Other achievements of the model related to nuclear binding energies and the properties of isobars will now be considered.

calculation of Nuclear Binding Energies.

Since nuclear forces are of a short range character each nucleon will be held strongly by those in the immediate vicinity. But each will be unaffected by the others. As a result, to a first approximation, there will be an attractive (or volume) energy, proportional to the number of nucleons in the nucleus; in other words the energy term will vary approximately as the mass number, A . This energy can be represented as $a_1 A$, where a_1 , is a constant. This value of energy of attraction is correct when the number of protons is equal to the number of neutrons. But most nuclei contain an excess neutron. These extra neutrons are inevitably in higher quantum states, than the other nucleons and they contribute a smaller amount (Per nucleon) to the total binding energy. Statistical calculations indicate, the energy corresponding to this 'asymmetry effect' or composition effect, can be represented as $-a_2 (A-2Z)^{2/A}$, where $(A-2Z)$ is the neutron excess and ' a_2 ' is a constant. Long range electrostatic forces due to repulsion of protons, decrease the binding energy by a quantity proportional to $-a_3 (Z^2/A^{1/3})$, where ' a_3 ' is a proportionality constant.

The nucleon at the surface of the nucleus will be less tightly bound than those in the interior. The binding energy is reduced by an amount, proportional to the surface area of the nucleus. This 'surface effect' is given by the term $-a_4 A^{2/3}$ ($A^{2/3}$ is the area). The influence of even or odd-odd nuclei can be represented a term $= \pm a_{5/A}$ + sign corresponds to even-even nuclei and - sign to odd-odd type.

by adding all the above mentioned terms, the binding energy B.E can be written as:

$$\text{B.E.} = \frac{a_1 A}{A} - \frac{a_2 (A-2Z)^2}{A^{1/3}} - a_3 Z^2 - a_4 A^{2/3} \pm \frac{a_5}{A} \quad \text{---- (1)}$$

the five constants must be known for calculating B.E. a_1 can be obtained from electrostatic theory. The other four constants are empirical and can be obtained from experimental data. Differentiating with respect to Z and equating to zero, ' a_2 ' can be calculated. a_5 is zero for an odd-even or an even-odd nuclei, the two remaining constants, and a_4 can be calculated from the known binding energies of any two nuclides of this type. The spin-effect constant a_5 is obtained empirically from binding energies of even-even nuclei.

Inserting these constant in equation (1) we have:

$$\text{B.E. (MeV)} = 15.75A - 23.7 \frac{(A-2Z)^2}{A} - 0.710 \frac{Z^2}{A^{1/3}} - 17.8A^{2/3} \pm \frac{130}{A} \quad \text{.....(2)}$$

The relative effects of the various factors on binding energy can be seen by performing calculations for nuclides of low, medium and high mass numbers.

40

Ca, B.E. per nucleon is about 8.52MeV.

20

The estimated binding energies for

40	120	238	
Ca	Sn and	U	are
20	50	92	

342, 1019 and 1805MeV, compared with values 342, 1026 and 1800 MeV, respectively derived from atomic masses.

Self Check Exercise – 1

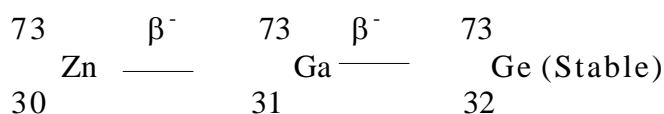
Calculate the binding energy/nucleon for ${}_{50}^{120}\text{Sn}$ and ${}_{92}^{238}\text{U}$ using the above equation and tabulate the values corresponding to the different effects.

The Values agree well with the observed binding energies upto three significant figures.

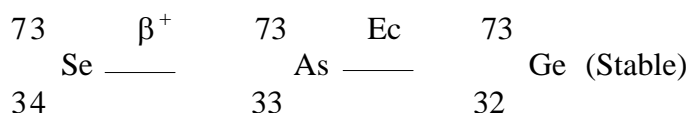
For elements of high atomic number, the decrease in binding energy/nucleon is mainly due to the marked increase in the electrostatic repulsion of the protons. This is responsible for the α -particle emission, by elements of high atomic numbers and also for the liberation of energy accompanying nuclear fission.

By plotting the binding energy against atomic number, of nuclides of odd mass numbers, a parabolic curve can be obtained. All isobaric nuclides whose binding energies are less than that of the stable nuclides, will lie on the two arms of the parabolic curve. They will be unstable and decay in an appropriate manner. The nuclides of lower atomic numbers (on the left arm of parabola) would exhibit negative β -decay.

For e.g.,



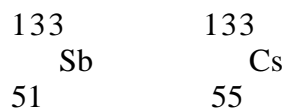
Isobars on the right arm of the parabolic curve have more protons and decay either by the emission of positron or by electron capture.



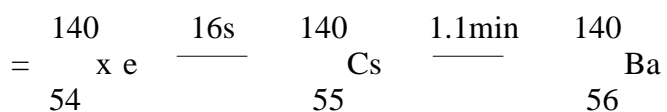
For isobars of even mass number, the results are different due to the inclusion of the odd-even (spin effect). For all nuclides with even numbers of protons and neutrons, the binding energy is increased, and for those with

odd numbers of protons and neutrons, it is decreased. This indicates that no stable odd-odd nuclide should exist. For isobars of odd mass numbers, the instability is greater and hence the half life should be shorter.

In a chain of β -disintegration, the half-life increases regularly as stability is approached. For e.g., in the chain (β -decay)



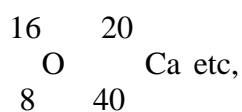
(stable) – the half life increases from 2.3min to 5.3days as Cs is approached. For even mass numbers also a similar effect is noticed



11.2.2 NUCLEAR SHELL – MODEL

This model is sometimes referred to as 'independent particle model'. It is based on the fact that there are specific numbers of protons and neutrons, generally known as magic numbers or shell numbers, for which the nuclei exhibit exceptional stability. This is like atoms containing certain numbers of closed shells of electrons. T.H.Bartlett indicated the possibility that nucleons might occupy quantum groups or shells just as electrons in an atom.

It was pointed out that the concept of nuclear shells could explain the magnetic moments of nuclei. Magic numbers of nucleons are 2,8,20,50,82 and 126. These apparently represent closed shells in the nucleus. Elements having the largest numbers of stable isotopes are those containing 20 and 50 protons or 20, 50 and 82 neutrons. Sn-50 has ten isotopes and also three isotopes of odd mass numbers (115,117 and 119). The more abundant nuclides in the universe are those with magic numbers of neutrons or protons



Nuclides containing magic numbers of neutrons, have small cross sections for neutron capture (they are stable). When the neutron numbers are 50,82 or 126, the cross sections for neutron capture are much lower for 1MeV neutrons.

Similarly for thermal neutrons, extremely low cross sections for (n, γ) reaction are observed, when the nuclei contain 20, 50, 82, or 126 neutrons.

Excited nuclides $\begin{matrix} 17 & 87 & 137 \\ & \text{O} & \text{kr} & \text{xe} & \text{lose neutrons} \\ & 8 & 36 & 54 \end{matrix}$

readily to get the magic number of neutrons. The alpha particle energy is exceptionally large, when the decay product (daughter nuclide), belongs to the magic number category, during the radioactive decay of the heaviest nuclides.

The end products of the four radioactive series,

$\begin{matrix} 206 & 207 & 208 & & 209 \\ \text{Pb} & \text{Pb} & \text{Pb} & \text{and} & \text{Bi} \end{matrix}$, contain magic numbers.
 $\begin{matrix} 82 & 82 & 82 & & 83 \end{matrix}$

The following also can be correlated with the special stability of magic numbers.

- 1) High binding energy of the last neutron in such nuclides.
- 2) The departure of the total binding energy determined from the atomic mass from that calculated using equation (2)
- 3) α - particle emission among isotope of certain elements of medium mass number.
- 4) The non existence of stable isotopes of elements – 43 and elements – 61.
- 5) The variation of quadruple moments with the numbers of neutrons and protons.

Hence the behaviour of atomic nuclei, can be correlated with excess or deficiency of nucleons, with respect to closed shells of magic numbers just as

the chemical and spectral properties of atoms are dependent on excess or deficiency of electrons.

In the shell model each nucleon is essentially independent of the other. The other nucleons provide the potential energy field which determines the quantum states and hence the numbers in closed shells. In the shell model the coupling (l-s) concept is employed to account for the total number of nucleons (magic numbers) in different shells. Each 'l' levels is split into two sublevels characterized by the j term.

$j=l+1/2$ and $j=l-1/2$ (except $l=0$). Each of these sublevels can accommodate $(2j+1)$ neutrons and $(2j+1)$ protons. For eg., when $l=1$, $j=3/2$ and $1/2$ $(2j+1) = (2 \times 3/2 + 1) = 4$ nucleons with $j = (3/2)$ and $(2j+1) = (2 \times 1/2 + 1) = 2$ nucleon with $j = 1/2$, written as $(3/2)^4$ and $(1/2)^2$; arranged in this manner each shell can have a magic number of nucleons such as 2,20,50,82, and 126 $l=0$ will have '2' nucleons $l=1$ will have 8 nucleons etc

The spin of a nucleus with odd mass number, in the ground state should

123

depend only on the odd nucleon. The nuclide Sb has one proton beyond

51

the closed shell of 50 and its spin is $7/2$, as expected $l=4$ and $j=l-1/2 = 4-1/2 = 7/2$.

The shell model gives a qualitative interpretation of the observed nuclear magnetic moments, by relating this property to the j value of the odd proton, certain groups of two or three isotopes of odd atomic number and odd mass number have identical spins and closely similar magnetic moments e.g. ^{107}Ag and ^{109}Ag ; In - 113 and In - 115;

The quadrupole moment is a measure of the deviation of the charge distribution, in a nucleus from the spherical form. Nuclei with closed shells of nucleons should have a spherically symmetric charge distribution, and therefore zero quadrupole moment. Experiments indicate that this is true.

For nuclei beyond closed shells, the quadrupole moment is negative. The quadrupole moment of an odd proton is not very different from that caused by an odd neutron. The shell model predicts that a proton would produce a greater distortion in the spherical charge distribution and give a larger quadrupole moment. This is a failure of the shell model.

11.2.3 Collective and unified model

This model differs in a fundamental respect from the independent particle model by postulating, a mutual interaction between nucleons. As a result of the collective or co-operative action among the particles, the nucleus behaves like a drop of liquid and may suffer permanent deformation. The deformation is not stationary. This travels around the nucleus producing motions which are equivalent to oscillations and rotations of the nucleus as a whole. The collective model requires a distortion of the nuclear core, and an associated quadrupole moment, when the odd particle is a neutron. When the numbers of nucleons are in between the values for closed shells, the collective model predicts larger quadrupole moments than expected from the independent particle model.

On the basis of collective models, the nuclear-rotational energy levels have been postulated. The levels have integral values of rotational quantum number. Consider the nuclei with mass number from 150 to 190 (and over 220). They lie between closed nucleon shells, such nuclei, with large deformation, have their nuclear rotational energy levels very close.

For nuclei with numbers of nucleons, near to closed shells, the spacing of rotational energy levels are large. In such nuclei, the vibrational energy levels should also be considered. Vibrational and rotational energy levels are superimposed, like ordinary molecules.

Rotational energy values for Pu-238 have been determined and are very close to the theoretical ratios of the energies.

The unified model of the nucleus is an attempt to combine the desirable features of both the concepts. According to this model the individual nucleons move in a potential field that can be deformed, especially in the regions between closed shells. Because of this distortion, the order of filling of the nucleon quantum states is often different from that required by the independent particle model. Other states have also been introduced to explain the various energy levels. These are known as "Nilsson States". Thus this model has been able to explain the behaviour of nuclei, such as magic numbers, spins, quadrupole moments, low energy excited states etc.

Self check exercise –2

1. Discuss the liquid drop model and indicate how binding energies can be calculated on the basis of this model.
2.
 - a) Write an account of the magic numbers.
 - b) Discuss the shell model on the basis of closed shells of magic numbers.
3. Write a note on collective model.

11.3 Let us Sum Up

The different types of nuclear models are discussed in details. Their successor and failures in explaining the behaviour of nucleus are also indicated. Calculation of binding energy and the various effects involved is illustrated.

11.4 Points for discussion

- 1) Different types of nuclear models and their successes and failures in explaining the behaviour of nucleus
- 2) Calculations of binding energies and the various effects involved.

11.5 References

- 1) Source book on atomic energy. Glass tone – East West press – New Delhi.

LESSON-12**CONTENTS**

12.0 AIMS AND OBJECTIVES

12.1 INTRODUCTION

12.2 NUCLEAR PARTICLES

12.2.1 NEUTRON

12.2.2 ELEMENTARY PARTICLES

12.3 LET US SUM UP

12.4 POINTS FOR DISCUSSION

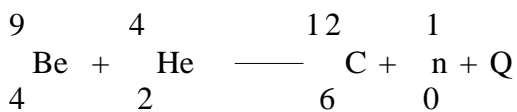
12.5 REFERENCES

12.0 AIMS AND OBJECTIVES

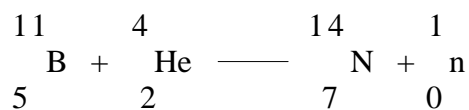
The aims and objectives of this lesson are is to learn, the discovery of neutron and understand a few other elementary particles.

3.1 INTRODUCTION

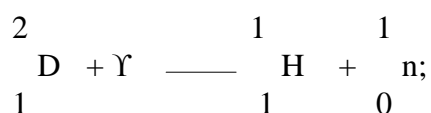
This lesson describes the discovery and properties of neutron. A few elementary particles such as mesons etc are also described. The primary radiation arising from the bombardment of 'Be' by α - particles was thought to be γ -rays. But Chadwick proved that the particle obtained in the above reaction was uncharged, with a mass approximately that of the proton.

**3.2.1 NEUTRONS**

Chadwick obtained the mass of the neutron using the reaction:



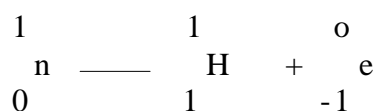
Since the atomic masses of the nuclides B-11, He-4 and N-14, are known the mass of the neutron can be calculated using the Q value of the reaction. The α -particle (He-4) obtained from polonium had an energy of 5.25MeV. The mass equivalent of this will be 0.00565amu 'Q' of the reaction in mass unit = -0.00154. For B-11, He-4 and N-14, Chadwick used the values of 11.00825 amu, 4.00106 and 14.0042 amu respectively. From the Q value and the other atomic masses, Chadwick obtained a value of 1.0067amu. For the neutron mass. From the reaction.



more accurate value of the mass of the neutron was obtained as 1.00867am. In the C-12 scale the value is 1.008665amu.

Radioactivity of the Neutron:

In the β -decay, a neutron is converted into a proton and an electron together with an antineutrino. If the mass of the antineutrino is zero then,



would involve an energy release of 0.782MeV.

1.008665 amu (for 1 n) and 1.007825 amu for proton i.e., (1.008665-
0
1.007825)= 0.000840amu.

This corresponds to the energy of 0.782MeV. Since the energy is released in this reaction, it would occur spontaneously. The half-life for this β -decay can be shown to be about 20min. Experimental values of half-life has been found to be 700sec. This is in agreement with the calculated value (~20min). Hence it can be proposed that the free neutron is radioactive and disintegrates with the emission of an electron, leaving proton as a residual particle.

Diffraction Neutrons

Neutrons like other particles (proton, α -particle etc) should exhibit diffraction. In other words neutron should have wave properties like electrons, in accordance with Debroglie's relation $\lambda = h/mv$.

Experimentally neutrons were found to be diffracted by crystals like sodium chloride, like X-rays. The energy 'E' of the neutron is kinetic energy equal to $\frac{1}{2} MV^2$; $\lambda = h$

$$\sqrt{2mE}$$

$$\lambda = \frac{6.627 \times 10^{-27}}{\sqrt{2 \times 1.67 \times 10^{-24} \times 1.6 \times 10^{-12} E}}$$

$$1.67 \times 10^{-24} = m \text{ (mass of neutron)}$$

$$\lambda = \frac{2.87 \times 10^{-9}}{\sqrt{E}} \text{ cm, where 'E' is in electron volts}$$

For neutrons to be diffracted λ would have to be 2×10^{-8} cm and hence neutrons having 0.02ev would exhibit diffraction phenomenon with crystals.

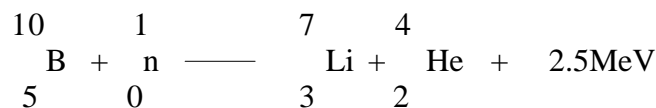
Self Check Exercise – 1

Calculate the wavelength of neutron having an energy of 0.06ev. Compare this with that of an electron, having the same energy.

X-ray diffraction depends only on the number of orbital electrons of the atom. Hence it is not feasible to detect positions of hydrogen and other light atoms, by X-rays. In the diffraction of neutrons, however, it is in the scattering by the nucleus, which determines the extent of diffraction. In this respects, the effect of hydrogen, is quite considerable. Hence neutron diffraction makes possible the location in crystals of hydrogen and other light atoms. Alloys of cu and Ni are studied easily by neutron diffraction.

A fair yield of neutron can be obtained by (α, n) reaction with Beryllium.

$^2\text{D} (\gamma, n)^1\text{H}$ and $^9\text{Be} (\gamma, n)^8\text{Be}$ have been largely used to produce neutrons. These are photo neutron reactions. Slow neutrons can be detected by their reactions with B-10;



This energy is carried off by Lithium and alpha particle. These produce considerable ionization in their tracks. By using a chamber of suitable and using enriched B-10, every neutron entering the chamber can be counted by a counter.

3.2.2 ELEMENTARY PARTICLES

i) Antineutron

The antineutron, like the positron and antiproton, however would not be a constituent of ordinary matter. After the availability of a fair source of antiprotons, antineutron was discovered. When a proton and antiproton, meet mutually annihilation takes place. If the two particles come fairly close to each other, although not close enough for annihilation to occur, it is possible for electric charge to be transferred from positive proton to the negative antiproton or vice versa. Because of this both particles would become electrically neutral.



Antiprotons produced by means of Bevartron, were allowed to enter a vessel of liquid hydrogen. About three out of every thousand antiprotons interacted with hydrogen to form antineutron. The neutron annihilated the antineutron produced, and energy was released. A flash of light in a detector accompanied the release of energy. Although neutron is electrically neutral, it has the properties of a small magnet, associated with a spinning negative charge. It is possible that the neutron has some structure in which, an electrically charged centre is surrounded by a region of opposite charge. It can be assumed then, while spinning in the same direction, the neutron and antineutron will produce oppositely directed, magnetic fields. It has been established that an antineutron can exist so that there is an attractive force between antiproton and antineutron.

ii) Muons and Mesons:

The existence of both positive and negative particles having masses heavier than electrons and lighter than protons, in cosmic rays was established. These particles were produced in the laboratory and were found to have a mass about 206.8times that of an electron.

These particles are now known as "muons' (μ^- particles) Both positive and negative muons are singly charged particles. They carry a charge positive and negative equal in magnitude to that of an electron.

A negative muon interacts with a proton in an atom producing a neutron plus energy. If this does not occur within 2×10^{-6} seconds, negative muon breaks down spontaneously into an electron, together with a neutrino and antineutrino, and energy. Mean life time of a negative muon is about 2.3×10^{-6} seconds. Positive muon does not generally interact with matter. It has the same mean life time as negative muon. It decays to positron and energy.

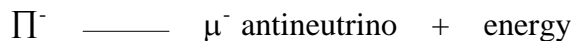
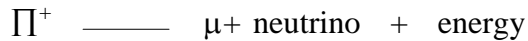
μ^+ (or μ^-) \longrightarrow e^+ (or e^-) + neutrino + antineutrino + energy

Pi-Mesons (or pions)

Pions having masses intermediate between the electron and proton were found in cosmic rays. These particles called pi(or Π) Mesons have also been produced in the laboratory. They occur in three forms Π^+ , Π^- and the third is electrically neutral, Π^0 . Π^+ and Π^- mesons have masses 273.2 times heavier than electron. Π^0 is lighter (264.3 times that of electron) $\Pi(-)$ interacts with proton more readily than μ^- to form a neutron.



They decay giving muons thus:



Π^+ and Π^- mesons have a mean life time of 2.6×10^{-8} sec (less than 100 times that of a muon) Π^0 mesons have a very short life and hence are not observed in cosmic rays. In the laboratory Π^0 was produced by bombarding Beryllium, carbon or other element with protons of high energy. Neutral pion has a lifetime of 10^{-16} seconds. Π^0 decays very rapidly; all its mass is converted into energy. In Π^0 , the particle and antiparticle are indetical.

K-Mesons or KAONS

Another particle having mass between electron and prton It is the Kmeson or kaon. K-meson exists as positive and negative and in two neutral forms. The charged K-mesons have the same mass, namely 966.6 electron masses. They have the same life time: 1.2×10^{-8} sec. Each type of charged kaon can decay in six different ways, the products being pions, muons, sometimes with e^- or e^+ and a neutrino (or antineutrino) negative kaons can inter act readily with protons in atoms.

12.3 Let us Sum Up

i) Neutron; its discovery and different types of neutron reactions are discussed. Neutron diffraction method is explained.

ii) Elementary particles like a) antineutron; b) muons and mesons; c) pions; d) kaons are discussed.

12.4 Points for Discussion

1) Write notes on:

a) Neutron its discovery, reactions and diffraction methods.

b) Different types of elementary particles.

12.5 References

1) Source book on atomic energy. Glass tone – East West press – New Delhi.

UNIT – V

LESSON – 13

CONTENTS

13.0 AIMS AND OBJECTIVES

13.1 INTRODUCTION

13.2 ALPHA, BETA, GAMMADECAY, NUCLEAR ISOMERISM

13.2.1 ALPHA, BETA-AND GAMMA DECAY – THEORIES

13.2.2 NUCLEAR ISOMERISM

13.3 LET US SUM UP

13.4 POINTS FOR DISCUSSION

13.5 REFERENCES

13.0 AIMS AND OBJECTIVES

The aims of this lesson are to study and understand the theories concerned with the decay of α , β and γ particles. After going through this lesson you would be able to learn the existence of nuclear isomers.

13.1 INTRODUCTION

Radio elements either in the pure state or as compounds emit radiations quite spontaneously and without any preliminary treatment. In this lesson, the properties of α , β and γ rays would be reviewed and theories of concerned with the decay of these particles would be studied. In the magnetic field γ - rays are not affected at all, the β - particles are considerably deflected and the direction of, deflection indicates that they are negatively charged. The α -rays are also deflected in a magnetic field and the direction of deflection indicates they are positively charged. Certain radio elements emit α -particles which are identified with Helium nuclei. Since outside the nucleus except nothing electrons exist, the α -particles must be supposed to proceed out of

the nucleus itself. β -particles identified with electrons should also arise from the nucleus. The emission of β -particles is irreversible and the β -decay gives rise to a new atom, which is different from the parent atom. Hence β -particle cannot be extra nuclear electron. γ -rays have been identified with electromagnetic radiation. γ -rays emitted are of extremely short wave length. Any radiation of shorter wavelength, as at least some of the γ -rays are, must therefore come from nucleus.

Another type of radioactive decay i.e., by isomeric transition, has been brought to light by a study of artificial radionuclides, although it is actually an aspect of the familiar gamma-ray emission. F.Soddy predicted the existence, of isobaric isotopes having different radioactive properties. Substances of this type have become known as nuclear isomers. The phenomenon is known as nuclear isomerism.

THEORY OF ALPHA DECAY

In experiments on the scattering of α -particles, it was found that even the fastest of such particles from radioactive sources, having an energy of 10MeV, are generally repelled by atomic nucleus. It is an undoubted fact that radioactive nuclei emit alpha particles, hence such particles must be able to exist, at least for a short time within such nuclei. The interaction between a radioactive nucleus and an alpha particle (inside or outside the nucleus) can be understood by a potential energy diagram i.e., a plot of potential energy vs distance from centre of nucleus. The diagram shows increasing electrostatic repulsion of an alpha particle as it approaches the nucleus. The sharp fall in potential energy indicates the region within the nucleus. This implies attraction of the alpha particle by the nucleons in the nucleus. The potential barrier represents a repulsive force. It can be shown that the force of repulsion between a proton and a nucleus is less than for an alpha particle, whereas there is essentially no repulsion between a nucleus and a neutron. Calculations indicate that an alpha particle must have an energy of 25MeV to

get into the nucleus from outside. Therefore an alpha particle must have the same out of energy to escape from the nucleus.

In other words a potential barrier prevents the escape of the α -particle from the nucleus. But α -particle are produced from radioactive sources with energy as low as 4 MeV, and for no natural element does the α -particle energy exceed 10.6MeV. wave mechanics shows that there should be a definite, if small, probability that such a particle from the interior will be found outside the nucleus. In other words, there is a definite probability that the alpha particle will escape from the nucleus even when its energy is less than that of the top of the hypothetical barrier.

It follows, therefore, that greater the energy of the alpha particle in a radioactive atom, the more likely is it to be found outside the nucleus. This is the fundamental basis of the fact that radio elements which disintegrate rapidly emit alpha particles, of high energy and long range, whereas the long lived elements produce particles of relatively low energy and short range. An approximate value of the frequency with which alpha particles reach the exterior surface of the nucleus can be obtained by dividing the radius of the nucleus by the estimated speed of the alpha particle. If this frequency expressed as the number per second is multiplied by the probability of escape, the result would give the frequency with which alpha particles actually escape. The value of λ (decay constant) will in general be larger the greater the energy of the α -particle. Using simplifying assumptions, the wave mechanical treatment leads to a relationship between the decay constant, λ and the energy of the alpha particle. This equation is similar to the Geiger Nuttall rule.

$\log \lambda = \frac{3}{2} A \log E_0 + B^1$. 'A' is the slope when $\log \lambda$ is plotted against E_0 . B^1 is a constant for each radioactive series. The wave mechanical theory of α -decay shows that for naturally occurring radio elements, the energy of the alpha particle must be at least 3.8MeV, if the decay constant is to be

greater than $10^{-20} \text{ sec}^{-1}$. Thorium with a half life of 1.39×10^{10} years emits alpha particles with the lowest energy, 4 MeV.

Assuming the radius of the nucleus is about 10^{-12} cm and the speed of the alpha particle moving in the nucleus as 10^8 cm/sec , then an alpha particle would find itself at the exterior of the nucleus. $10^8/10^{-12} = 10^{20} \text{ time/sec}$.

If the decay constant say for Th-C' is 10^7 sec^{-1} , then the alpha particle escape probability would be:

$$10^{20} \times \text{escape probability} = \lambda$$

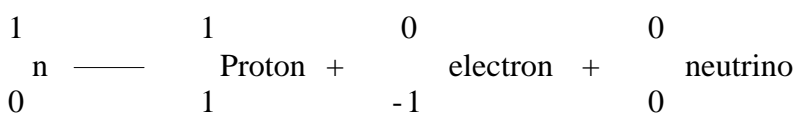
$$10^{20} \times \text{escape probability} = 10^7$$

$$\text{then escape probability} = 10^7/10^{20} = 10^{-13}$$

This means even with a very short-lived radio element Th-C', an alpha particle with an energy of 9 MeV, makes on the average, 10^{13} attempts to escape from the nucleus. For Th the escape probability is $1/10^{38}$

THEORY OF β -DECAY

When the energy of β -particles is plotted against the number of β -particles emitted a maximum is observed (E_{max}). From the energy distribution it can be shown that the average energy of the β - particles from a given source is considerably less than the maximum energy. Energy considerations during the emission of β -particles indicated that the electrons which are emitted as β - rays by radioactive nuclei must result from the spontaneous conversion of a neutron into a proton and electron. Pauli suggested that this process was accompanied by the emission of another particle, called a neutrino, this was assumed to be electrically neutral and to have very small rest mass, compared to that of the electron.

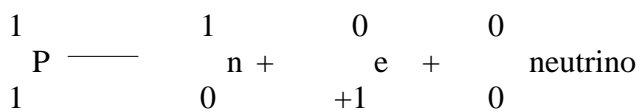


In the β -decay process the proton remains in the nucleus, but the electron and neutrino are ejected. In order to account for the continuous distribution of energy among β -particles Pauli suggested that the total available energy, equal to E_{\max} , was divided between the electron (β particle) and the neutrino. Thus the difference between E_{\max} and the actual value for any β -particle would be carried off by neutrino. If a spin quantum number of $\frac{1}{2}$ is assigned to neutrino, spin can be conserved in the conversion of a neutron into a proton and electron (β - particles).

β -decay is an example of the phenomenon known as weak interaction in contrast to the stronger electromagnetic interaction and the even stronger interaction between nucleons. For emission of β -particles no barrier exists and relatively long half lives are accounted for by the weakness of the interaction between the neutron and proton with the electron – neutrino field.

POSITIVE β -DECAY:

Nuclei having too many protons, for stability emit positive β -particles, called positrons.



The energies of positive β - particles have a continuous distribution of energy. The emitted neutrino shares energy with positron and also conserves spin.

GAMMA RAY EMISSION

Gamma rays are electromagnetic in nature like other radiations, one might say these rays emitted by radioactive nuclei are merely the excess of energy radiated away in the form of quanta by the excited nucleus returning to a more stable state-Experiments indicate that this is actually the case. The γ -ray emission is usually accompanied by α or β - disintegration, of a radioactive nucleus. Owing to the emission of α or β particle from the

nucleus, the nucleus becomes excited and hence transition can take place from this excited state to another of lower energy with the consequent emission of the excess of energy as a γ -ray. If there are several lower states transitions may take place to these states giving rise to γ -ray spectra. γ -ray spectrum has been experimentally observed. Certain atoms are known to disintegrate without emitting γ -ray e.g, RaE emits β -particles without γ -ray emission. After the β - particle is ejected the resulting product nucleus is left in an excited state, which therefore returns to the normal state by the emission of γ -rays. As regards the γ -rays associated with α disintegration, there are reason to believe that the γ -rays may be emitted either before or after the departure of α - particles.

INTERNAL CONVERSION OF GAMMA RAYS.

Information concerning gamma ray energies has been obtained from the phenomenon now known as 'internal conversion'. In emerging from a nucleus the γ -ray (photon) may produce a kind of photo electric effect with one of the orbital (or extra nuclear) electrons of the same atom. As a result, the energy of the photon is transferred to the electron. The γ -ray is then said to be 'internally converted'. The electron which interacts with the γ -ray photon is ejected from the atom with kinetic energy 'E-P' where 'E' is the γ -ray energy and 'P' is the binding energy of the electron in the atom of the element emitting the γ -radiation. This is presumed to be the daughter element in the given disintegration. If the ejected electron came from the K-level of the atom then, 'P' can be replaced by E_k . E_k is the energy of the K-line of the characteristic X-rays of the daughter element. Hence kinetic energy of the ejected electron is $E - E_k$. If the electron comes from the L-Level, then kinetic energy of the ejected electron is $E - E_L$.

As a result of internal conversion a number of groups of electrons having discrete energies are emitted. Because of their definite energies, the internal conversion electrons are said to give a line spectrum, which is super imposed upon the continuous spectrum of beta particles. As a general rule

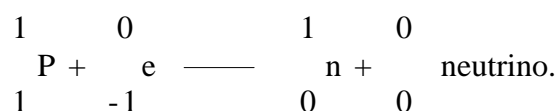
only a small proportion of the γ -ray photons have their energies internally converted. The fraction of the energy so converted, called the internal conversion coefficient depends on the energy of the gamma rays.

The energies of the internal conversion electrons have been determined by the magnetic spectrograph. If to these are added the energy values for the appropriate K,L etc., lines of the characteristics X-rays spectrum of the daughter element, the sum should give the energies of the γ -ray prior to conversion. For example in the conversion of Ra-B \longrightarrow Ra-C, the energy of the electron emitted is added to the characteristic X-ray energies (say K.L etc) of the daughter element (Ra- C), the γ -ray energies are obtained. These values are in excellent agreement with the accepted values for the energies of gamma rays. For eg: Energy of ejected electron = 0.0368 MeV; 'L' line of Ra-C has the energy = 0.0161 MeV. The total $0.0368 + 0.0161 = 0.0529$ MeV is the γ -ray energy.

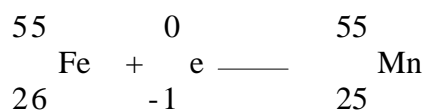
The binding energies of the electrons, obtained by subtracting their measured kinetic energies from the known gamma ray energies, and the observed frequencies of the characteristics X-rays are definitely those of the daughter and not of the parent. These facts provide clear proof that the γ -rays are emitted from the excited daughter nucleus, which remains after the parent has ejected either an alpha or β - particles.

ORBITAL ELECTRON CAPTURE

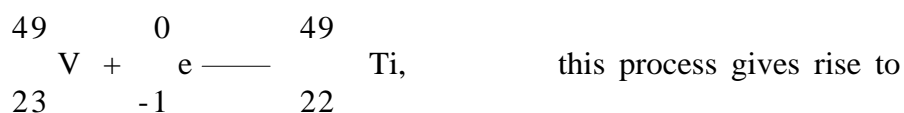
In some instances, where N/P ratio is low, positron activity is expected. Another type of decay has been found to occur with artificial nuclides. Instead of a proton being converted into a neutron with the emission of a positron, the nucleus capture one of the extra nuclear (orbital) electrons, which immediately combines with a proton to form a neutron, thus with a neutrino being formed at the same time.



This process increases N/P ratio. This gives rise to a product with the same mass number and the atomic number decreases by one unit.



This process is known as decay by orbital electron capture. The electron is usually captured from the K-level, for such an electron is more likely to be found near the nucleus. This process is also known as K-electron capture or K-capture. Examples of L-level capture are known but they are not common. Due to K-capture, characteristic X-rays of the product nucleus are emitted. For eg.,



K-series of X-rays belonging to 'Ti'. This shows that vanadium decays by K-electron capture. If as a result of orbital electron capture, the product nucleus is left in the ground state, the change will not be accompanied by γ -rays. The decay of ^{49}V , by K-capture is not accompanied by gamma-rays. Such a K-capture is known as pure K-capture. In most instances, however the product nucleus is found in a high-energy excited state and the excess energy is given off in the form of gamma radiation. This γ -radiation is internally converted; the energy of the gamma ray photon is transferred to an orbital, which is consequently ejected. Thus characteristics X-rays lines of the product nucleus are produced. It is possible to show that for positron emission a minimum of 1.02MeV energy is required. If the energy is less than this value, then K-capture would occur. When the energy is less than 1.02MeV K-capture is favoured. Positron emission is unknown among the heaviest elements. In these cases several cases of K-capture have been recorded.

13.2.2 NUCLEAR ISOMERISM

Study of radioactive decay of artificial nuclides, indicates a transition known as Isomeric transition. Nuclides having the same mass number and same atomic number, but having different radioactive properties are known as nuclear isomers. This phenomenon has been called nuclear isomerism. O.Hahn found U-Z to be isotopic with and also to have the same mass number as U-X₂. But both differ in the rates of decay. Later several isomers had been reported; for e.g., Br₂. When a target containing bromine was bombarded with slow neutrons, the product was found to exhibit three different half life periods of radioactive decay, Viz, 17.6 min, 4.5hr and 35.3hr. The reaction is of (n, γ) type. The explanation for this behavior is as follow:

⁸⁰Br exhibits nuclear isomerism; each isomer has a different half life. The difference between the nuclear isomers of ⁸⁰Br, and in fact of all other cases of nuclear isomerism is attributed to difference in the nuclear energy states. One isomer represents the nucleus in the ground state, whereas the other is the same nucleus in an excited state of higher energy. Frequently the transition from a higher to a lower energy state (associated with γ-rays) requires a very short time, less than about 10⁻¹³ sec. The excited state then has an extremely short life. If the transition is "forbidden", the high-energy state (excited state), referred to as 'meta stable state', will have an appreciable half-life. This half-life varies from small fraction of a second to several days. Such a metastable state represents one isomeric form of the particular nuclear species, whereas the ground state, ie., the state of the lowest energy, represents the other. For eg, in the case of ⁸⁰Br, the meta stable form is represented as ⁸⁰Br^m. Nuclear isomers can be obtained by various ways.



Three types of nuclear isomers may be distinguished. Isomers of independent decay each; isomer decays independently of the other with its

own particular half-life. In such cases transition from metastable to ground state is highly forbidden

examples: ^{52}Mn (β^+ , 5.7 days, β^+ , 21 min)

^{71}Zn (β^- , 4.1 hr, β^- 2.4 min)

^{115}Cd (β^- , 43 days, β^- , 2.3 days)

The second class of isomers are called genetically related isomers. The parent meta stable state decays to the ground state with a definite half life, a γ -ray photon is expelled. This decay process is known as isomeric transition (IT). In most cases the gamma rays are internally converted characteristic X-rays are emitted. The ground state decays to form the product with another half-life. Examples are:

^{44}Sc (IT, 2.44 days, β^+ 3.91 hr)

^{80}Br (IT, 4.5 hr; β^- 17.61 min).

Half life of IT is longer than that of the β decay (+ or -).

The third category of nuclear isomerism is that in which, the active species are isomers of stable nuclei. The decay process now involves an isomeric transition from the meta stable excited state to the ground state of the stable nuclide, accompanied by the emission of γ -ray emission. More than 30 stable species are known. Examples, ^{83}Kr , Sr-87, Ag-107, Sn-117, Ba-137, are known to form metastable states of appreciable half-life. Isomers of short life are also known.

Self Check Exercise – 1

- 1) Discuss the theories of α and β - decay
- 2) The speed of the α - particle moving in a nucleus is 10^5 cm/sec. if the radius is assumed to be 10^{-12} cm and decay constant 10^4 sec^{-1} , calculate the escape probability of the α -particle.

Self Check Exercise – 2

- 1) Discuss the theory of γ -ray decay.
- 2) Discuss the different types of nuclear isomers

- 3) Discuss the orbital electron capture. How are characteristic γ -rays produced in an orbital capture?

13.3 Let us Sum Up

α and β decay and the theories of α , β and γ -decay are discussed in detail. Different types of nuclear isomers and their production are explained. Internal conversion of γ -ray is explained.

13.4 Points for Discussion

- i) The production of different types of nuclear isomers
- ii) Internal conversion of γ -ray
- iii) The α and β decay theories.

13.5 References

- i) Atomic Physics by J.B.Rajan S.Chand & CO, New Delhi–1972
- ii) Source book on atomic energy – Glasstone – East – West press- Delhi.

LESSON – 14**CONTENTS**

14.0 AIMS AND OBJECTIVES

14.1 INTRODUCTION

14.2 Q-VALUE IN NUCLEAR REACTIONS, COULOMBIC BARRIER,
NUCLEAR CROSS SECTIONS

14.2.1 NUCLEAR REACTIONS – Q VALUES

14.2.2 COULOMBIC BARRIER AND NUCLEAR CROSS SECTIONS

14.3 LET US SUM UP

14.4 POINTS FOR DISCUSSION

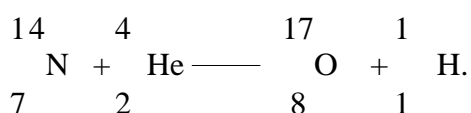
14.5 REFERENCES

14.0 AIMS AND OBJECTIVES

The aims and objectives of this lesson are to understand the calculation of 'Q' values of different types of nuclear reactions and also to understand the concepts of coulombic barrier and cross sections.

14.1 INTRODUCTION:

The bombardment of nitrogen by α -particle was the first artificial transmutation reaction studied. The nuclear reaction may be represented as



The reaction energy corresponding to such reaction is termed as the 'Q' value. The best value of reaction energy obtained for the above reaction was about – 1.26MeV. From the masses and kinetic energies of the reactant nuclei and product nuclei, one can calculate the reaction energies. High energies are required to surmount the coulombic barrier. To reach the nucleus of an atom an α - particle should have energies of the order of 20 to 30MeV, according to classical electrostatic theory.

Nuclear cross sections represent the effective area of cross section of a single nucleus of a given species for a particular reaction.

14.2.1 NUCLEAR REACTIONS – Q VALUE.

A nuclear reaction equation, satisfying the universal principle of conservation of energy can be written in a general way:

$$M_0 + (M_1 + E_1) = (M_2 + E_2) + (M_3 + E_3)$$

M_0 , is the rest mass of the nucleus bombarded, M_1 and E_1 , the mass and kinetic energy, respectively of the projectile, M_2 and E_2 and M_3 and E_3 similar quantities of the two products of transmutations, viz, the outgoing particle and the product nucleus. It is to be noted that the two sides of the above equation can be expressed in terms of either energy or mass.

In the nuclear reaction equation, the reaction energy is known as Q value.

$Q = (M_0 + M_1) - (M_2 + M_3) = E_3 + E_2 - E_1$ Hence 'Q' can be calculated using the masses of the particles involved or by means of the kinetic energies of the particles. Q may be positive or negative, depending on the nature of the process. Thus, if Q is positive, that is if the process is accompanied by liberation of energy, there must be a decrease of mass – the total mass of the products will then be less than that of the interacting nuclei by an amount equivalent to this energy. A negative value of 'Q' means that the energy is absorbed and there is a gain of mass on the nuclear reaction.

When ${}^7\text{Li}$ is reacted with ${}^1\text{H}$, the energy liberated 'Q' value was found to be 17.2 MeV; hence the mass equivalent of this energy is $17.2 = m(\text{amu}) \times 931$ $m = 0.0185$ amu ; since Q is positive, it can be calculated that sum of the masses of the products will be less than the interacting nuclei by 0.0185 amu



increases with the atomic number. Hence nucleus having high atomic number would repel strongly an energetic alpha particle. Therefore alpha particles of energies in the range 20 to 30 MeV, would only be able to surmount the potential barrier required to react with nuclei of high atomic numbers. The application of wave mechanics, to the problem of nuclear penetration showed that particles could both leave and enter the atomic nucleus even though their energies are considerably less than the top of the hypothetical barrier. G.Gamow showed that not only was the energy barrier lower, but the probability of penetrating it and reaching an atomic nucleus also increased, as the charge and mass of the incident particle decreased. Thus for a given value of the particle energy, a proton with unit charge and unit mass, is much more likely to enter the nucleus than an alpha particle, carrying two charges and having a mass of four units.

NUCLEAR REACTION CROSS SECTIONS

The efficiency of a nuclear reaction can be defined in terms of the number of particles emitted (or of nuclei undergoing transmutation). The interaction probability is expressed in terms of a quantity known as 'nuclear cross section'. when the probability of the process is high, the nuclear cross section will be large; on the other hand when the probability is low, the cross section will be small.

If 'I' is the number of incident particles striking in a given time a certain area of target material, containing 'No' target nuclei per sq cm and 'A' is the number of these nuclei that undergo interaction in the specified time, then the nuclear cross section 'σ' expressed as sq cm per nucleus, is defined by:

$$\sigma = \frac{A}{N_0 \times I} \quad \text{cm}^2/\text{nucleus}$$

σN_0 is the fraction of the surface, which is capable of taking part in the nuclear reaction ($N_0 = \text{atoms/sq cm}$)

This also represents the fraction of the incident particles 'I' falling on the target surface. The number actually reacting is $=\sigma Na I$ and this is equal to 'A', the number of target nuclei undergoing transmutation.

$$A = \sigma \times Na \times I \quad \text{i.e.,} \quad \frac{A}{NaI} = \sigma$$

Hence ' σ ' gives the effective cross section of a single nucleus for a given nuclear reaction. The larger the fraction of the incident particles reacting, the greater is the probability that the process will occur under the given conditions. The value (σ) of the nuclear cross section depends on i) the nature of the target element, ii) on the particular reaction under consideration and iii) the energy of the incident particle. The total cross sections for all processes in which the incident particles are removed, can be determined by a simple procedure. Let I_0 be the number of incident particles, in a narrow (or collimated beam), falling in a given time on the target material, which is on the form of a sheet of thickness 'x'cm, and 'I' is the corresponding number of these particles, emerging from the other side of the sheet in the narrow beam, the difference $I_0 - I$ has been removed in various nuclear reactions then

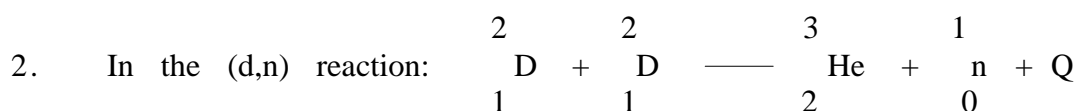
$\frac{I}{I_0} = e^{-N \times \sigma}$ - 'N' is the number of target nuclei/cc and ' σ ' is the total cross section. Hence it is possible to determine ' σ ' from measurements of the intensity of the beam of incident particles before and after passage through the target material.

Experimental values for nuclear cross sections are usually in the neighbourhood of 10^{-25} to 10^{-23} sq cm per nucleus. ' σ ' may be as high as 10^{-18} $\text{cm}^2/\text{nucleus}$. The average diameter of the nucleus may be taken as 10^{-12} cm and the actual area of cross section is approximately 10^{-24} cm^2 . ' σ ' is expressed in the unit of barn equal to 10^{-24} $\text{cm}^2/\text{nucleus}$. Nuclear cross sections are frequently in the range of 0.1 to 10 barns.

A curve showing the variation of ' σ ' with the energy of the incident particle is called the excitation function, of that reaction. In the case of Cu-63 with protons in the energy range upto 35MeV, the excitation function curves show, that at the lowest energies (p,n) reaction predominates; at about 15MeV the (p,pn) and (p,2n) reactions start to replace the (p,n) process. The cross section for a given nuclear process increases with the energy of the incident charged particle, provided there is no competitive reaction. Competing reactions cause the cross section to decrease at high energies.

Self Check Exercise – 1

1. Discuss the principle of Q-value



Q has been to and to be 3.16MeV. Using this value indicate how you would obtain the mass of the neutron.

Self Check Exercise – 2

1. Write a note on coulombic barrier
2. Discuss nuclear cross section.

14.3 Let us Sum Up

Q-values is defined – calculation of Q-value is illustrated. Nuclear cross section and Coulombic barrier are discussed in detail. The use of Q value in calculating the mass of ^{17}O is illustrated.

14.4 Points for Discussion

- i) Q-Value and its uses
- ii) Evaluation of nuclear cross section
- iii) Coulombic barrier

14.5 References

- 1) Atomic physics – J.B.Rajan – S.Chand & Co New Delhi (1972)
- 2) Source book on a atomic energy – Glasstone East-West press.

LESSON – 15

15.0. AIMS AND OBJECTIVES

15.1. INTRODUCTION

15.2 NUCLEAR REACTIONS

15.2.1. Different types of nuclear reactions

15.2.2 Spallation

15.3 LET US SUM UP

15.4 POINTS FOR DISCUSSION

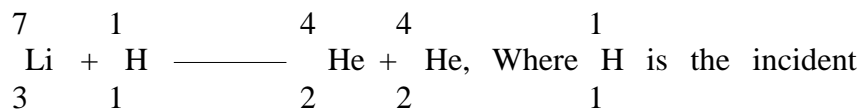
15.5 REFERENCES

15.0. AIMS AND OBJECTIVES

The aims and objectives of this lesson are to learn, the different types of nuclear reactions and to know how they are brought about.

15.1. INTRODUCTION

The first successful nuclear transformation using artificially accelerated protons was achieved by Rutherford. The nuclear reactions thus achieved can be written as,



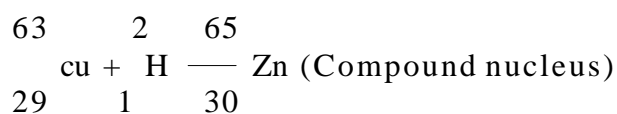
proton and the two helium nuclei are the alpha particles formed. The process occurred to a detectable extent with protons of 125,000 eV ie., 0.125 MeV, a value considerably less than the height of the potential barrier between a lithium nucleus and a proton, namely about, 0.45 MeV. Artificial nuclear reactions have been classified in six general categories. The various types of processes are (i) transmutation (ii) stripping and pick up (iii) fission (iv) spallation (v) fragmentation and (vi) scattering.

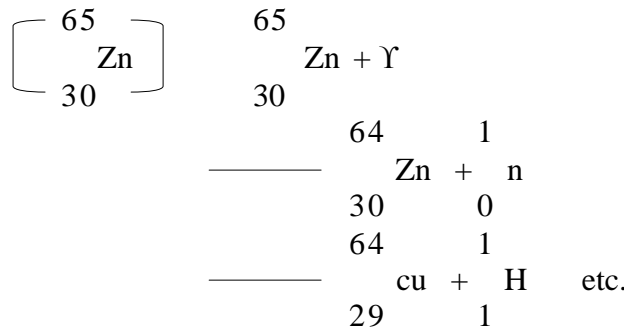
Nuclear reaction is represented by a simple method for e.g. ^{14}N (α, p) ^{17}O , is the reaction in which ^{14}N , is the target nucleus; the ' α ' particle is called the incident particle or projectile; a proton is ejected (P) and an ^{17}O , nucleus known as the recoil nucleus, remains. The general group of nuclear reactions studied by Rutherford can be referred to as (α, p) type.

i) Transmutation reactions :

These reactions involve particles of energy 50 MeV. In the first step the target nucleus completely absorbs the projectile to form what is called, a 'compound nucleus'. Before forming the compound nucleus, the projectile must overcome the barrier due to electrostatic repulsion forces. It has been found that the deuteron is capable of initiating several nuclear transformations, through the formation of the compound nucleus, at relatively low energies. In the compound nuclear redistribution of additional energy takes place rapidly.

The average life of a compound nucleus, i.e. the average time elapsing between the capture of the projectile and the emission of a particle is estimated to be 10^{-14} sec or less. The nature of the particles expelled from the compound nucleus, depends on i) its excess or excitation energy ii) the heights of the various coulomb barriers, iii) stability of the remaining (recoil) nucleus. Since no barrier exists for neutrons, these particles will in general be able to escape from the compound nucleus, much more readily than either, protons, deuterons or alpha particles. This is especially true when the target nucleus has high atomic number. For target elements of small atomic number, neutrons are more strongly bound in the compound nucleus than protons. The energy barrier is not also too high and the ejection of a proton or α -particle may occur. The compound nucleus can give rise to different reactions, depending on the available energy.



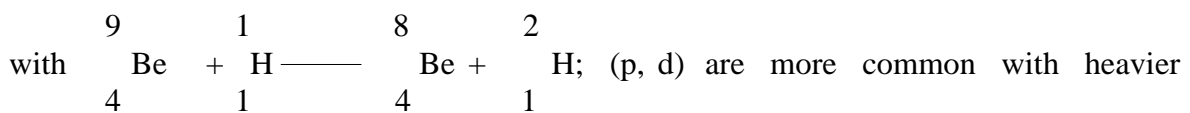
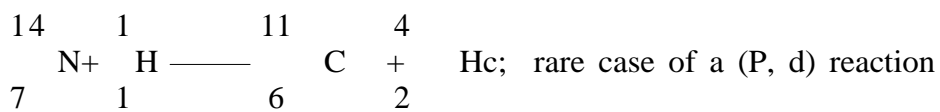


a) Transmutation by protons :

In these reactions the projectile has less than about 50 MeV energy. For a number of lighter elements (P, γ) process is observed for eg 27 Al (P, γ) 28 Si, other examples are ⁷Li (P, γ) ⁸Be, ¹⁴N (P, γ) ¹⁵O, ¹⁹F (P, γ) ²⁰Ne, ⁵⁰Cr (P, γ) ⁵¹Mn.

If the incident proton has an energy in excess of 20 MeV, the compound nucleus has sufficient excitation energy to permit the expulsion of two or more nucleons. Examples are : ⁶³Cu (p, pn) ⁶²Cu, ⁶³Cu(P, 2n) ⁶²Zn, ⁸⁸Sr (P, 3n) ⁸⁶Y.

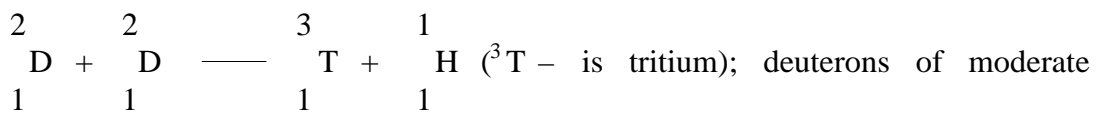
If proton energies are more than 50 MeV, more than three nucleons may be emitted. (P, α) reaction is expected only with targets of low atomic number, for eg.



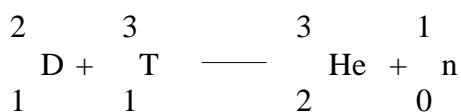
elements and protons of fairly high energy, but they appear to be pick-up reactions not involving compound nucleus formation.

b) Transmutation by deuterons:

The deuteron is a particularly effective projectile for causing nuclear transmutations, because a relatively small amount of energy, about 2 Mev, is sufficient to cause its rupture into a neutron and proton. This small binding energy of the nucleons of a deuteron facilitates nuclear changes. In the (d, p) reaction, the efficiency of the process increases with increasing energy of the incident particle. Oppenheimer– Philips mechanism, explains the ease of the (d, p) reaction. According to this the deuteron behaves as a relatively loose combination of a neutron and a proton, since the binding energy is relatively small. When the deuteron approaches a nucleus, the electrostatic forces of the positive charges tends to force the proton away, but the neutron is not affected. If the energy of the incident deuteron exceeds about 2 MeV, the proton portion breaks off and be repelled, but the neutron will enter the target nucleus. If enough energy is available neutron may also be expelled. Then the reaction (d, pn) occurs. (d, p) reactions are observed with all elements. Examples :

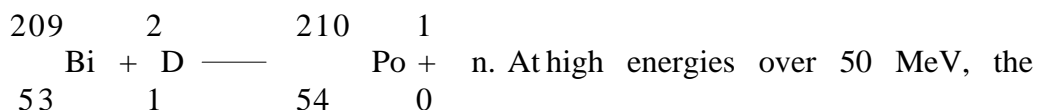


deuterons of moderate energies give neutrons i.e., (d,n) type.





method for producing neutrons with 14MeV energy. Other examples are:

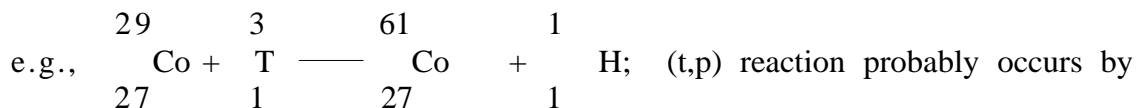


(d,n) reaction like the (d,p) reaction, becomes a stripping process, that does not involve compound nucleus formation to any extent (d α) are observed only with deuterons of moderately high energy and elements of fairly low atomic weight.

$\begin{array}{cccc}
 40 & 2 & 38 & 4 \\
 \text{Ca} & \text{D} & \longrightarrow & \text{K} + \text{He}; \text{ others are } {}^6\text{Li} (d, \alpha) {}^4\text{He}, \\
 20 & 1 & 19 & 2
 \end{array}$
 ${}^{20}\text{Ne} ((d, \alpha) {}^{18}\text{F}, {}^{26}\text{Mg}((d, \alpha) {}^{24}\text{Mg}, \text{Na}, ((d,2n), (d,3n), (d,2p) and ((d,p α)) are also known when high energy deuterons (about 20 MeV or more) are used.$

c) Transmutation by ${}^3\text{T}$:

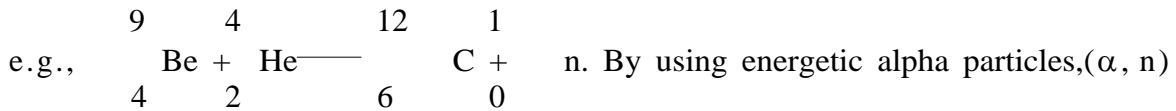
When tritons obtained by the action of 10MeV deuterons on Be, are used as projectiles, (t,p) reactions occur.



oppenheimer – Philips mechanism. The proton present in the triton is repelled by the target– nucleus, leaving the two neutrons to combine with the target nucleus to form a compound nucleus. In ${}^6\text{Li} (t,d) {}^7\text{Li}$ and ${}^{63}\text{Cu} (t,d) {}^{64}\text{Cu}$ also the oppenheimer – Philips mechanism operates.

d. Transmutation by alpha particles:

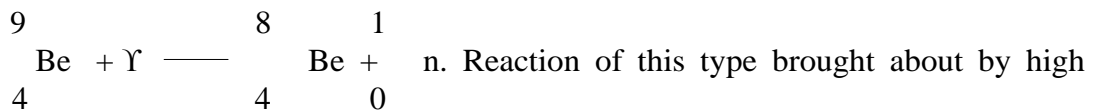
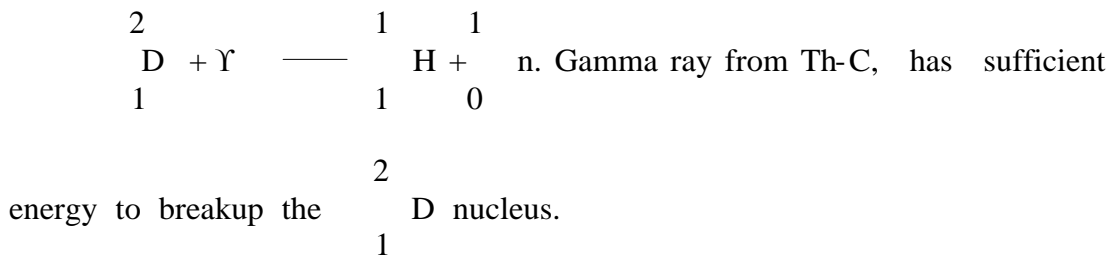
(α , p) process was the first artificial transmutation studied. This occurs in common with elements of low atomic number. With highly accelerated α -particles this reaction occurs even with elements of higher atomic numbers (above potassium) (α ,n) reaction:



reactions have been observed with the heaviest elements, including uranium and artificial elements of higher atomic numbers with increase in energy of the α -particles, (α ,np), (α ,3n), (α ,4n), (α ,3np) have been detected.

e. Transmutation by radiation:

By using gamma radiation, deuterium nucleus could be disintegrated into a neutron and a proton:

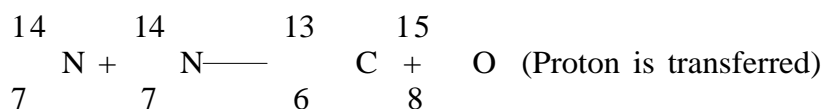
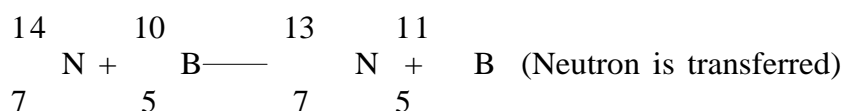
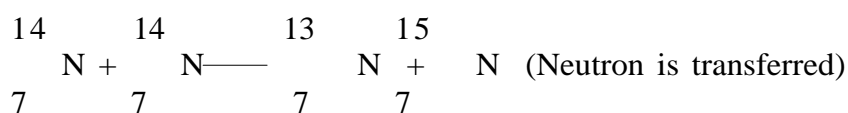


energy radiation, have been described as photo disintegrations or as photo nuclear reactions. When the 17-MeV, radiations produced by the bombardment of lithium by protons were employed, number of nuclei exhibited photo nuclear reactions of the (γ ,n) type. A neutron can be removed from any nucleus by γ -rays of about 10MeV, energy. If the γ -ray energy is not sufficient, to remove a neutron, the nucleus may enter into one

of its excited states; the excess energy is then emitted as radiation. Such a process is described as $(\gamma-\gamma^1)$, where the energy of γ^1 is equal to or less than that of the incident photon.

f) Nuclear reaction with heavy ions:

Accelerated carbon ions and 'Al' target is an example of a nuclear reaction with heavy ions. $^{27}\text{Al} (^{12}\text{C}, \alpha n)^{34}\text{Cl}$ and $^{197}\text{Au} (^{12}\text{C}, 4n)^{205}\text{At}$. The particle energy is relatively high (about 10 MeV) per nucleon, certain reactions in which heavy ions take part are called transfer reactions'.



15.2.2 Fission, Spallation and Fragmentation Reactions

Fission can also be initiated by charged particles of high energy (compare with neutron). Fission with energetic charged particles can occur with many nuclides of lower mass number. Alpha particles of about 400 MeV, energy can cause fission of Bi, Pb, Tl, Pt and Ta and 200 MeV deuterons are effective for Bi, Pb and Tl. The lightest element that is known to undergo fission by α -particles is Ta (Z-73). In the fission of Ta-181 by high energy protons, the masses of the product nuclei vary from about 60-120. The distribution of the products depends to some extent on the energy of the projectile particles. Another type of reaction, different from fission, but also leading to many different product nuclei, was discovered in 1947 by

G.T.Seaborg. When bombarded by high energy charged particles e.g., 400MeV protons or 200-MeV deuterons, many target nuclei do not break up into two parts of similar mass, as in fission. Instead such nuclei emit various numbers of nucleons commonly 10 to 20 and to a lesser extent up to 30 or more, singly or in clusters, leaving a series of products, with mass numbers lower than that of the target nucleus.

The name "Spallation" is used to describe this type of reaction. Spallation is known to occur with many different nuclei from the lightest e.g, Mg to the heaviest using charged particles with energies of several million electron volts. With heavier elements, fission and spallation often occur at the same, time as indicated by the masses of the product nuclei. In spallation most of the products have masses that differ from that of the product by up to 10 to 20 units, smaller amounts of lighter products. The mass with distribution of the products is the only way of distinguishing between fission and spallation.

75

For example when arsenic ($^{75}_{33}\text{As}$) is bombared by high energy α -particles (^4_2He), one of the mirror products is $^{38}_{17}\text{Cl}$, the net decrease in

the number of protons is 18 and that in the number of nucleons is 41; this

particular mode of spallation is expressed as $^{75}_{33}\text{As} (\alpha, 18Z41a) ^{38}_{17}\text{Cl}$. Some

writers use the equivalent representation $^{75}_{33}\text{As} (\alpha, 9 \alpha 23n) ^{38}_{17}\text{Cl}$,

but this is misleading as it implies the emission of 9α particle, which may or may not occur. The mechanism suggested for high energy fission and spallation, by R.Serber is generally accepted. The high energy projectile enters the target nucleus and strikes a single nucleon; the latter known as the knock-on particle, may be ejected or it may strike another nucleon, which may in turn be ejected or it may share its energy with other particles in the nucleus. The incident particle may still have enough energy to strike or

possibly eject another nucleon, or again the energy may be shared and so on. This stage of the process is cascade in which several knock-on nucleons may be expelled from the target nucleus. When the cascade is over within 10^{22} sec or so, the remaining nucleus is left in a highly excited state. It is similar to a compound nucleus, but with a much larger amount of excess energy. A distribution of energy then occurs, over a period of about 10^{14} sec, and several individual nucleons (or small groups of nucleons) are emitted. The result would then be a spallation reaction. Alternatively and simultaneously, after expelling a few nucleons the excited nucleus may split into two parts in various ways, thus undergoing fission.

In reactions of some nuclei, particularly of medium or high mass number, with high energy particles, the products include finite quantities of nuclei with mass numbers from 18 to 32, e.g., ^{18}F , ^{24}Na , ^{28}Mg and ^{32}P . These are apparently too light to be fission either or spallation products. Reactions leading to the formation of such species are called nuclear fragmentation. After the cascade stage mentioned above but before there has been time for the energy to be distributed in the excited residual nucleus, a relatively large amount of energy may be concentrated in a limited region of the nucleus. As a result, there is a rapid break up of the nucleus, leading to the formation of nuclei consisting of 20 or 30 nucleons.

Self Check Exercise - 1

1. Discuss the different types of nuclear reactions
2. Explain the oppenheimer – Philips mechanism

Self Check Exercise – 2

1. Compare the fission and spallation reactions
2. Write a note on fragmentation

15.3 Let us Sum Up

Nuclear reactions brought about by different types of particles are explained open Himer-Philips mechanism is discussed. Spallation reaction and its mechanism are explained.

15.4 Points for discussion

- 1) Compound nucleus formation in nuclear reactions
- 2) Philips-oppenheimer mechanism
- 3) Mechanism of spallation reaction.

15.5 References

- 1) Atomic Physics – J.B.Rajan S.Chand & Co
- 2) Source book on atomic energy – By Glasstone East West press.

UNIT VI

LESSON – 16

CONTENTS

- 16.0 AIMS AND OBJECTIVES
- 16.1 INTRODUCTION
- 16.2 NUCLEAR FISSION AND FUSION
 - 16.2.1 FISSION – THEORIES
 - 16.2.2 FISSILE AND FERTILE NUCLIDES
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- 16.3 LET US SUM UP
- 16.4 POINTS FOR DISCUSSION
- 16.5 REFERENCES

16.0 AIMS AND OBJECTIVES

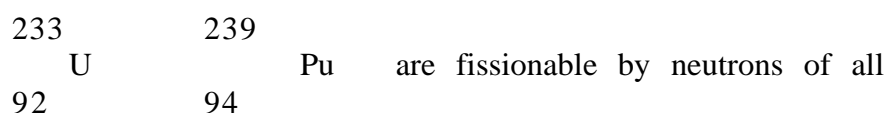
The aims and objectives of this lesson are

- i) To learn and calculate the energy released in nuclear fission and fusion reactions.
- ii) To study the theories of fission

16.1 INTRODUCTION

In the fission process a nucleus, after interacting with a projectile particle, breaks up into two nuclei of roughly similar mass plus a few nucleons. The nucleons obtained in the fission process are invariably neutrons. The most important of fission is that caused by neutrons. But fission can also be initiated by charged particles of high energy. The neutron fission is restricted to a few heavy nuclei, whereas fission with energetic charged particles can occur with many nuclides of lower mass number. Thus alpha particles of about 400MeV can cause fission of bismuth, lead, thallium and platinum.

The fission process is accompanied by the liberation of large amounts of energy. The important point to remember is that fission, which is initiated by neutrons, is also accompanied by the emission of neutrons. These emitted neutrons cause a chain reaction to occur and more energies and neutrons are produced. Uranium can be split by neutrons of all energies, i.e., by slow, intermediate and fast neutrons. Fission of more abundant U-238 requires fast neutrons with energy exceeding 1MeV,



energies. Fission cross sections are generally high for slow neutrons. Fission of Th requires fast neutrons of energies of about 1 MeV. Protactinium also requires fast neutrons. The combination of two or more of the lightest nuclei by a process of fusion, like fission, result in the liberation of energy.

Many reaction between nuclei of low mass number can be brought about by accelerating one or other of the nuclei in a suitable manner. These are fusion reactions, accompanied by the release of energy. The energy of the sun is due to the fusion reaction.

The power production corresponding to the fission of 1 g of Uranium or Plutonium per day would be 1 mace Watt. To obtain the same amount of power by combustion would require more than 3 tons of coal per day or 600 gallons of fuel oil per day.

16.2 NUCLEAR FISSION AND FUSION

16.2.1 FISSION THEORIES

Before studying the theories of nuclear fission one should know the amounts of energy liberated in a nuclear fission reaction. In the fission reaction we have to calculate the mass loss, in a nuclear fission reaction. But we know the energy corresponding to the mass loss of 1 a m u = 931 MeV.

$$\begin{aligned}
 \text{I a m u} &= \frac{1}{6.0225 \times 10^{24}} \\
 &= 1.6604 \times 10^{-24} \\
 E &= m \times c^2 \\
 &= 1.6604 \times (2.998 \times 10^{10})^2 \times 10^{-24} \\
 E &= 1.6604 \times 10^{-24} \times (2.998 \times 10^{10})^2 \text{ g cm}^2 / \text{sec}^2 \times \text{cm} \\
 &= 1.6604 \times 10^{-24} \times (2.998 \times 10^{10})^2 \text{ ergs} \\
 &\quad (\text{note } \text{g cm}^2 / \text{sec}^2 = \text{ergs}) \\
 &= 1.4924 \text{ ergs} \\
 &= 1.602 \times 10^{-12} \text{ ergs} = 1 \text{ ev} \\
 \text{hence } E &= \frac{1.4924 \times 10^{-3} \text{ ev}}{1.602 \times 10^{-12}} \\
 E &= 931.4 \text{ MeV / amu}
 \end{aligned}$$

Although U-235 splits in many different ways, the nuclei obtained in the greatest yield in fission by slow neutrons have mass numbers of about 95 and 139. The initial products are radioactive and undergo several stages of negative β -decay ultimately, after the emission of a total of seven beta particles (electrons), the stable nuclides Mo-95 and La-139 are formed.

The fission process in this particular case can be represented as:



Some neutrons are always liberated in the fission process. The atomic mass of U-235 is 235.0439 amu and the mass of neutron is 1.0087 amu.

The total mass on the left hand side of the equation is 236.0526 amu. The masses of Mo-95 and La-139 are 94.9058 and 138.9061 amu, respectively

and the mass of the electron is 0.00055amu; the total mass on the right side is 235.8332 amu. The mass loss is equal to $236.0526 - 235.8332$
 $= 0.219\text{amu}$

Energy equivalent of this mass is

$= 0.219 \times 931.4\text{MeV}$
 $\sim 204 \text{ MeV}$

The actual process of fission is probably accounted for by the large value of repulsive force in heavy nuclei, and so it is responsible both for fission and for the release of energy accompanying the nuclear reaction.

The energy released in the fission process appears in several different forms. The major part occurs as kinetic energy of fission fragments and a substantial amount as radioactive decay energy of the fission products. In addition, neutron and gamma rays liberated at the instant of fission carry appreciable amount of energy. Thermal neutron fission of U-235 is far from symmetrical. If the compound nucleus splits into two equal of fragments, the mass of each is 117 or 118, only 0.01% of the nuclei undergoing fission by thermal neutrons break up in this manner. There are 90 possible mass numbers in the range of from 72 to 161, it is understandable that this may represent the total number of different nuclides formed as direct fission fragments. The amount of symmetrical fission by thermal neutrons is about 0.02% for U-233 and 0.04% for Pu-239.

Experimental studies indicated that for each atom of uranium undergoing fission between three and four neutrons were emitted on the average. The average number of neutrons released per fission increases with the energy of the neutrons inducing fission. Thus in the fission of U-235 by 14MeV neutrons, an average of 4.5 neutrons are produced per fission. The average number of neutrons increases in general with the number and the atomic number of the fissioning nucleus. The great majority (over 99%) of the neutrons produced in fission are released within about 10^{-14} sec. These are referred to as prompt neutrons. A small proportion of fission neutrons are

delayed neutrons, which are emitted sometime after the fission process has taken place. In the fission of U-235 by neutrons upto atleast 1MeV energy, 0.65% of the neutrons emitted is delayed. The emission of delayed neutrons is an important factor in the control of nuclear fission reactors. For thermal neutron fission of plutonium – 239, about 0.21% of the neutrons are delayed, and for U-233, about 0.26% are delayed.

THEORY OF NUCLEAR FISSION

A useful approach to understanding the mechanism of fission is by means of the liquid – drop model of the nucleus. It is postulated that, just as the surface tension forces tend to maintain a liquid drop in a stable form which resists distortion, so the nuclear forces serve to keep the nucleus in a stable state. Only if considerable distortion occurs due to the addition of energy a drop of liquid can be broken into two smaller drops. Similarly for a nucleus to undergo fission, there must be considerable distortion, which will be possible only if additional energy is available. This is the basis of the interpretation of fission indicated by Meitner and Frisch.

The general idea of the proposed mechanism for fission may be understood by considering a drop of liquid which is made to break up into two smaller droplets, by the application of a suitable force. The system passes through a series of stages. The drop is at first spherical, it is then elongated into an ellipsoid. If insufficient energy is available to overcome the surface tension, the drop will return to its original spherical shape. But, if the deforming force is sufficiently large, the liquid acquires a shape similar to a dumbbell. Once it has reached this stage, it is unlikely to return to the spherical form, but it will rather split into two droplets.

The situation in nuclear fission is regarded as analogous to that just considered for a liquid drop. A large nucleus combines with a neutron to form a compound nucleus; the energy gained by the nucleus is equal to the binding energy of the additional neutron plus any kinetic energy the neutron may have possessed. The excitation energy may then be emitted as gamma

radiation or the compound nucleus could, if sufficient energy were available split in to one or more nucleons.

If the nucleus has obtained enough energy to permit it to form the dumbbell shape, (like the liquid drop), the restoration to the initial shape (spherical) becomes very improbable. The reason is that the electrostatic repulsion between the positive charges on the two ends of the dumbbell, can now overcome the relatively small portion of the nuclear binding force, operative in the constricted region of the dumbbell. Consequently the dumbbell shaped nucleus, undergoes fission to two separate nuclei. The series of changes just described can occur only if it is accompanied by a net decrease of mass, that is, by an emission of energy. The state, consisting of two separate nuclei is then more stable.

CRITICAL ENERGY FOR FISSION

The critical energy (or activation energy) required for fission to occur is the energy that must be supplied to the original nucleus in order to deform the nucleus to the dumbbell state.

The repulsive energy is proportional to $Z^2/A^{1/3}$, whereas the surface energy depends on $A^{2/3}$. Therefore the ratio of these two energies namely, Z^2/A , for a given nucleus is a measure of the ease with which, it will undergo fission.

The larger the value of Z^2/A , the smaller the amount of energy that must be supplied from outside sources to cause fission to occur.

It was shown that if the electrostatic repulsion energy was more than twice the surface energy, a nucleus should undergo instantaneous fission. The condition for instantaneous fission was shown to be.

$$0.710 \quad Z^2 > 2 \times 17.8 \times A^{2/3}$$

$$A^{1/3}$$

$$\text{or} \quad \frac{Z^2}{A} > 50$$

The closer Z^2/A for a particular nucleus is to 50, then shorter should be the half life for spontaneous fission. If Z^2/A is approximately less than 40 fission cannot occur at a significant rate unless energy is supplied to the nucleus; this is the 'Critical energy' of fission. For plutonium-239, Z^2/A is 37.0, for Uranium-233 it is 36.4 and for Uranium-235 it is 36.0, these are fairly high, but they are sufficiently less than the limiting values to require appreciable energies for fission. The critical energy for U235 after absorbing a neutron has been estimated to about 5.5 MeV. Similar values have been estimated for the other two fissile species. For lighter elements such as bismuth, lead and tantalum Z^2/A is about 30 or less and critical energy for fission is large. It can be understood, why fission does not occur with these substances.

Fission process has also been explained by potential energy diagram. In this diagram, the energy of the fragments is plotted as a function of their distance apart. The exact shape of the curve depends on the target nucleus. At the extreme left of the diagram, the fission fragments are supposed to be brought together (i.e.) the point at the left of diagram represents the energy of the target nucleus and an incident neutron. At the extreme right the fission fragments are at a considerably distance apart and their interaction is zero. This diagram is similar to the activation energy diagram. The top of the barrier corresponds to the state of critical deformation of the nucleus. If fission is to occur then the target nucleus plus neutron (i.e.) the compound nucleus, must acquire sufficient energy to reach the top of the barrier. By using neutrons of 1 MeV energy, the energy of the system is increased so that it now lies above the barrier and fission takes place.

The critical energy depends on the quantity Z^2/A for the given nuclide. The larger the value of Z^2/A , more closely will the energy of the compound

nucleus, approach that of the critical deformation energy. Calculations indicate the U-235 could be fissioned by slow neutrons. Whereas fast neutrons are required for fission reaction when U-238 is used U-233 and Pu-239 would also undergo fission by means of thermal neutrons. Their critical deformation energies are about 5.1MeV and 4.8MeV for U-233 and Pu-239 respectively. In the case of Th-232, Pa-231 and Np-237, critical deformation energies are about 6.0 to 6.6 MeV. In these three cases neutrons of about 1.1 MeV energy must be absorbed to produce critical deformation leading to fission. Thus U-235, U-233 and Pu-239, which contain even numbers of protons and odd number of neutrons, are called fissile nuclides. Np-237, with an odd number of protons and an even number of neutrons, and Th-232 and U-238 which are of the even-even type are fissionable species requiring fast neutrons to induce fission.

NUCLEAR POWER PRODUCTION

A large amount of energy is released in a fission reaction which is a chain reaction induced by neutron. Hence power can be produced by means of a nuclear reactor. It can be shown that 1gm atom of U-235 (235grams) by means of a fission reaction, would produce 1.93×10^{13} watt-sec energy. It follows that the complete fission of 1 gram releases 8.2×10^7 ergs. It is equivalent to 8.2×10^{10} watt-sec or 8.2×10^7 kilo watt-sec. This is equivalent to 2.3×10^4 (Kw-h) or $2.3 \times 10^4 / 24 = 0.96 \times 10^3$ kilo watt days.

The (heat) power production corresponding to the fission of 1gm of uranium or plutonium/day would thus be 0.96×10^3 kilo watts, roughly 1000 kilo watts or 1 mega watt. The same amount of power can be obtained only by the combustion of about 3 tons of coal or about 600 gallons of fuel oil per day.

The total number of nuclei 'A' undergoing fission per second in the reactor is given by the expression.

$$A = nvN\sigma V$$

Where 'n' is the average neutron density, ie the number per cc, U is the average speed, so that, 'nv' is the average neutron flux; 'N' is the number of fissile nuclei (U-235) per cc, σ square cm is the cross section for fission, and 'V' cc is the volume of the reactor. 3.1×10^{10} fission per cc produce 1 watt of power, hence the power 'P' of a nuclear reactor in watts is obtained upon dividing the fission rate 'A', by 3.1×10^{10} (ie)

$$P = \frac{nvN\sigma V}{3.1 \times 10^{10}} \quad \text{Watts} \quad \dots (1)$$

The product 'NV' is equal to the total number of fissile nuclei in the reactor and this is related to the mass 'm' grams by

$$m = \frac{235 \times N \times V}{6.02 \times 10^{23}} \quad \text{where 235 is the atomic weight of U-235.}$$

The fission cross section σ of U-235, for thermal neutrons is 577 barns (ie) $577 \times 10^{-24} \text{ cm}^2$ and upon inserting these values in equation (1), we have,

$$P = 4.8 \times 10^{-11} mn$$

This equation shows that the power output of a given reactor, containing a definite amount of fissile material, is proportional to the neutron flux-nv. Therefore reactor power is generally determined by measuring the appropriate neutron flux, by means of a suitably calibrated instrument. In the reactor the chain reaction has to be controlled. Controls are necessary to prevent the chain reaction from becoming too violent. Once the desired energy level is reached, control rods of Cd, boron steel or other material with a large capture cross section for slow neutrons are used. These rods are inserted in the reactor to such a depth as will permit them to absorb all excess neutrons. In other words, when the reactor has reached a predetermined power level, the control rods serve to keep the effective multiplication factor to unity. If it is required to increase the power, the

controls are partially removed, the multiplication factor then exceeds unity and then neutron flux increases.

When this attains the desired value the controls are inserted to the extent necessary to keep the flux (or power level) constant.

When the shutting down the reactor, the control rods are inserted to a considerable depth, the rods then capture so many neutrons than the effective multiplication factor becomes less than unity. Then neutron flux thus decreases and the nuclear chain reaction then is no longer maintained. A reactor consists of an active core in which the fission chain is maintained and in which most of the energy of fission is released, as heat. The core contains the fissile material in a suitable form i.e the reactor fuel, and also a moderator if it is required to slow down the neutrons. The relative amounts of and nature of the fuel and moderator determine the energy of the neutrons causing most of the fission. The core is surrounded by a reflector of a material which is largely dependent on this neutron energy. The combination of core and reflector, together with other components present, e.g, coolant and structure must be capable of maintaining a fission chain.

The operation of the reactor at appreciable power levels depends on the ability to remove the heat produced by fission as fast as it is liberated. This involves the use of a coolant, which must circulate through the reactor core in such a manner as to maintain a temperature distribution that is as uniform as possible. If the energy generated in the reactor is to be converted into electrical power, then the heat must be transferred to a working fluid to produce steam or hot gas. The resulting vapour or gas can be used to generate power in a conventional manner, for example by means of a turbine.

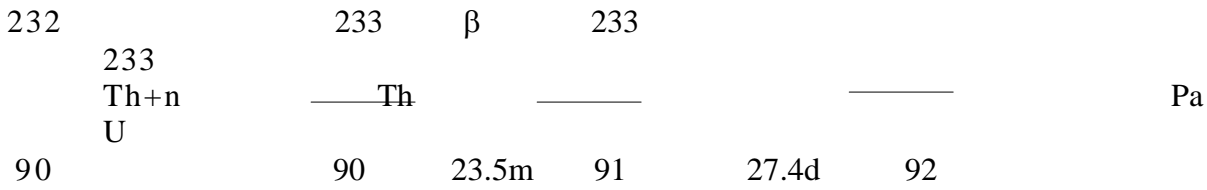
Reactors are classified as "thermal", "Fast" or intermediate "according to the neutron energy region in which the majority of the nuclear fissions occur. In thermal reactors most fissions are due to the absorption of slow neutrons. In order to slow down the fast neutrons released in fission a sufficient amount of moderator must be included, in the core of the reactor.

Thermal reactors have the great advantage of flexibility in size. The size can be attained by Varying the nature and properties of the fuel and the moderator size. For example a reactor with natural uranium as fuel and graphite as moderator, is roughly 20 feet across at least with a fuel material highly enriched in U-235 and ordinary water as moderator, a thermal reactor may have linear dimensions of not more than one or two feet. An important draw back to thermal reactors is the loss of neutrons due to parasitic capture by constructional and other materials as well as by fission products.

In a fast reactor, the majority of fissions occur by interaction of fissile material with neutrons of high energy. The use of a moderator or of any material of low mass number, which might slow down the neutrons, must consequently be avoided as far as possible. Parasitic capture of neutrons is a relatively minor problem in a fast reactor. On the other hand there is some limitation in the choice of fuel materials. A fast reactor requires an enriched fuel containing about 20 to 25% of fissile material, e.g, U-235, U-233 or Pu-239. A disadvantage of a fast reactor is the larger mass of fissile material necessary to attain criticality. Because there is no moderator, the critical size may be quite small e.g, a foot or less across, and then the heat removal is difficult when the operating power is high. The outstanding aspect of certain fast reactors is their ability to breed fissile material, Plutonium- 239, in particular. It is mainly for this reason that such reactors are alternating interest.

An intermediate reactor is one in which fissions are caused mainly by neutrons slowed down into a broad energy range between fast and thermal energies. Some moderation is necessary, but not as much as in a thermal reactor. In a sense an intermediate reactor is compromise between thermal and fast reactors. Parasitic capture of neutrons can be less than in a thermal reactor. An intermediate reactor also offers the possibility of breeding P - 239.

U-233 is fissionable by slow neutrons and it is obtained from Th-232 by means of neutrons available in a reactor.



16.2.2 FISSILE AND FERTILE NUCLIDES

U-235 will undergo fission by neutrons of any energy, from almost zero upward, but U-238, requires neutrons of at least 1 MeV to induce fission. U-233 and P - 239 are like U-235 in the respect that neutrons of any energy can induce fission, such species are known as fissile nuclides. On the other hand, U-238, Th-232 and certain other species, which have a fission threshold at about 1 MeV are said to be fissionable nuclides. In general fissile nuclides have either an even number of protons and an odd number of neutrons or odd numbers of both. Of the fissionable nuclides, only the even-even species U-238 and Th-232 are of practical interest, because they can be converted into fissile nuclides by reaction with neutrons. Both U-238 and Th-232 will undergo fission by fast neutrons with energy greater than 1 MeV, but it is not possible to sustain a chain reaction in these isotopes. Since both U-238 and Th-232 can be converted into fissile species, however, they are referred to as 'fertile materials'.

One of the remarkable aspects of nuclear reactors is that they can be designed so as to produce their own fuel, by conversion of fertile to fissile material. Such reactors are called regenerative reactors or converters. Plutonium production reactors fall in this category. In these reactors U-235 serves to maintain the fission chain, but some of the neutrons are captured by the fertile U-238 with the ultimate formation of plutonium-239. A regenerative reactor can produce useful energy while converting fertile material into new fissile material, to replace that consumed. Consider a reactor with U-233 as the fissile material. For every one of these nuclei undergoing fission, more than one would be produced by the capture of neutrons in Th-232. Such reactors are called breeders and the regeneration process is known as breeding. By the use of breeding, the stock pile of fissile

material could be steadily increased. Thus not only would all the fertile material be converted into fissile material, but the amount of the latter available, and hence the rate of power production could be steadily increased.

This would not go on indefinitely, because a time would be reached in the ultimate future when all the fertile material was consumed.

16.2.3 FUSION STELLER ENERGY

The energy obtained by the fusion of light nuclei would be more practical than the energy that would be obtained by the fission of heavy nuclei. The liberation of energy in fission is due-essentially to the binding energy per nucleon being less in the heavy elements, than it is in those of intermediate mass number formed in fission. In the case of fusion, the combination of two more of the lightest nuclei should result in the liberation of energy.

Many reactions between nuclei of low mass number can be brought about by accelerating one or other of the nuclei, in a suitable manner. These are often fusion processes accompanied by release of energy. To have practical value, fusion reactions must occur in such a manner as to make them self sustaining, that is more energy must be released than is consumed in initiating the reaction.

Some indication of how this might be achieved can be obtained by considering the source of the enormous amounts of energy produced continuously in the stars. A.S. Eddington suggested that the energy of the sun resulted from the mutual annihilation of positive and negative charges. Eddington proposed that stellar energy was liberated in the formation of helium from hydrogen.

Energy might be liberated in the stars as a result of nuclear fusion reactions occurring at the very high stellar temperatures, from 15 to 30 millions, degrees Kelvin. Such processes are called thermonuclear reactions and these

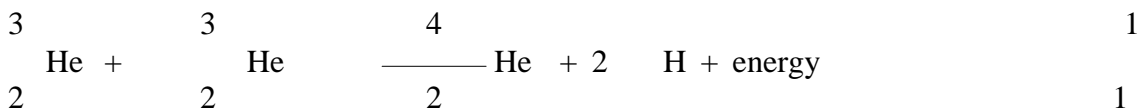
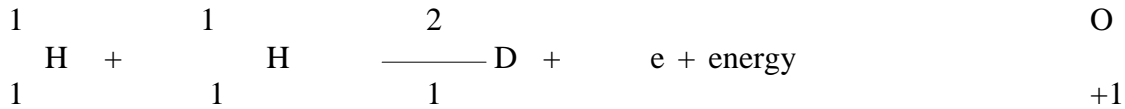
reactions can occur at rates sufficient to account for the release of large amounts of stellar energy.

In order for two nuclei to interact, they must have enough kinetic energy to overcome the electrostatic repulsion barrier which tends to keep them apart. Simple calculations indicate that for the nuclei of the lowest atomic number e.g., the isotopes of hydrogen the energy required to make the nuclear reactions occur at a detectable rate is about 0.1 MeV. But the temperature would have to be as high as 1000 million degrees Kelvin, if the average energy of the particles is to be 0.1 MeV. Such temperatures are considerably higher than those existing in stars. At any given temperature, there is a Maxwellian distribution of energies among the molecules of a gas. At temperatures of millions of degrees a gas does not consist of molecules, but rather of a completely ionized system called a 'Plasma'. A plasma contains equal quantities of positively charged nuclei (ions) and negative electrons. The concept of distribution of energies should be applied. Therefore there will always be a certain proportion of nuclei, which have energies greatly exceeding the average. Thus at a temperature of 20 million degrees, for example, where the average kinetic energy is only 0.002 MeV, there are an appreciable number of nuclei with energies of 0.1 MeV or more. These have sufficient energy to permit them to take part in thermonuclear fusion reactions, resulting in the release of energy.

Most of the thermonuclear reactions are due to nuclei with energies in excess of the average. H.H. Bethe suggested the following to explain nuclear reactions at high temperatures. Two sets of nuclear reactions have been found to account for the energies of what are called "Main Sequence" stars. The first is known as the 'Carbon Cycle', in which the carbon acts as a sort of catalyst in facilitating the combinations of four protons to form a Helium nucleus. The second is known as the proton-proton chain, since the first step involves the combination of two protons. Other nuclear reactions accompanied by the release of energy undoubtedly occur in older (holter) stars.

The net result is thus the conversion of four hydrogen atoms into a helium atom, plus energy amounting to a total of about 26.7MeV.

In the Proton – Proton chain, two protons fuse to produce a deuterium nucleus and a positron:



The energy released is the same as in carbon- cycle, namely 26.7 MeV for each helium nucleus. at low temperatures (Stellar), the proton-proton chain predominates, but as the temperature is raised, the carbon cycle rapidly becomes of increasing significance. Thus in hotter stars (larger), all the energy comes from the carbon cycle but in the smaller (cooler) stars, the proton-proton chain is the main source of energy.

Self Check Exercise-1

1. Discuss the theory of nuclear fission
- 2.a) Show that 1 amu = 931 MeV
- b) Calculate the energy released in the fission reaction.



Self Check Exercise – 2

1. Discuss the different types of nuclear reactors
2. Write a note on fissile and fertile nuclides
- 3.a) Discuss the fusion reaction by using Bethe's carbon cycle and proton–proton chain.
b) Explain how power production is feasible using fusion reactions?

16.3 Let us Sum Up

Fission theory is discussed in detail. Fusion reactions in stars are explained. Bethe's carbon cycle is illustrated. Nuclear power production is discussed. The feasibility of power production using fusion reaction is indicated.

16.4 Points for Discussions

- i) Theories of fission
- ii) Fusion reactions in stars
- iii) The feasibility of power production from fusion reactions.

16.5 References

- 1) Source book on atomic energy – Glass tone – East, West, New Delhi.
- 2) Theory and problems of physical chemistry- Schaum's Outline Series – McGraw – Hill New Delhi.

LESSON – 17

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17.0 AIMS AND OBJECTIVES

The aim of this lesson is to study the synthesis of elements by artificial means. After going through this lesson you would be able to learn the methods by which several transuranium elements have been obtained.

17.1 INTRODUCTION

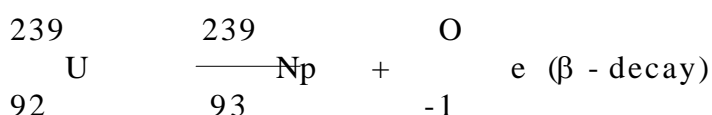
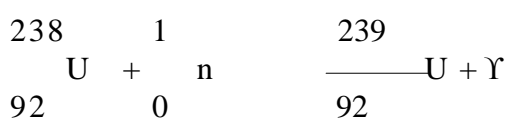
In view of the existence of the lanthanide series, there has been much speculation concerning the possibility of the occurrence of an analogous 'actinide series', beginning with the element actinium, atomic number 89. The four elements of this possible series, whose properties were generally known at the time, namely actinium, thorium, protactinium and uranium are placed in groups IIIA, IVA, VA and VIA. Prior to 1945, most chemists would have doubted the existence of an actinide series. A study of the chemical properties of the new "artificial" elements, Np(93), Pu(94), Am(95), Cm(96), Bk(97), Cf(98), Es(99), Fm(100), and Md (101), has shown clearly that these elements have properties, which would make them members of a series similar to the lanthanide series. The nearly studies of the transuranium elements led to the development of the remarkable techniques of quantitative ultramicro chemistry, this made possible experiments with fractions of a

cubic centimeter of solutions containing a few millionths of a grain of dissolved substance.

17.2 SYNTHETIC ELEMENTS

Neptunium (93)

A thin layer of uranium oxide was exposed to slow neutrons. A non recoiling beta emitting product ($t_{1/2} = 23\text{min}$) was obtained. This was shown to be U-239. This U-239 decayed emitting β rays to give, Np (93) ($t_{1/2} = 2.3$ days)



This new synthetic element does not precipitate with H_2S in acid solution; it is not reduced to the metallic state by Zn. In a reducing SO_2 solution, Np would be precipitated with Ce (III) as fluoride ie, NpF_3 or NpF_4 . The neptunium activity could be separated with sodium uranyl (VI) acetate. Np resembles U; both exist in III, IV, V and VI oxidation states. NpO_2 and NpF_4 are more stable.

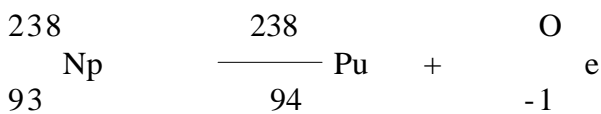
Another isotope of Np, Np-238 ($t_{1/2} = 2.1$ days) was obtained by Seaborg:



Eight Np isotopes with mass numbers ranging from 231 through 241 have been obtained by the bombardment of either one or other of the isotopes of Uranium by deuterons or alpha particles. Tracer techniques are used to

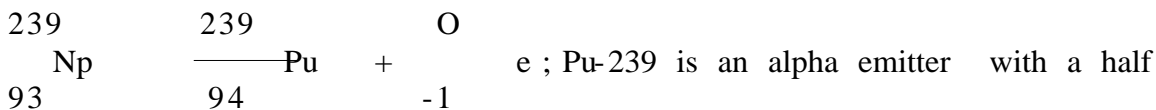
identity the synthetic elements like the transuranium, elements. In this technique an inactive carrier is used to follow the behaviour of a radio active element present in tracer amounts. Provided the material has a reasonably strong activity, it is possible to, trace quantities as small as 10^{10} gm or less. For example if an appreciable quantity of 'Th' is added as carrier to a solution containing a tracer amount of Np, in the reduced state in aqueous hydrofluoric acid, it will be found that the Thorium fluoride (ThF_4) precipitated contains essentially those of the neptunium activity. From this it followed that Np forms an insoluble fluoride namely NpF_4 . Using ultramicro chemical techniques extremely small amounts (from $1\mu\text{g}$ to $0.02\mu\text{g}$) of synthetic elements are analysed. Quantitatively Np has oxidation states III, IV and VI in solutions.

Pu : Plutonium – 238 named after Pluto is an alpha emitter and is formed from Np-238:

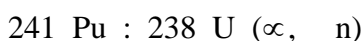
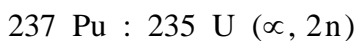
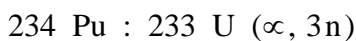
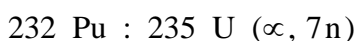


Tracer techniques showed that plutonium like neptunium is precipitated as fluoride or iodate with a rare earth element or thorium as a carrier.

Pu -239 is an important fissile material. It is formed from Np-239.



life of 24, 360 years. Several isotopes of Pu have been obtained by nuclear reactions.



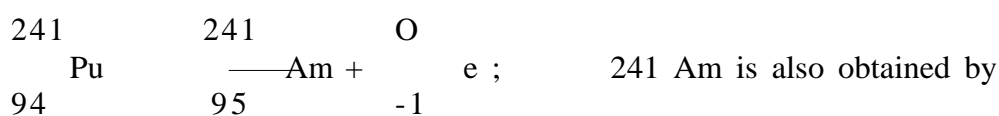
Pu has four oxidation states, III, IV, V and VI. Like Np Pu resembles Uranium in many of its chemical properties. The IV state of Pu is more stable than VI state. The stable oxide of Pu is PuO₂.

PuO₂ $\xrightarrow{1500^\circ\text{C}}$ Pu^{IV}O₃. PuF₄, Pu(IO₃)₄ and Pu(OH)₄ are insoluble like those of thorium.

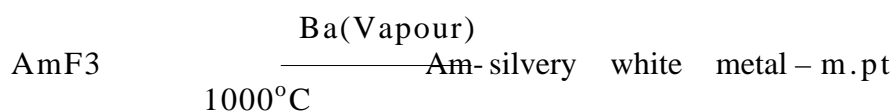
Plutonium metal (used as a reactor fuel) is made by heating the PuF₄ with calcium in a closed vessel:



Am: Americium: Third transuranic element obtained as follows: U²³⁸ is bombarded with 40-MeV 'α' particle to get Pu-241.

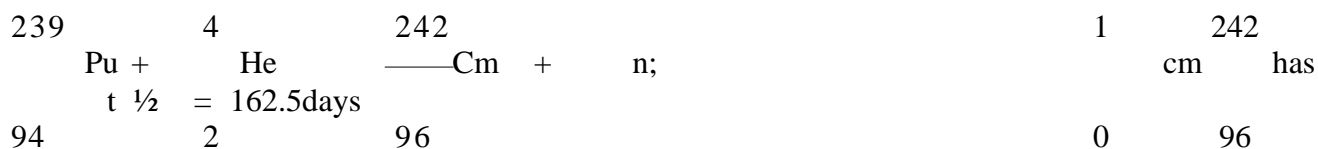


(α,2n) reaction with Pu-239. Am has the stable III state. Am is separated from the rare earth carriers by Ion-exchange methods. Am x 3 (x=Cl, Br,I) are known.

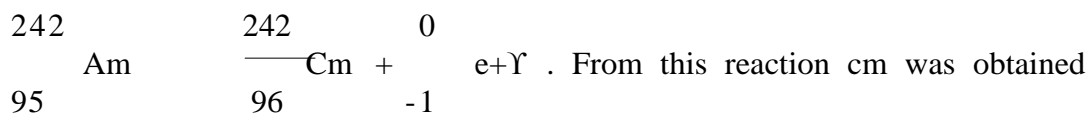


1340°C

cm: curium obtained by bombarding Pu-239 using cyclotron with α - particle.



It was also obtained from metastable Am-242



as cm₂O₃. 13 isotopes of Cm (from 238 to 250) are known.

Bk and Cf: Berkelium (is analogous to terbium)



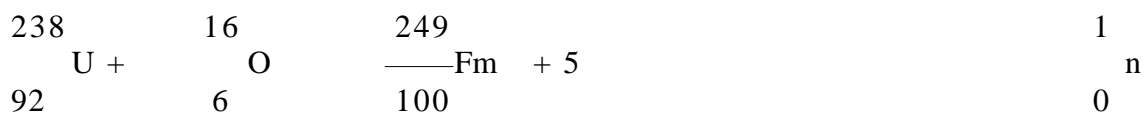
from Am by ion exchange methods. Bk exists predominantly in the (III) state. eight isotopes (mass numbers 243 through 250) are known t_{1/2} of Bk is 4.5hrs.

Californium (Cf) is obtained by the action of 35MeV alpha particle on cm-242. The reaction is (α,n)



Cf exists only in the (III) oxidation state. Es(Einsteinium) and fermium (Fm): Es-247 is obtained by the reaction: 238U (14N, 5n) 247 Es. It has 11 isotopes from 245 to 256. Es-254 (t_{1/2} = 270days) is obtained in weighable amounts. Fm-248 is obtained using.

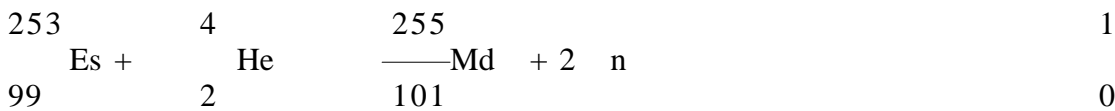
240 Pu (12C,4n) reaction





Mendelevium (Md): atomic no 101. A very small amount of Es253 is bombared with 48MeV alpha particles. The product nuclei were collected by recoil on a gold foil, so that they were free from Es. The gold foil was dissolved and the new element isolated by the ion-exchange method.

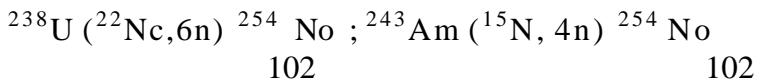
Md-256has a t $\frac{1}{2}$ of 1.5hrs



No: Nobelium (102): produced by the bombardment of cm-246 with C-12 ions using the heavy ionaccelerator



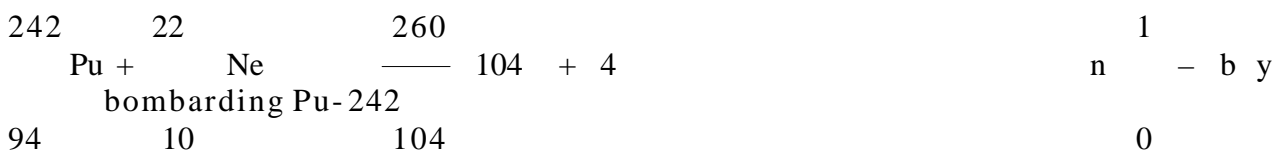
Obtained also by:



No-252 produced from Cm has t $\frac{1}{2}$ of 2.5sec.

LW: Lawrencium (103): The method used to obtain the new element was to bombard a mixture of californium, with mass numbers 249, 250, 251 and 252, with a beam of B-10 and B-11 ions from the heavy ion accelarator . Lw was found to be an alpha particle emitter. By counting the alpha particles, its t $\frac{1}{2}$ was found to be about 8 sec.

Element 104 (Kurchatovium):



using Ne-22 ions, $t_{1/2}$ was given as 0.3sec. The chloride of the new element was reported to be more volatile than the chlorides of other transuranium elements.

Self Check Exercise – I

- 1) Discuss the synthesis of transuranium elements
- 2) Compare the properties of transuranium elements with those of rare earths.

17.3 Let us Sum Up

The synthesis of transuranium elements is explained in detail. Several nuclear reactions are illustrated. The synthesis of Pu-239 (an important fissile material) is indicated. The oxidation states of transuranium elements are also explained.

17.4 Points for Discussion:

- i) Discussion of several nuclear reactions
- ii) Discoveries of transuranium elements and their separation.

17.5 References

- 1) Source book on atomic energy – Glass tone – East, West, New Delhi.
- 2) Theory and problems of physical chemistry- Schaum's Outline Series – McGraw – Hill New Delhi.

LESSON – 18

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18.0 AIMS AND OBJECTIVES

After going through this lesson you would be able to understand the simple principle of hot atom chemistry and you would be able to learn about and use in future, the radio isotopes.

18.1 INTRODUCTION

Several isotopes both radioactive and inactive have been employed to investigate various chemical processes. The isotopic method represents a powerful tool for the solution of numerous problems in biology, physiology, chemistry, physics and other sciences. Some of these problems, particularly those having an important bearing on life processes, could not have been solved without the use of isotopes.

It is only in recent years that isotopes have become available in such variety and in such quantity as to make their use as wide spread as it is at present time.

The more important applications of isotopes depend on the fact that the chemical properties of isotopes of a given element are essentially identical. A radioisotope can be detected by its radioactivity, and an inactive isotope of particular mass can be identified by means of the spectrometer. Therefore, the characteristic property of the isotope namely, its activity or mass can act as a 'tag' or 'label'. The element which has been tagged or labeled is consequently called a tracer element.

In general an element can be labeled by changing its natural isotopic composition. For example ordinary 'C' contains 1.1% of C-13, but if the proportion of this isotope in a particular compound is increased, the carbon has become labeled.

Suppose that acetic acid, in which only the CH₃ carbon is labeled, is supplied to an organism then among the metabolic products, appears CO₂ gas. Upon testing the gas it is found to be inactive, This shows that the carbon in the 'CO₂' originated from the – COOH group and not from the CH₃-group.

This example is a simple illustration of the type a problem for which an unequivocal solution could not possibly be obtained without the use of an isotopic tracer.

18.2.1 HOT ATOM CHEMISTRY

The name "hot atom chemistry" is given to the study of chemical reactions resulting from the transfer to valence bonds of energy produced in nuclear processes of various kinds.

Isomeric transition is sometimes accompanied by the breaking of a chemical bond.

This may make possible a separation of the isomeric nuclei. An interesting example is provided by the isomers of tellurium, for (eg) Te-131. If to a Tellurate solution (Te (VI), containing this species, is added some ordinary

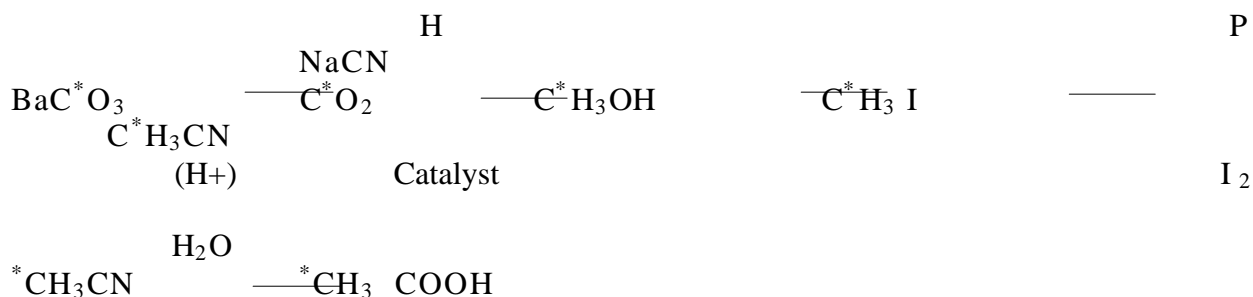
inactive tellurite (Te(IV)), then upon separating the latter chemically, it is found to contain the 25-minute isomer. This is explained as follows: the gamma ray emitted by the upper (1.2 days) isomeric state undergoes internal conversion, resulting in the ejection of an electron from a K or L level of the product atom, that is from the lower (25 min) isomeric state. As a result of what is known as the "Auger effect", the high energy of this inner (K or L) electron is transferred to one or more of the outer electrons (valence electrons), which are consequently removed from the atom. This detachment of valence electrons from the 25-min isomer results in the breaking of some of the bonds between the tellurium and oxygen atoms, consequently the isomeric transition is accompanied by a change from the VI to the IV oxidation state i.e., from tellurate to tellurite.

L. Szilard and T. Chalmers employed this type of hot atom chemistry to separate the product of an (n, γ) reaction from the target material. The emission of a γ -ray photon following the capture of a neutron causes the residual nucleus to recoil; the recoil energy is sufficient to break the chemical bond attaching this particular atom to the remainder of the molecule. The product atom, although isotopic with the target atom, will thus be in a different chemical form, and a separation from the original material becomes possible. For example, if an aqueous solution of NaClO₃ is subjected to the action of slow neutrons, the reaction $^{37}\text{Cl}(n, \gamma)^{38}\text{Cl}$ takes place, but many of the Cl-38 atoms formed are detached from the chlorate and pass into solution as Cl(-) ions. By adding a small amount of inactive chloride to the solution and precipitating with silver nitrate, the resulting AgCl is found to carry the whole of the Cl-38 activity.

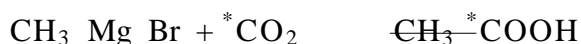
18.2.2 APPLICATIONS OF RADIO ISOTOPES

In much of the work in which an isotope is used as a tracer it is necessary to introduce the tracer element into a certain compound to be studied. In biochemical investigations the object of the study is to determine the fate of the different portions of a given compound. The preparation of labeled

compounds has become an important aspect of tracer studies. For example consider the synthesis of C-14 labeled acetic acid (CH₃ – group is to be labeled) BaCO₃ containing C-14 is employed. The sequence of reactions can be represented as:



To Label – COOH, carbon, consider the reaction:



TRACER APPLICATIONS:

The use of isotopic tracers in biological studies is to obtain information that will make possible a better understanding of many complex processes which take place in living organisms.

Linseed Oil, which contains fats derived from doubly and triply unsaturated acids, was partially "hydrogenated" by means of deuterium as as to give a mixture of both saturated and unsaturated fats, in which two or four of the hydrogen atoms attached to the carbon were replaced by deuterium. The resulting deutero fats were fed to animals. The analysis showed that the major part of the deuterium was found to have been deposited in the fatty portion of the body. Further studies indicated that the saturated fats are desaturated by the removal of deuterium and at the same time the unsaturated fats are saturated by the addition of hydrogen (or deuterium) from water.

Deuterium studies indicate tat only singly unsaturated fats could take part in the equilibrium. Such deuterium studies in animals indicate that the highly unsaturated fats are indispensable in the sense that they must be supplied in the diet, the body being unable to synthesis them. By lebeling various dietary

amino acids with both isotopic nitrogen and deuterium it has been shown that the formation of creatine in the body requires contributions from three amino acids, namely glycine, arginine and methionine. The creatine is produced in this manner and is converted into creatine at a fairly steady rate, Creatine is the an hydride of the amino acid creatine, an important constituent of animal tissue. An approximately constant amount of creatine is excreted daily in the urine. Tracer studies using radio active iron as tracer indicate that iron is stored in the body in the form of an iron-protein combination known as ferritin. When the store of ferritin has attained its normal value it does not increase further, no matter how much iron may be supplied orally. If the iron reserves decrease, then the amount of ferritin decreases, the body is able to absorb iron.

Radio iron studies that indicate iron remains in the hemoglobin as long as the red blood-corpuses are intact. But when the corpuses are destroyed, the iron is not lost, it is almost wholly retained in the body and is rapidly incorporated into the hemoglobin of new red corpuses. It is this phenomenon which accounts for the small absorption of iron from the food under normal conditions.

Radioactive isotopes have become a valuable tool in the diagnosis and understanding of many diseases. A simple instance is provided by the use of radio sodium to study cases of restricted circulation of blood. A small quantity of sodium chloride solution, in which the sodium has been labeled with Na-24, is injected into a vein of the patient's fore arm, a gamma ray counter is then placed in contact with one of the feet. If the blood circulation is normal, the presence of radioactivity is very soon detected in the foot, it increases rapidly and reaches a maximum value within less than an hour. If there is a circulatory impairment of some kind, however, the radioactivity will increase slowly, showing that blood has difficulty in reaching the foot. By moving the counter to different parts of the body the position of the restriction can be located, and the necessary treatment applied.

It has been found by introducing iron-59 into the blood of a normal human being that the iron is deposited in and then removed from the marrow, the spleen and the liver in a manner that is specific for the particular organ. In cases of anemia (deficiency of red blood cells) and polycythemia (excess red cells), the normal behaviour is changed in a manner typical for each disease. In the case of anemia the activity of iron-59 increases with time. But in the case of a normal human being the activity increases and then decreases with time. In refractory anemia associated with hypoplastic (under developed marrow), for example, the iron is found preferably in the liver rather than in the marrow where the red blood cells are formed.

The tracer experiments have also demonstrated that red cell formation is controlled by a hormone called erythropoietin, which circulates in the blood stream. At normal conditions are associated with an excess or deficiency of this hormone.

Vitamin B-12 (complex organic compound containing cobalt) has been prepared with the cobalt as a radioactive isotope, either Co-57, -58 or -60 and its rate of absorption and loss from the body has been studied with the whole body counter. From the results it is possible to distinguish three types of behavior, normal, second, inability to absorb B-12 from the intestine and third pernicious anemia, in which there is a deficiency of the vitamin in blood. Whole-body radiation measurements with labeled B-12 are being used in the study of pernicious anemia. The position of tumours have been identified using radio isotopes. I-131 has been used to study the functioning of thyroid gland. Brain tumor is detected using tracers like the positron emitter Ga-58 and the isomer of technetium-99 in the form of pertechnetate ion. After injection of the radioactive tracer the location of the brain tumor can be found by means of a suitable scintillation camera or a multiple detector scanner.

Co-60 obtained from the reaction $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$, is used in cancer therapy.

Brain tumors are destroyed using an internal source of alpha particles (and lithium ions). α - particles are obtained from B-10 by means of (n, α) reaction.

Radio active isotopes have been extensively employed in agricultural research. The use of P-32, is indicated below. Phosphoric acid containing a known proportion of P-32, is converted into a phosphate such as calcium superphosphate, tricalcium phosphate or hydroxyapatite suitable for use as a fertilizer. A definite quantity of the labeled phosphorous is then applied to the soil, in which plants are grown. At certain intervals a number of these plants are harvested and the total phosphorous derived from both soil and fertilizer, is determined by chemical analysis of their ash. The radioactivity of the plant ash, combined with the measured specific activity of the fertilizer, gives the amount of phosphorous which the plant takes up from the fertilizer.

It has been shown by such studies that (in poor soil conditions) corn requires most of its phosphorous fertilizer at the beginning and less toward the end of the growth with potatoes on a similar soil, from 50 to 60% of the phosphorous uptake came from the fertilizer during the whole period of the growth.

Radioactive tracers have been employed in several industrial processes. Wetting, detergency and floatation of minerals, adsorption and lubrication are examples of surface phenomena upon which work has been done with radioactive tracers. Age hardening, annealing, quenching and cold rolling of alloys have been subjected to radio tracer studies to understand the effects of such treatments.

Activation Analysis is a powerful tool in many aspects of science and industry. The basic principle of activation analysis is that one (or more) of the stable isotopes of a given element is activated "i.e, converted into a radioactive nuclide, by a suitable nuclear treatment e.g, bombardment with

neutrons, with accelerated particles or by high energy X-rays. The product can then be identified by its radiation, i.e, beta particles, or gamma rays and by its half life. By using a comparison sample containing a known amount of the particular element and treating it in exactly the same way as the unknown specimen, the analysis can be made quantitatively. The most common application of the techniques is probably in testing highly purified substances for traces of impurities. Construction materials and moderators for nuclear reactors, for example, must be exceptionally free from elements that capture neutrons to a significant extent. Activation analysis provides a sensitive means for detecting such impurities. Small amount of oxygen present in the steel is detected by measuring gamma ray from $N-16$ produced by the reaction $^{16}O(n,p)^{16}N$

Tracer Analysis

Tracer analysis involves the addition of a known amount of an isotopic material (a known amount refers to a known rate of particle emission as determined by a suitable counter) suppose it is required to analyse a solution for the element 'A', present in very small amount. Let the element B be one which forms an insoluble compound AB; a solution of 'B' is prepared with one of its radio isotopes in known proportion i.e, known specific activity. The solution 'B' is then added to 'A', to precipitate all of the 'A' as the insoluble 'AB'. The precipitated AB is separated and counted. From the observed count rate the total quantity of 'B' in the precipitate can be calculated, this is equivalent to the amount of 'A' in the precipitate.

Solubilities of a sparingly soluble salts can be determined by tracer method. A sample of $Pb(NO_3)_2$ is prepared containing a known ratio of the alpha emitting isotope Ra-D. The nitrate is dissolved in water and a solution of sulphate is added. The solid $PbSO_4$ containing Ra-D as tracer is then used to prepare a saturated solution in water. This solution is evaporated and its α -activity measured. The total amount of lead in the solution and hence the

solubility of lead sulphate can be calculated from the known proportion of Ra-D.

The dilution principle has been applied to determine the volume of water in the body. For this purpose either the stable isotope D_2 or tritium can be used as a tracer. A definite volume of water containing one of these isotopes is injected into the body and after allowing about an hour for uniform mixing to take place, a sample serum is withdrawn and its isotope content is measured.

From the change in concentration, the volume of water in the body can be calculated. If the isotope concentration is found to be decreased by a factor of 1000, for example the volume of water in the body is 1000 times that originally injected.

Age of uranium can be estimated as follows:

$N_t = N_0 e^{-\lambda t}$; $N_0 = \text{U-238}$ originally present in the mineral and N_t is the amount left after the lapse of time 't'. This represents the age of the mineral. Since essentially all the U-238 has been converted into $Pt-206$, the quantity of $Pt-206$ present is equal to:

$(N_0 - N_t)$ Therefore = $(^{238}\text{U} = ^{238}\text{U} + ^{206}\text{Pb}) e^{\lambda t}$ knowing the amount of U-238 and $Pt-206$ present and knowing λ of U-238, 't' the age of the mineral can be estimated.

By means of radio carbon dating the age of a dead wood or animal can be estimated.

Several radio nuclides have been employed as heat sources for power generation in satellites. $Pu-238$ is the heat source in the 25-watt thermo electro generator used in some satellites.

Self Check Exercise – 1

- 1) Explain the term 'hot atom chemistry' and discuss its applications.
- 2) Discuss the uses of radio isotopes in the fields of
 - i) Biology
 - ii) Medicine
 - iii) Agriculture.
- 3) Discuss tracer analysis

Self Check Exercise 2

- 1) A sample of ^{14}C CO_2 was to be mixed with ordinary CO_2 for a biological tracer experiment. In order that 10 cm^3 of the diluted gas at STP should have 10^4 dpm, how many μCi of radioactive C-14 are needed to prepare 60L of the diluted gas? (Ans: $\sim 27\ \mu\text{Ci}$).
- 2) In order to determine the volume of the blood in an animal, a 1.00ML of an aqueous solution containing tritium is injected into the animal's blood serum. The sample injected has an activity of 1.8×10^6 CPS (Counts/sec). After sufficient time, 2.00ML of blood are withdrawn from animal and the activity of the sample of blood is found to be 1.2×10^4 CPS. Calculate volume of animal's blood (Ans: $\sim 300\text{ML}$).
- 3) A sample of uraninite, was found to contain 0.214g Pb-206, for every gram of uranium. If all the lead came from the disintegration of U-238, estimate the age of the mineral ($T_{50}\ \text{U-238} = 4.5 \times 10^9$ yrs)

18.3 Let us Sum Up

Hot atom chemistry is defined. The uses of radio isotopes in the fields of biology, medicine and agriculture are discussed in detail. Tracer studies are illustrated.

18.4 Points for Discussion:

- 1) Hot atom chemistry – definition and other examples.

- 2) Several uses of radio isotopes

18.5 References

- 1) Source book on atomic energy – Glass tone – East, West, New Delhi.
- 2) Theory and problems of physical chemistry- Schaum's Outline Series – McGraw – Hill New Delhi.

UNIT – VII

LESSON – 19

CONTENTS

- 19.0 AIMS AND OBJECTIVES
- 19.1 INTRODUCTION
- 19.2 EXPERIMENTAL METHODS FOR DETECTION OF NUCLEAR RADIATIONS
 - 19.2.1 CLOUD CHAMBER
 - 19.2.2 BUBBLE CHAMBER
- 19.3 LET US SUM UP
- 19.4 POINTS FOR DISCUSSION
- 19.5 REFERENCES

19.0 AIMS AND OBJECTIVES

The lesson describes the various experimental techniques such as cloud chamber, bubble chamber for the detection of nuclear radiations, After going through this lesson you would learn how such instruments like Wilson's cloud chamber made possible the discovery of particles like positron, muon, various mesons and other particles.

19.1 INTRODUCTION

Instruments like cloud chamber are useful for the study of artificial transmutation. A single cloud chamber photograph can demonstrate with compelling evidence how many fragments are formed in a single transmutation, process and the directions in which they fly away and how far they are able to travel through the gas in the chamber.

19.2.1 CLOUD CHAMBER

In 1911, Wilson showed that the path of a single ionizing particle could be made visible. The apparatus is known as cloud chamber. Air contained in an enclosed space can be saturated with the vapour of water or any other liquid the amount of the vapour necessary to produce saturation decreasing as the temperature is lowered. Imagine a vessel containing air saturated with water vapour enclosed by a piston. The piston is maintained in position by the pressure of air below it. If the pressure under the piston is suddenly released, so that it falls, it will result in the immediate expansion of the air or gas in the vessel. The sudden adiabatic expansion causes the air to be cooled and it now contains more vapour at this lower temperature. If particles of dust are present in air, they will act as condensation nuclei, and the excess of water vapour will separate out as fine droplets of liquid in the form of a cloud or mist.

The air is saturated with water vapour and the piston is allowed to drop to such an extent as will expand the volume of the air by a factor of 1.25 to 1.37 this being the range in which cloud formation can occur. If an ionizing particle enters the chamber, either immediately before, during or immediately after the expansion, the ions left in the path will act as condensation nuclei, a close array of fine droplets, ie. a kind of linear cloud, called a cloud track will thus be formed. By using strong illumination from the side, the track appears as a white line on the dark background. This can be photographed by means of two cameras at right angles, so that a record can be attained from which the path of the single ionizing particle in three dimensions can be studied. Cloud chamber photographs have shown that alpha particles travel in straight lines.

In the earlier cloud chambers a layer of water or oil was used on the floor of the chamber as a seal for the piston and this meant that the piston could be used only in the horizontal position. Wilson constructed a cloud chamber in which the piston was replaced by a thin rubber diaphragm fixed at its edge. The diaphragm was maintained in a state of tension by means of

compressed air in the back or lower part of the chamber, and when this was released the gas in the chamber underwent sudden expansion. A cloud chamber of this type can be used in any desired position. To saturate air in the Wilson's chamber water was initially used. But ethyl alcohol or propyl alcohol or a mixture of alcohol and water can be employed to saturate the air in the chamber. The use of alcohol gives better condensation on positive ions, than does water alone and in addition, the extent of expansion necessary for droplet formation is diminished from 1.25 to 1.10 at ordinary pressure. Cloud chambers containing argon are also employed. The pressures range from below atmospheric to about 200 atm. The higher pressures are desirable for the study of high energy (or long range) particles which might otherwise pass right through the chamber without taking part in an event of interest.

For the study of radioactive radiations and for many similar purposes, relatively simple cloud chambers, with air at ordinary pressure, are quite adequate. Because of the low penetrating power of alpha particles, the source of the radiation, must be inside the chamber. But a substance emitting ' β ' particles can be placed outside and the rays allowed to enter through a 'window'. Gamma rays and x-rays, yield cloud tracks because they liberate electrons which produce ionization in their paths. These tracks are however very faint. By making visible the track of an ionizing particle, the range of the particle and its energy can be calculated.

$$E_0 = 2.12 \cdot R^{2/3} \quad \text{-----(1)}$$

E_0 = initial energy of the alpha particle in MeV and R is its range in cms of air .

By counting the drops in the cloud track the specific ionization can be determined and the nature of the particle identified, it is thus possible to distinguish between an alpha particle, a proton, a meson and an electron. The α particle has the highest specific ionization and gives a short dense track,

while an electron, unless it is moving with very high speed, leaves a track which is diffuse. By determining the radius of curvature of the cloud track in a magnetic field of known strength, the momentum of the particle can be estimated. The direction of curvature indicates the sign of the electric charge of the ionizing particle. The discovery of the position was made in this manner.

The basic disadvantage of the condensation cloud chamber is that, because of the low density of the gas, the significant phenomena are not very frequent.

19.2.2 Bubble Chamber

In 1952 D.A. Glaser at the University of Michigan conceived the idea of using superheated liquid to display the track of ionizing particles, just as a cloud chamber uses a superheated vapour. The instrument based on this concept is called a bubble chamber, because the tracks consist of a series of closely spaced bubbles, analogous to the small droplets of liquid in the cloud chamber.

Glaser found that when such a superheated liquid was exposed to nuclear radiation, the resulting ions acted as nuclei for the production of small bubbles. The bubbles are spaced at something like a hundredth of an inch apart depending on the specific ionization of the ionizing particle, so that they appear as a fairly continuous track which indicates the path of the particle. As in the cloud chamber, the tracks can be photographed against a dark background.

The medium in the first bubble chambers was diethyl ether, but liquid hydrogen, D_2 , He, propane and other liquids have been used successfully. For studying the interaction of particles with protons, the liquid in the chamber is hydrogen. Along with liquid H_2 , C_3H_8 is also used, in the chamber.

For neutron interactions liquid deuterium is employed in the chamber. For studying ' γ ' rays, liquid containing heavy atoms is favoured. Freon type compounds such as trifluoro bromomethane and liquid xenon have been employed in the chamber.

The operation of a bubble chamber is similar in many respects to that of an expansion cloud chamber. The liquid is compressed and the temperature is raised to well above the normal boiling point at atmosphere pressure. For (eg) propane has a normal boiling point of -42°C . It is compressed to about 21 atmospheres and heated to a temperature of 58°C . The pressure is then decreased suddenly and the liquid becomes super heated. In this condition it is sensitive to the passage of ionizing particle. Even if no such particles enter the chamber, boiling with bubble formation would invariably occur within a short time. Regardless of whether a particle track is formed or not, the liquid must be recompressed before it is again ready for operation.

The earliest bubble chambers had linear dimensions of only one inch or two and were made with smooth glass or lined internally with glass. Larger bubble chambers (upto 14 feet in length) have been designed for tracking particles of higher and higher energies. Bubble chambers are almost invariably placed in a magnetic field, of known strength. The momentum of the charged particles can then be determined from the radius of curvature of the bubble track. For particles of high momentum, the curvature is small, and difficult to measure unless a strong magnetic field is used.

In many studies with high energy particles, it is necessary to analyze a large number of bubble chamber events and then to plot the data in a suitable manner to obtain the probability distribution of various events. This statistical analysis can also be performed by a computer. The results are then displayed in some convenient graphic manner for use of interpretation.

Nuclear Emulsion

In 1909 Miigge (Germany) and S.Kinoshita (Japan) observed that the blackened regions of a developed photographic plate, resulting from exposure to alpha particles, appeared to be made up of individual grains. It was later realized that the positions of the grains were related to the path of the alpha particles. It was found that ionizing particles, in general record their tracks in a photographic emulsion, as a series of closely spaced black specks of silver.

Because of the relatively high density (and stopping power) of the photographic emulsion, the tracks produced by charged particles are very short compared with those found in a cloud chamber. These tracks do not differ greatly from bubble tracks. Due to the development of special nuclear track emulsions this method is largely employed in tracking charged particles. They were widely used in cosmic ray studies and led to the discovery of Pi-and K- mesons.

The composition of emulsion had been changed so as to make it more suitable for the study of various ionizing particles, such as alpha particles, protons, mesons and even electrons. By adding Boron or lithium to the emulsion neutrons can also be detected. The modern emulsion contain silver bromide to the extent of 80% or more of the dry weight, this being about ten times the quantity present in plates or films used for normal photographic purposes. The silver halide grains are extremely small. The smaller the grain, the more sensitive is the emulsion to ionizing radiations originally the emulsions were deposited (roughly one eighth of a centimeter thick) on glass plates. Now, stripped emulsions are available without backing.

The tracks produced in a photographic emulsions are very short, (eg) a few thousandth's of an inch for alpha particles from radioactive sources, but they can be magnified and photographed.

The photograph emulsion resembles the Wilson cloud chamber in the respect that it can record individual events involving atomic nuclei and other

charged particles. Information concerning the particles involved can be obtained from measurements on the photographic tracks. Tracks caused by heavy, strongly ionizing particles have numerous thin wavy tracks projecting from their sides. These are called delta rays and are produced by electrons ejected from the nuclei in the path of the particle. From the number of delta rays per unit track length, the magnitude of the charge in the particle can be estimated.

By the use of very strong magnetic fields, the deflection of long (but not short) tracks in photographic emulsions has been observed. This gives the sign of the charge, but the large amount of scattering makes the deflected tracks useless for calculation of momentum. This is a disadvantage of nuclear emulsion.

Self Check Exercise – 1

- 1) How is a cloud formed in the cloud chamber?
- 2) What are the other compounds that can be used in the cloud chamber? Indicate the advantage.

Self Check Exercise – 2

- 1) How does a bubble chamber work? Discuss the advantages when compared to the cloud chamber.
- 2) Write a note on nuclear emulsion method, in tracking nuclear particles.

19.3 Let us Sum Up

The designs of cloud chamber and applications are explained in detail. The advantages of bubble chamber and nuclear emulsion techniques are indicated.

19.4 Points for Discussion

- i) The designs of the cloud chamber and applications
- ii) The advantages of the bubble chamber and nuclear emulsion techniques.

19.5 References

- 1) Source book on Atomic Energy by Glass tone – East West press India.

LESSON – 20

CONTENTS

20.0 AIMS AND OBJECTIVES

20.1 INTRODUCTION

20.2 THE DIFFERENT TYPES OF COUNTERS

20.2.1 Proportional Counters

20.2.2 Scintillation counters

20.3 LET US SUM UP

20.4 POINTS FOR DISCUSSION

20.5 REFERENCES

20.0. AIMS AND OBJECTIVES

After going through this lesson, you would be able to understand

- i) some of the most useful procedures for the detection and measurement of radiations like Alpha & Beta particles.
- ii) the way in which the measurements of radiations are carried out.

20.1. INTRODUCTION

Becquerel found that gases become electrical conductors that is they are ionised, as the result of exposure to radiations from radioactive substances. The amount of radioactivity could be measured, by measuring the extent of ionisation by a radioactive source.

A rapidly moving charged particle like alpha or beta particle has the ability to eject – orbital electrons from the atoms or molecules of a gas through which it passes, thus converting them into positive ions. The ejected electrons attach themselves to other atoms or molecules, to form negative ions. Thus the passage of a charged particle, through a gas results in the formation of Ion-pairs consisting mainly of positive ions and free electrons. A term 'Specific ionisation' is used to express the intensity of ionisation

produced by a charged particle in its path. It is the number of ion-pairs formed per cm of path. For particles of same mass and energy, the specific ionisation increases with the magnitude of the charge, and for particles of the same energy and charge it increases with the mass.

The total number of ion-pairs produced by a charged particle is determined largely by the energy.

20.2.1 PROPORTIONAL COUNTERS :

One has to understand the behaviour of ion-pairs in electric fields. Quantitative measurements of radiations are based on counting of individual particles, as well as on the determination of total radiation received in a given interval of time. For these purposes instruments have been developed in which the positive and negative ions formed by the ionising radiations are driven towards the collecting electrodes, by means of an applied potential under various conditions.

Consider for example an apparatus consisting of a vessel, containing gas or air, in which two electrodes, connected to a battery are fixed. The circuit also contains a current measuring instrument. Normally the air in the vessel does not conduct electricity and hence no current is observed. If any ionising radiation such as alpha or beta particle enters the vessel and when a small electric potential is applied to the electrodes, the ion-pairs produced and the applied potential would produce a pulse of current. The magnitude of the charge collected and therefore the size of the current pulse will depend on two factors viz.

- i) the number of ion-pairs produced between the electrodes and
- ii) the applied voltage.

When logarithm of pulse size is plotted against applied voltage a number of regions could be obtained. A few these regions have been employed to measure the radiations.

The proportional counter is based on the fact that, for a given applied voltage across the electrodes, the size of the current pulse is proportional to the number of Ion-pairs produced between the electrodes. This condition is best obtained by using a cylindrical chamber, which acts as the negative electrode, with a central wire, is the positive electrode.

When the voltage is high enough, the electric field near the central wire becomes so large that the electrons, produced by the primary ionization of the gas, by an alpha or beta particle, would move toward it with very high speed. When the speed becomes very high the electrons would cause the ionization of the other atoms or molecules in the gas, this produces more electrons which cause further ionization. This multiplication effect is often known as 'Townsend avalanche or Townsend Cascade.

The total number of ion-pairs produced by a single primary ion-pair is called the gas amplification factor. The size of the current produced by a single particle is thus increased to a very great extent, so that considerably less external amplification is required. Pulse counting is employed in a proportional counter.

In the proportional counter the magnitude of the potential ranges from 500 to 800 volts. Various gases have been employed for filling proportional counter tubes. A mixture is used consisting of a simple gas such as hydrogen or Argon, which favours high amplification and a gas like carbon dioxide, methane or pentane, to provide stability of operation For (eg) a typical gas mixture consists of methane and 10 to 20% by volume of argon.

The total pressure is always less than 1 atm. Because of the proportional character of the amplification, an alpha particle will give a larger pulse than a Beta particle or a gamma ray photon. Hence proportional

counting instruments are particularly useful for counting alpha particles in the presence of beta particles and gamma rays.

Geiger – Muller Counter

This counter is widely used in radioactive counting. It is known as G-M counter. Because the detecting portion is commonly in the form of a tube, the names Geiger - Muller tube or G-M tube are commonly used.

The essential difference between the proportional and the GM counter is that, in the proportional counter an electron from an ion-pair, produces an avalanche at one point only, whereas in the G.M. Counter, the avalanche spreads along the whole length of the central wire. In the Geiger counter, the amplification is so great that the size of the pulse is almost independent of the number of Ion-pairs. When the applied potential in the instrument reaches a value known as 'Geiger threshold potential', the number of pulses per minutes (due to the production of ion-pairs by the entering alpha or beta particles), becomes essentially constant. The range of potential over which this occurs is known as 'Geiger– plateau'. Beyond this plateau, continuous discharge occurs and counting is not possible. Most G.M counters are filled with gas at pressure below atmospheric pressure, when the plateau may extend over a range of two or three hundred volts in the region from about 800 to 1500 volts. The trouble with GM counter is that, the separate pulses produced by different particles entering the Geiger tube are not resolved. To improve the resolving power of the G.M counter a mixture of gases like argon and methane is used for filling the Geiger tube. This quenches the discharge (self quenching) and resolution is improved.

When properly quenched (internally or externally) a G.M counter will have a resolving time of about 200 micro second, in other words, particles arriving at intervals of not less than 2×10^{-4} seconds will give separate pulses. If the particles were produced at a uniform rate, a maximum of 5000 pulses could be counted per second. Actually the practical counting rate is less-than this maximum.

The GM tube is almost invariably used to determine the rate at which radiation is being received at a particular point. For this purpose the output of the GM tube, generally without amplification is applied to a counting rate meter.

Because of their versatility GM tubes have been made in great variety of sizes and shapes from 1 cm to 1 m in length and from 0.3 cm to 10 cm in diameter. The walls can be of metal, e.g., copper, or a metal cylinder may be supported inside a glass tube. In another form of GM tube the interior surface of the glass tube is coated with a thin layer of an electrical conductor like silver or graphite. The central wire of the GM tube (which acts like anode) is usually made of tungsten, with a thickness of 0.02 to 0.05 mm the pressure in the GM tube is usually less than atmospheric pressure.

G-M counters are mainly used for counting beta and gamma rays, partly because it is difficult to make tubes with windows thin enough to be penetrable by alpha particles. When the penetrating power of the beta radiation is small, the tube may have a very thin glass or mica window through which the particles can pass.

In health protection operation, it is required to know that radioactive material is present and to know a rough indication of the quantity of radiation. For this purpose the GM counter with a rate meter is very convenient. GM tubes are rarely designed to detect alpha particles, because of their short range in air and small penetrating power.

For the detection and rough measurement of the intensity of alpha particles, some form of proportional counter is generally used.

20.2.2. SCINTILLATION COUNTER :

This is one of the oldest methods of counting particles. It is based on small flashes of light (or scintillations), which are produced when certain materials are exposed to nuclear radiations. The production of these

scintillations, involves the initial formation of high energy (or excited) electronic state of the molecules (or atoms). The excess energy which has been obtained from the nuclear radiation, is then emitted within a very short time as a flash of light. Each particle produces a flash of light.

The first attempt to count alpha particles by observing the scintillations they generated in a diamond was made by E. Regener in Germany in 1908. Rutherford and Geiger, at the same time compared the number of pulses, produced by Ra-c source, in an ionization counter and the number of scintillations produced by the same source, on a ZnS screen and they found that the numbers were the same. Thus if each alpha particle gives one pulse in the counter, it also gives one flash in the scintillation counter.

In this manner, Rutherford and Geiger established the reliability of the scintillation method of counting, alpha particles. Certain organic and inorganic phosphors which produce scintillations when exposed to nuclear radiations, are transparent to the light they emit. Therefore large quantities of the scintillator can be used in the counter. This ensures high probability of interaction with the radiation and high detection efficiency. Thus using a photo multiplier tube in a scintillation counter along with the phosphor, helps in the counting of particles from a radio active source. A large clear crystal of naphthalene as phosphor was employed with a phototube in the scintillation counter.

The crystal of the phosphor, surrounded by thin aluminium foil, is attached to the top, close to the cathode of the phototube. The purpose of the foil is to reflect the light flashes on to the cathode. A particle of nuclear radiation (or gamma ray photon) entering the phosphor causes a flash of light, which falls on the photo cathode. As a result electrons are emitted and these are subsequently multiplied to produce a relatively large electric pulse at the output of the tube. Of the solid organic scintillators, anthracene and transstilbene appear to be the best. Liquid scintillators (solution containing xylene as the solvent and a few percent of diphenyl oxazole as the solute) have also been employed in scintillation counters. One of the best inorganic

scintillators especially for gamma rays, is crystalline sodium iodide with 0.1% Thallium as activator. Zns, activated by Ag is an excellent scintillator and is made in thin layers. Its chief application lies in the study of alpha particles. Inert gases have also been used as scintillators.

When rapid response is required NaI scintillator cannot be satisfactorily used. (the light pulse produced has long decay time)

Scintillation counters have found many uses due to the following reasons :

- i) they are simple
- ii) Flexible and versatile
- iii) high sensitivity to all forms of nuclear radiations.
- iv) rapid response
- v) very short resolving time
- vi) can be used to measure photon energies
- vii) superior to GM counters for gamma ray detection.

Self Check Exercise –1

1. How are ion-pairs produced in an ionization chamber?
2. Discuss the design and uses of proportional counters.
3. Write a note on G.M. counter and also indicate its advantages

Self Check Exercise –2

1. Discuss the design and uses of scintillation counters
2. How many types of phosphors are used in the scintillation counters?

20.3 Let us Sum Up

The designs and advantages of different types of counters are explained in a detailed manner. The G.M. Counter is explained and its advantage is indicated. Examples of different types of phosphors used in Scintillation counter are given.

20.4 Points for discussion

- i) The designs and advantages of different types of counters
- ii) A comparative study of different types of phosphors employed in scintillation counters.

20.5 References

- i) Inorganic chemistry J.D. Lee
- ii) Source book on atomic energy – glasston – East west press
- India

LESSON – 21

CONTENTS

- 21.0 AIMS AND OBJECTIVES
- 21.1 INTRODUCTION
- 21.2 PARTICLE ACCELERATORS
 - 21.2.1 CYCLOTRONS
 - 21.2.2 BETATRON- BEVATRON
- 21.3 LET US SUM UP
- 21.4 POINTS FOR DISCUSSION
- 21.5 REFERENCES

21.0 AIMS AND OBJECTIVES

The aim of this lesson is to make an in depth study of different types of particle accelerators.

After going through this lesson one would be able to understand

- i) The design and the uses of accelerators for accelerating the various types of particles
- ii) The energies attained by different particles, when particles are accelerated by various types of accelerators.

21.1 INTRODUCTION

A particle accelerator is a device for increasing the kinetic energy of electrically charged particles. Upto about one tenth of the velocity of light, the kinetic energy can be calculated by means of $\frac{1}{2} m_0 V^2$, where m_0 is the rest mass of the particle and V its velocity.

Since 'm' is constant, increase of kinetic energy implies increase of velocity. It is for this reason that the machine employed for increasing kinetic energy, is called an 'accelerator'. As the velocity of the particle approaches the velocity of light, its mass also increases. Under these

circumstances, an accelerator can increase the kinetic energy with very little increase in velocity.

Many nuclear reactions have been studied by high energy particles. Accelerators have been used in the creation of new particles. The muon and mesons have been discovered using high energy particles. Several additional particles not previously known have been found using high energy particles. Calculations indicate that protons with energy of 5.6 billion electron volts would be required to create antiprotons and antineutrons. The anti protons and antineutron are not known to occur in nature. For the discovery of antiprotons and antineutrons. Beaverton accelerator was designed at the University of California.

Accelerators have also been designed to study the nuclear structure, the nuclear forces and strong and weak interactions.

Protons of 400 to 1000 MeV energy are used to produce intense beam of pions. Natural decay of pions may in turn yield muons and neutrons of high energy.

The growth of high energy particle physics is due to the particle accelerators.

21.2.1 CYCLOTRONS

Lawrence modified the 'Wideroe' Cylindrical (linear accelerators) accelerator by using a magnetic field to make the charged particles follow a spiral path, of increasing radius. The length of the path would then increase automatically with the speed of the particles. The 'cyclotron' was designed on the basis of this principle.

The first accelerator to yield protons of energy in excess of 1 MeV— was the cyclotron constructed by Lawrence and Livingston in 1932. It had a magnet with pole faces 11 inches in diameter. The energy to which a particle

can be accelerated in a cyclotron increases with the radius of the magnet and with the strength of the magnetic field.

The cyclotron consists of two flat semicircular boxes known as 'dees' because of their shape. These dees are surrounded by a closed vessel, containing a gas at low pressure, placed between the poles of a magnet. A radio-frequency alternating potential, of about 10 to 20 mega cycles per second, is applied between the dees, which act as electrodes. An electrically heated filament in the vessel, produces a stream of electrons, which cause ionization of the gas such as deuterium or helium contained in the vessel. The filament thus can be regarded as the source of positive ions (protons), deuterons or alpha particles. Suppose that at any particular instant the alternating potential is in the direction which makes the first 'dee' positive and the second 'dee' negative. A positive ion from the source would be attracted to the second D (which is negative), but as a uniform magnetic field acts in a direction at right angles, the particle will move in a circular path. The radius 'r' of the particle is given by $r = mv/Be$ (1) where 'm' is the mass of the ion, 'e' is its charge 'v' its velocity and 'B' is the strength of the magnetic field.

While it is in the interior of the dee, the speed of the ion remains constant. But after describing semicircular path through the second dee, the particle reaches the gap between the dees, where it becomes subject to the action of the applied potential difference. When the first dee, becomes negative, (because of the alternating potential) the positive ion will be accelerated toward the first dee. Since its energy is consequently greater than it was originally the ion will move faster, i.e, 'v' will increase. Therefore the circular path in the first dee will have larger radius, under the influence of the magnetic field, as per equation (1). The significant property of the cyclotron is that the time taken by the particle to traverse the semicircular path is independent of the velocity of the particle or of the radius of the path. In other words, the increase in length of the path, due to the larger radius, is exactly compensated by the increase in velocity of the ion. The time taken to

traverse the path 'T' is given by $T = \pi r / V$ ----- (2); r = radius of the path.
 from (1) $T = \pi m / Be$ ----- (3).

Thus 'T' is independent of both V and r . This means that if the frequency of oscillation is adjusted to the nature of the ion and to the strength of the magnetic field, the charged particle will always keep in phase with the changes of electric potential between the dees. Thus each time the particle crosses the gap from first dee (D_1) to second dee, (D_2) it will receive an additional impulse toward D_2 ; on the other hand when it crosses from D_2 to D_1 it will be accelerated toward D_1 , for the direction of potential will then be reversed. The result of these repeated impulses is that the energy of the ion is steadily increased, and at the same time it describes a flat spiral of increasing radius. Eventually the ion reaches the periphery of the dee and it can be brought out of the dee chamber by means of a deflecting plate, which is charged to a high negative potential. The attractive force acting on the positive ion draws the latter out of its spiral path, and it can be used to bombard any desired material. Although the above description refers to a single particle, the source supplies ions continuously, thus a stream of high energy particles will emerge from the cyclotron.

The maximum velocity at the periphery is given by : BeR/m (R is the radius of the dee).

Therefore the kinetic energy 'E' of the ion, coming out of the cyclotron is: $E = \frac{1}{2} M (BeR/m)^2$ $E = B^2 R^2 / 2 \times e^2 / m$. It can be seen from this equation that the maximum energy acquired by a particle is determined by $B^2 R^2$. Therefore in order to obtain ions of high energy, it is necessary to increase the strength and size of the magnet. By using a 60inch cyclotron alpha particles of 40MeV were obtained.

SYNCHROCYCLOTRON

At higher energies, the rest mass of the particle increases (due to increase in velocity). For example a deuteron having an energy of 20 MeV

(obtained from 60 inch cyclotron) has a velocity about 0.145 times the velocity of light. Its effective mass is 1.01 times the rest mass, as given by.

$m = m_0 / \sqrt{1 - V^2/C^2}$; V is the velocity of the particle, m_0 is its rest mass and 'C' the velocity of light.

At higher energies, the mass of the particle increases to such an extent that its effect becomes appreciable. As the mass of the ion increases, the time of transit 'T' also increases (T & m at constant B). Because of this the particle will no longer be in phase with the alternating potential, and consequently it will gain no additional energy.

For the 'T' to be unaffected by the increase in mass, the magnetic field is left unchanged but the frequency of the oscillating potential is decreased so that $fm = \text{constant}$, f = frequency m – mass of the particle. McMillan (1945) pointed that if the oscillation frequency is adjusted continuously to coincide with the decreasing frequency of revolution of the particle, the revolution of the charged particle is automatically synchronized with the changing frequency of the alternating of potential. The action is similar to that in a synchronous motor and hence the name 'Synchrotron' was proposed by Mc Millan.

The cyclotron was modified to permit variation of oscillation frequency to compensate for the increase in mass of the accelerated ions. Hence the machine is referred to as a 'Synchrocyclotron' or a frequency modulated cyclotron. It uses a single dee instead of two dees, the oscillating potential being applied between it and a ground connection. Every time a charged particle enters or leaves the dee, it acquires additional energy, so that it follows a spiral path (just as if two dees were employed) R.F frequency is decreased to compensate for the gain in mass of the particle as its speed increases. By using improved frequency modulators, protons of 720MeV energy were produced.

ELECTRON CYCLOTRON:

The conventional cyclotron is not used to accelerate electrons because of the large relativistic increase in mass even at fairly low energy. This is because m_0 for electron is very small compared with that of a proton or deuteron.

For a specified particle energy, a lower magnetic field strength is required in a cyclotron of a given size for the acceleration of electrons than for protons because of smaller mass. Electron cyclotrons have been designed without iron-core magnets, the necessary magnetic fields being provided by the passage of electric currents through suitably shaped coils.

21.2.2 BETATRON:

For the acceleration of electrons to high energies, above approximately 1 MeV, the cyclotron principle is not applicable. Electrostatic accelerators of the type 'van de Graff' generator are useful upto 10 to 20 MeV. For energies of the order of 100 MeV, other devices have to be employed. For this purposes, D.W.Kerst developed 'Betatron', since it was designed to accelerate electrons (which are identical with beta particles). The first useful induction accelerator, the betatron, accelerated an electron to an energy of 2.3 MeV.

The action of the betatron is based on the familiar principle of transformer. In the transformer an alternating current applied to a primary coil induces a similar current, usually with a higher or lower voltage, in the secondary windings.

In the betatron the secondary is an annular (ring shaped) evacuated glass (or ceramics) tube. It is often called a 'dough nut'. This is placed between the poles of a specially shaped electromagnet, energized by pulsed current passing through the coils. The purpose of this magnet is to produce a strong field in the central space or "hole" of the dough nut, and therefore it is constructed with a good amount of iron in the core. Heated filaments produce

electrons and these are given initial acceleration by application of an electric field having a potential difference of 20,000 to 70,000 volts. Even with low energies, thus obtained, the electrons travel at very high speeds, from nearly 1/5th to 1/2 the velocity of light.

As the field strength starts to increase, the partly accelerated electrons are injected into the doughnut. The energy of the moving electrons is increased due to an induced EMF, within the doughnut, caused by the growing magnetic field.

Since the electrons are moving in a magnetic field, the electrons are forced into a curved path. The increasing magnetic field keeps them moving in a circle of constant radius. The equation $r = mv/Be$ shows that as the field strength moves in proportion to the momentum of the electrons, 'r', remains constant. Thus, the electrons are kept moving around the doughnut in a fairly stable, circular path. In each turn the electron acquires energy. When the magnetic field reaches the maximum point of the sine wave cycle, a pulse current is sent through an auxiliary coil, which suddenly changes the magnetic field. The high energy electrons are displaced from their stable path and can be used to produce x-rays or can be used for other purposes.

Betatron can produce electrons with very high energies. Since the operation of the betatron is unaffected by the increase in mass of the electrons, due to increase in energy, it would appear that extremely high energies might be possible by means of betatron. But the accelerated electrons lose energy by radiation and hence there is a limit to the energy that can be acquired by electrons in the betatron. Energy losses have been minimized by means of large doughnut radius (120cms)

PROTON SYNCHROTRON

Attempts were made to produce particles of very high energies in the range of thousands of MeV ie billion electron volt (10^9). Radiation losses, in the case of electrons prevented from acquiring electrons of BeV range. But

with protons loss due to radiation is small. Hence protons can be accelerated to very high energies using cyclic accelerator.

By means of 'Proton Synchrotron' 2 to 3 BeV protons were produced. The proton synchrotron consists of four quadrants joined by straight pieces. In the Berkeley beavatron, the radius of each quadrant is about 55' and the connecting pieces are ~20' long. Alternating current is used for energing purposes. The magnet consists of a large number of plates surrounding only the quadrants of the doughnut. Protons accelerated to about 6 to 10 MeV, initially by vande Graff generator, is injected into the synchrotron. After having their energy increased, as a result of many revolutions, the protons are removed by a deflector. Injection and removal take place outside the magnetic field.

To keep the protons in the synchrotron moving in a circular path of constant radius, the strength of the magnetic field is increased in proportion to the momentum. Similarly for proper synchrotron action, the frequency of the radio frequency alternations is increased in such a manner that the condition of phase stability is maintained.

In proton synchrotron deviations from circular path, of particles occur, as a result of fluctuations. The deviations are observed both in horizontal and vertical direction. The magnet is designed in such a way that both the deviations are decreased.

Zero gradient synchrotron is designed to accelerate particles to higher energies by using a stronger magnetic field than in the conventional synchrotron.

Self Check Exercise – 4

1. Calculate the mass of an electron, when its velocity becomes equal to 1/5th the velocity of light.

2. Discuss the cyclotron in detail.

Self Check Exercise – 2

1. Discuss the principle of synchrocyclotron
2. Write briefly on
 - i) Betatron
 - ii) Bevatron

21.3 Let us Sum UP

i) Cyclotron and its design are discussed in detail. Synchrocyclotron is explained. Betatron and Bevatron are discussed in detail. Zero gradient synchrotron is explained.

21.4 Points for Discussion

- i) Cyclotron and its design
- ii) How does the mass increase affect the operation of cyclotron and the modifications introduced in Synchrocyclotron?
- iii) The different types of proton synchrotrons to be discussed.

21.5 References

- 1) Source book on atomic energy by Glass tone– East West press India.

UNIT VIII
THERMAL ANALYSIS
LESSON – 22

CONTENTS

- 22.0 AIMS AND OBJECTIVES
- 22.1 INTRODUCTION
- 22.2 THERMAL ANALYSIS
 - 22.2.1 TG – DTA
 - 22.2.2 APPLICATIONS
- 22.3 LET US SUM UP
- 22.4 POINTS FOR DISCUSSION
- 22.5 REFERENCES

22.0 AIMS AND OBJECTIVES

The aims and objectives of this lesson are to understand the methodologies of different thermal analyses techniques such as thermogravimetric analysis and differential thermal analysis . After going through this lesson you would be able to use these methods to

- Obtain information concerning the detailed structure and composition of different phases of a given sample.
- Understand how heats of reactions are obtained and used to determine the purity of materials.

22.1 INTRODUCTION

22.2.1 TG – DTA – RELATED TECHNIQUES

Thermal analysis includes a group of techniques in which specific physical properties of a material are measured as a function of temperature (Table 1.1). The production of new high– technology materials and the resulting requirement for a more precise characterization of these substances have increased the demand for thermal analysis techniques. Current areas of

applications include environmental measurements, composition analysis, product reliability, stability, chemical reactions and dynamic properties. Thermal analysis has been used to determine the physical and chemical properties of polymers, electronic circuit boards, geological materials, and coals. An integrated, modern thermal analysis instrument (Figure 1.1) can measure transition temperatures, weight losses, energies of transitions, dimensional changes, and viscoelastic properties.

Thermal analysis is useful in both quantitative and qualitative analyses. Samples may be identified and characterized by qualitative investigations of their thermal behaviour. Information concerning the detailed structure and composition of different phases of a given sample is obtained from the analysis of thermal data. Quantitative results are obtained from changes in weight and enthalpy as the sample is heated. The temperatures of phase changes and reactions as well as heats of reaction are used to determine the purity of materials.

Table 1.1

SUMMARY OF THERMAL ANALYSIS TECHNIQUES		
Techniques	Quantity Measured	Typical application
Differential scanning calorimetric (DSC)	Heats and Temperatures of transitions and reactions	Reaction kinetic, purity analysis polymer cures
Differential thermal analysis (DTA)	Temperatures of transitions and reactions	Phase diagrams, thermal stability
Thermo gravimetric analysis (TGA)	Weight change	Thermal stability compositional analysis
Thermo mechanical analysis (TMA)	Dimension and viscosity changes	Softening temperatures, expansion coefficients
Dynamic mechanical analysis (DMA)	Modulus, damping and viscoelastic behavior	Impact resistance, mechanical stability
Evolved gas analysis (EGA)	Amount of gaseous products of thermally	Analysis of volatile organic components of

	induced reaction	shale
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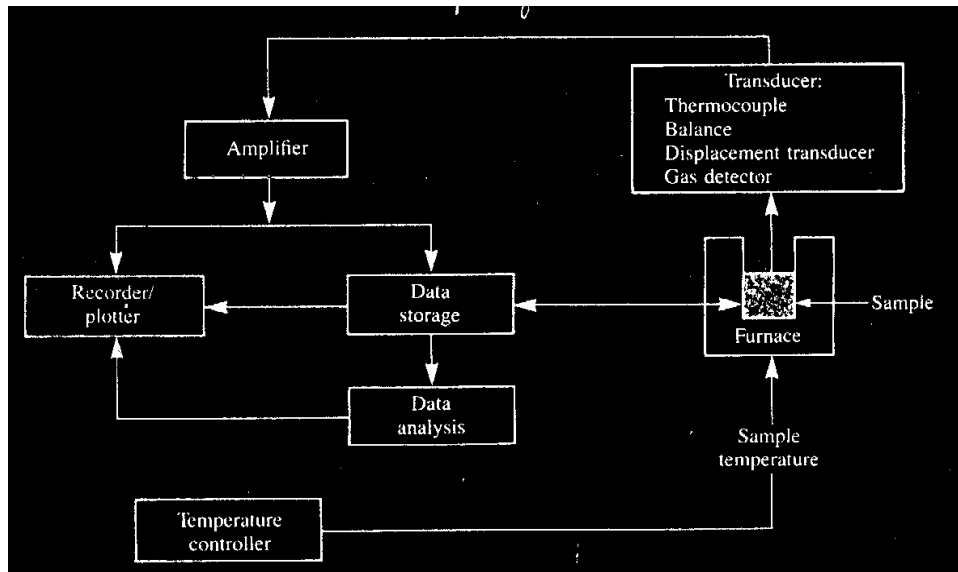


FIG -
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The use of microprocessors has both enhanced and simplified the techniques of thermal analysis. The sample is heated at a programmed rate in the controlled environment of the furnace. Changes in selected properties of a sample are monitored by specific transducers; which generate voltage signals. The signal is then amplified, digitized and stored on a magnetic disk along with the corresponding direct temperature responses from the sample. The data may also be displayed or plotted in real time. The microcomputer is used to process the data with a library of applications software designed for thermal analysis techniques. The multitasking capabilities of some computer systems allow a single microcomputer to operate several thermal analyzers simultaneously and independently.

A major advantage of microcomputer systems in thermal analysis is that the operator seldom, if ever, needs to repeat an analysis because of an improper choice of ordinate scale sensitivity. The software does this rescaling after all the data have been collected. In some systems both axes are automatically rescaled after the last data point has been received. When the amount of time necessary to obtain thermal data is considered, the advantage is obvious. For example, a differential scanning calorimetric run $10^{\circ}\text{C}/\text{min}$ from room temperature to 1100°C takes 100 min, and thus the rerun of the sample would take longer than 2hr including the time required for cooling and sample reloading.

DIFFERENTIAL SCANNING CALORIMETRY AND DIFFERENTIAL ANALYSIS

Differential scanning calorimetry (DSC) has become the most used thermal analysis techniques. In this technique, the sample and reference materials are subjected to a precisely programmed temperature change. When a thermal transition (a chemical or physical change that results in the emission or absorption of heat) occurs in the sample, thermal energy is added to either the sample, or the reference containers in order to maintain both the sample and reference at the same temperature (Figure 1.2(a)). Because the

energy transferred is exactly equivalent in magnitude to the energy absorbed or evolved in the transition, the balancing energy yields a direct calorimetric measurement of the transition energy. Since DSC can measure directly both the temperature and the enthalpy of a transition or the heat of a reaction, it is often substituted for differential thermal analysis as a means of determining these quantities except in certain high-temperature applications.

In differential thermal analysis (DTA), the difference in temperature between the sample and a thermally inert reference material is measured as a function of temperature (usually the sample temperature) (Figure 1.2(b)). Any transition that the sample undergoes results in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. A plot of the differential temperature, T , versus the programmed temperature, T , indicates the transition temperature (s) and whether the transition is exothermic or endothermic. DTA and thermogravimetric analyses (measurement of the change in weight as a function of temperature) are often run simultaneously on a single sample.

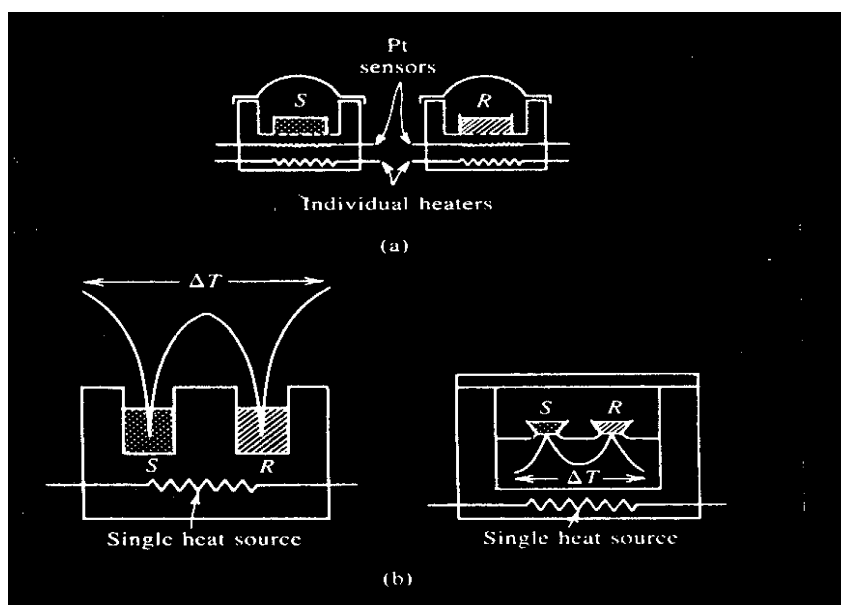


FIG -22.2(a) &

In DTA, the furnace contains a block with identical and symmetrically located chambers. The sample is placed in one chamber and a reference material such as α - Al_2O_3 , is placed in the other chamber. A thermocouple is

inserted into the centre of the material in each chamber. The furnace and sample blocks are then heated by a microprocessor– controlled heating element. The difference in temperature between sample and reference (S,R) thermocouples, connected in series opposition, is continuously measured. After amplification (about 1000 times) by a high– again, low– noise dc amplifier for microvolt– level signals, the difference signal is recorded as the y-axis. The temperature of the furnace is measured by an independent thermocouple and recorded as the x-axis. Because the thermocouple is placed in direct contact with the sample, DTA provides the highest thermometric accuracy of all thermal methods. DTA can be used in the temperature range from - 190 to 1600°C. Sample sizes are similar to those used in DSC.

Although the area of a DTA peak is proportional to the heat of reaction and the mass of the sample, it is inversely proportional to the sample's thermal diffusivity, which is a function of grain size and compactness. This inverse relationship prevents DTA peak areas from being used to provide direct calorimetric measurements. It is necessary to calibrate a DTA instrument for each type of sample and to carefully control experimental parameters to obtain useful thermodynamic data.

THERMOGRAVIMETRY

Thermogravimetry (TG) or thermogravimetric analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions. For example, TG can record directly the loss in weight as a function of temperature or time (when under isothermal conditions) for transitions that involve dehydration or decomposition. Thermogravimetric curves are characteristics of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. The rates of these thermally induced processes are often a function of the molecular structure. Changes in weight result from physical and chemical bonds forming and breaking at elevated temperatures. These processes may evolve volatile products or from reaction products that result in a change in weight of the sample. TG data are useful in

characterizing materials as well as in investigating the thermodynamics and kinetics of the reactions and transitions that result from the application of heat to these materials. The useful temperature ranges for TG is from ambient to 1200°C in either inert or reactive atmospheres.

In TG the weight of the sample is continuously recorded as the temperature is increased. Samples are placed in a crucible or shallow dish that is positioned in a furnace on a quartz beam attached to an automatic recording balance. Figure 1.3 shows a TG instrument that contains a taut-band suspension electromechanical transducer. The horizontal quartz beam is maintained in the null position by the current flowing through the transducer coil of an electromagnetic balance. A pair of photosensitive diodes acts as a position sensor to determine the movement of the beam. Any change in the weight of the sample causes a deflection of the beam, which is sensed by one of the photodiodes. The beam is then restored to the original null position by a feedback current sent from the photodiodes to the coil of the balance. The current is proportional to the change in weight of the sample.

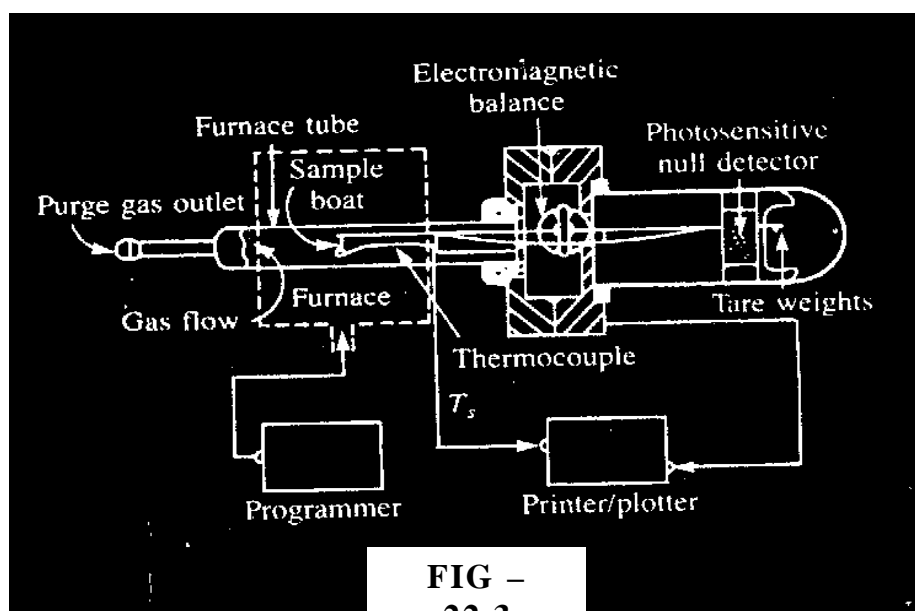


FIG -

Linear heating rates from 5 to 10°C/min are typical. Sample sizes range from 1 to 300mg. Computer software allows the computation of w/t , which is important in kinetic interpretations of reactions and processes. TG has been used in the kinetic analysis of polymer stability, Compositional

analyses of multi component materials, atmosphere analyses and corrosion studies, moisture and volatiles determinations, and accelerated tests of aging.

EVOLVED GAS DETECTION AND ANALYSIS

The analysis of the purge gas exit stream from differential thermal analysis, differential scanning calorimetry, and thermogravimetric analyzers is useful in establishing mechanism and stoichiometric relationship of thermal decompositions. In evolved gas analysis (EGA) the absolute identities of the gaseous components are determined, whereas in evolved gas detection (EGD) the presence of only a single, preselected component of the evolved gas is sensed. An appropriate analyzer may be coupled to a thermogravimetric system for performing either EGA or EGD. The resulting hyphenated methods are powerful analytical tools. Two analyzers that have been successfully coupled to TG systems are mass spectrometers (MS) and flame ionization detectors (FID). The TG-MS or TG-MS-MS combination is used for evolved gas analysis, whereas the TG-FID combination provides evolved gas detection. These hyphenated methods are used in studies of the volatile organic pyrolysis products of oil shales.

The simultaneous TG-DTA-MS analysis of copper sulfate-pentahydrate is shown in figure. 1.4. The quadrupole mass spectrometer detects the temperature- dependent intensity changes of water during dehydration to 300°C. The evolution of sulphur dioxide during the two-step sulfate decomposition to copper (II) oxide between 600 and 900°C is also clearly seen. Electron – impact ionization in the MS is responsible for the production of sulfur monoxide (SO) radical ions.

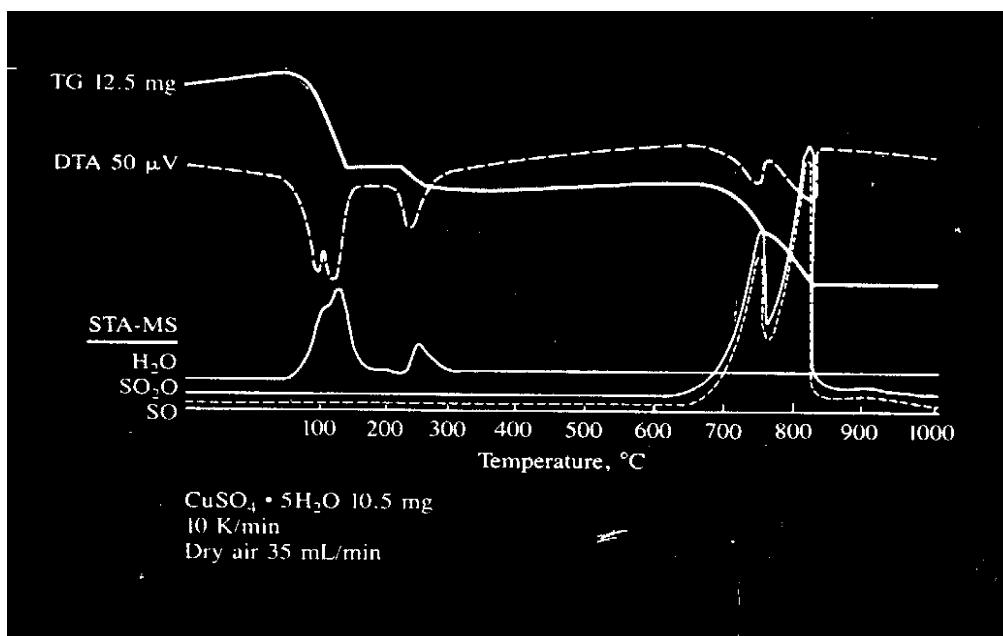


FIG -
22.5

22.2.2 APPLICATIONS METHODOLOGY OF THERMOGRAVIMETRY, DIFFERENTIAL SCANNING CALORIMETRY AND DIFFERENTIAL THERMAL ANALYSIS

Thermogravimetry (TG)

The weight-change TG curve for calcium oxalate monohydrate is shown in Fig-1.5. Water is evolved beginning slightly above 100°C. At about 250°C the curve breaks at the stoichiometry corresponding to that of the anhydrous salt. Further heating gives definite weight plateaus for the carbonate (from 500 to 600°C) and finally the oxide (hotter than about 870°C). Exact locations of the weight plateaus are dependent on the heating rate (a slower heating rate shifts values to lower temperatures) and the ambient atmosphere around the sample particles. The curve is quantitative in that calculations can be made to determine the stoichiometry of the compound at any given temperature.

Thermal analysis is affected by the experimental conditions. Deviations caused by instrumental factors include furnace atmosphere, size and shape of the furnace and sample holder, sample holder material and its

resistance to corrosive attack, wire and bead size of the thermocouple junction, heating rate, speed and response of the recording equipment, and location of the thermocouples in the sample and reference chambers. Another set of factors that influence the results depends on the sample characteristics; these include layer thickness, particle size, packing density, amount of sample, thermal conductivity of the sample material, heat capacity, the ease with which gaseous effluents can escape, and the atmosphere surrounding the sample.

Thermogravimetry, a valuable tool in its own right, is perhaps most useful when it complements differential thermal analysis studies. Virtually all weight-change processes absorb or release energy and are thus measurable by DTA or DSC, but not all energy-change processes are accompanied by changes in weight. This difference in the two techniques enables a clear distinction to be made between physical and chemical changes when the samples are subjected to both DSC (or DTA) and TG tests.

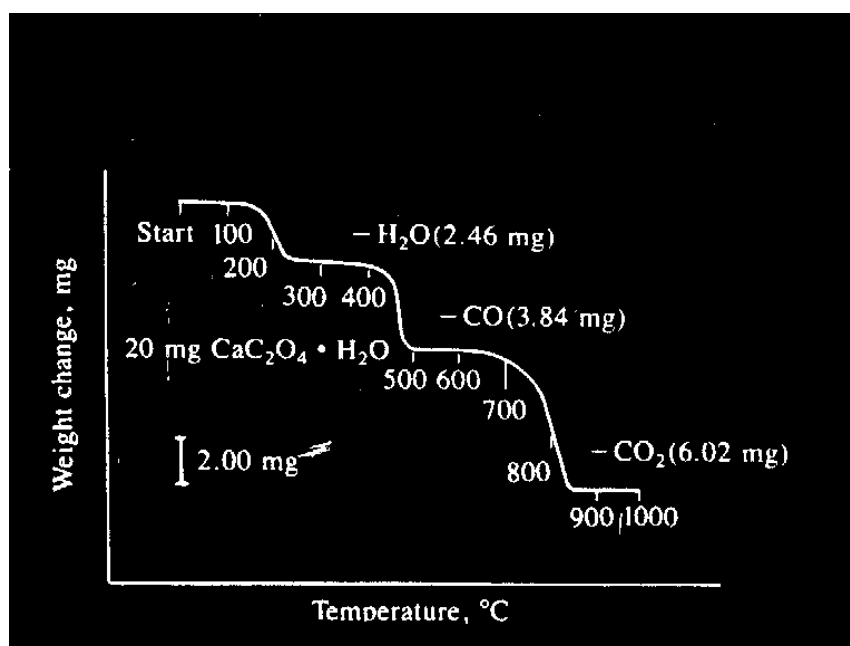


FIG -
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EXAMPLE - 1

Thermogravimetry can also be used to determine the composition of complex materials such as carbon black-filled rubber. Figure 1.6 shows the

result of rapidly heating a rubber sample in an inert atmosphere of nitrogen from room temperature to 950°C and then quickly changing the atmosphere to air. Heating the sample in an inert environment results in the

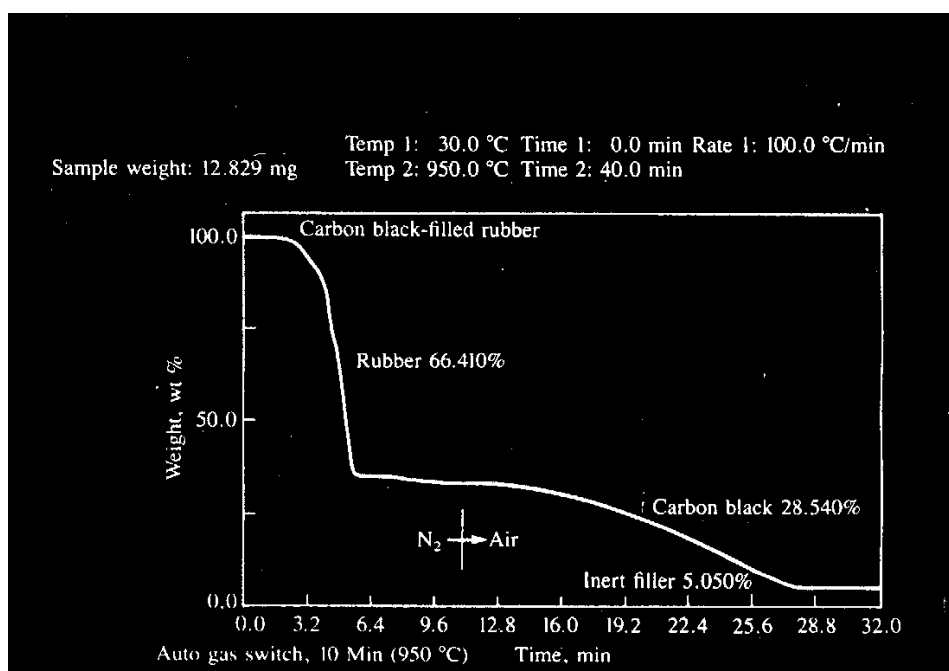


FIG -

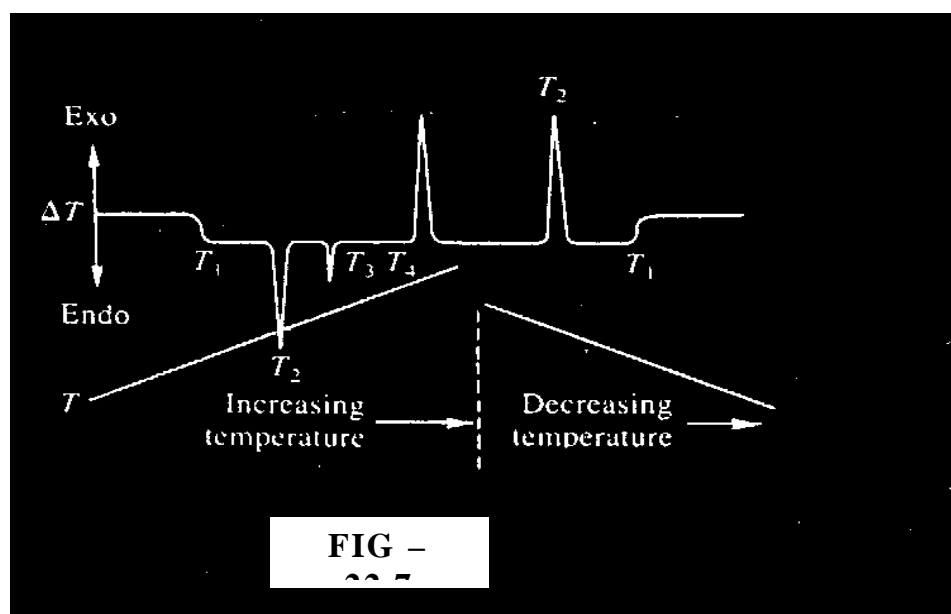
pyrolytic decomposition of the rubber and gives the first major weight loss observed in the scan. The addition of air at 950°C causes the carbon black to undergo combustion to produce the second loss in weight, leaving in the balance pan only inert filler. All the major components of the rubber sample were determined quantitatively from a single TG scan.

DIFFERENTIAL SCANNING CALORIMETRY (DSC) AND DIFFERENTIAL THERMAL (DTA)

In general, each substance gives a DSC or DTA curve in which the number, shape and position of the various endothermic and exothermic features serves as a means of qualitative identification of the substance. When an endothermic change occurs, the sample temperature lags behind the reference temperature because of the heat in the sample. The initiation point for a phase change or chemical reaction is the point at which the curve first

deviates from the baseline. When the transition is complete, thermal diffusion brings the sample back to equilibrium quickly. The peak (or minimum) temperature indicates the temperature at which the reaction is completed. When the break is not sharp, a reproducible point is obtained by drawing one line tangent to the baseline and another tangent to the initial slope of the curve.

Various behaviors deduced for a DTA curves are shown in Figure 1.7. The heat capacity at any point is proportional to its displacement from the blank



baseline. A broad endotherm indicates a slow change in heat capacity. A "Second - order or glass" transition observed as a baseline shift (T_1), denotes a decrease in order within the system. This is the temperature at which a polymer changes from a brittle, glasslike material to a tough, resilient material. The lower the glass transition temperature, the lower the temperature at which the polymer is useful in applications, such as adhesives or impact-resistant structures. In a thermoset, a high glass transition temperature indicates incomplete cure of the resin; In a thermoplastic, a high glass transition temperature indicates the use of the wrong plasticizer or incomplete reaction in the formation of the polymer itself. Endotherms generally represent physical rather than chemical changes. Sharp endotherms (T_3) are indicative of crystalline rearrangements, or solid-state transitions for relatively pure materials. Broader endotherms (T_2) cover behaviour ranging

from dehydration and temperature dependent phase behaviors to the melting of polymers. Exothermic behaviour (without decomposition) is associated with the decrease in enthalpy of a phase or chemical system. Narrow exotherms usually indicate crystallization (ordering) of a metastable system, whether it be supercooled organic, inorganic, amorphous polymer, or liquid, or annealing of stored energy resulting from mechanical stress. Broad exotherms denote chemical reactions, polymerization, or curing of thermosetting resins. Exotherms with decompositions can be either narrow or broad depending on the kinetics of the behavior. Explosives and propellants are sharpest, and the "Unzipping" of polyvinyl chloride is rapid, whereas oxidative combustion and decomposition are generally broad.

On cooling one would expect the reverse of features observed on the heating cycle (Figure 1.7). Since T_4 does not recur on cooling, the reaction is obviously nonreversible (perhaps a pyrolytic decomposition). Instead of taking the system up to T_4 , the cooling cycle be started before that temperature. As it cools, the substance is seen to lose its transition peak at T_3 . Judging from the area under the T_2 peak, the transition energy of T_3 has been added to T_2 . This indicates a metastable condition at T_3 , with the retained energy being released in one large step at a lower temperature. Further along the cooling curve, the glass transition at T_1 falls properly into place to complete the cycle.

Determining the significance of thermoanalysis curves is not always a straightforward task. A reference library of curves of specific interest to a particular laboratory is vital. Computerized systems offer the capability of storage and quick retrieval of data. Thermoanalysis data on commercial products or thermal transition points for pure substances reported in the literature are of little value for the comparison with a dynamically scanned thermal profile. Complementary techniques are valuable. The correlation of thermally evolved gaseous products with differential scanning calorimetry or differential thermal analysis transitions using evolved gas analysis or evolved gas detection often assists in elucidating the decomposition mechanism.

Running thermal decompositions in inert, oxidative, or special atmospheres can often provide valuable clues from changes in the curves.

Example -2

The TG and DTA curves of manganese phosphinate monohydrate are shown in Figure.1.8. The weight-loss data (TG curve) from a 200-mg sample run under vacuum and with the analysis of effluent gases showed the loss of 1 mole of water at 150°C, 1 mole of phosphine at

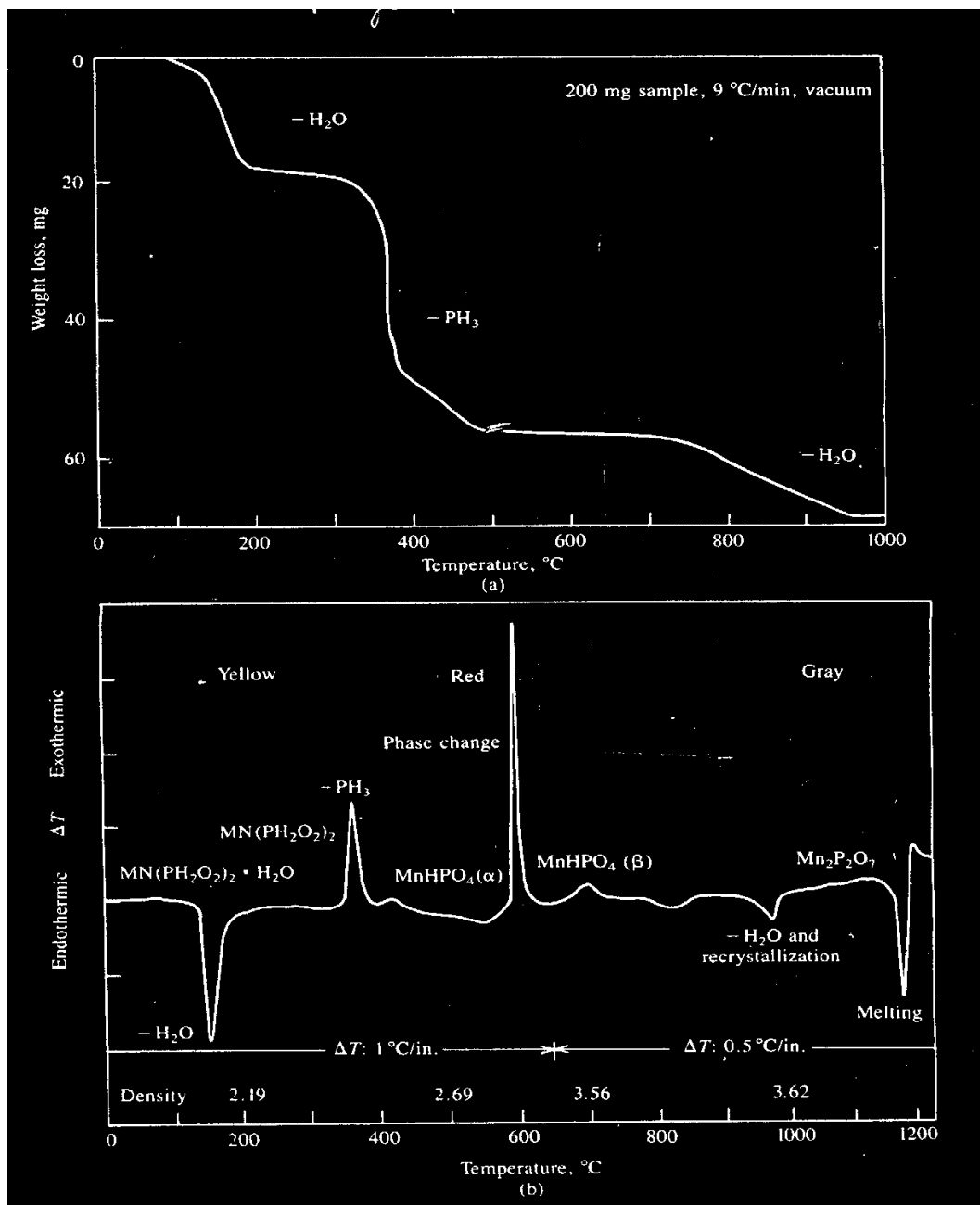
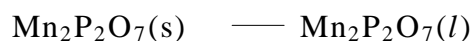
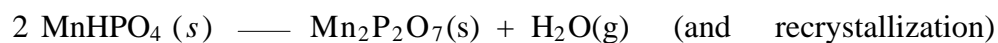


FIG -22.8(a) &

360°C, and the slow loss of another mole of water starting around 800°C. After comparison with the DTA curve, two major peaks remain unidentified: the large exotherm at 590°C and the endotherm at 118°C, plus several smaller thermal features. Thermogravimetric data obtained from runs performed under vacuum and in a nitrogen atmosphere failed to show any loss associated with these peaks. Each sample was measured for its real density. The resulting data are shown on the DTA curve, Undoubtedly the sharp DTA exotherm at 590°C represents a phase change. The relatively small endotherm starting above 900°C must represent a recrystallization exotherm following the elimination of water. Which is superimposed on the latter endotherm. The peak at 1180°C is due to melting. With this information the thermal decompositions reaction and phase changes are:



Thermal studies with polymers can predict a product's performance in use – that is, its stiffness, toughness, or stability. Melting point, Phase transition, Pyrolysis, and curing temperatures are accurately measured. Once a polymer has been broadly classified by other, methods, curves are often used to establish, by comparison with known reference materials, the degree of polymerization, the thermal history of the sample, crystal perfection and orientation, the effect of different coreactants and catalysts, the percentage of crystalline polymer, and the extent of chain branching. For example, curves for a low-molecular-weight, nonlinear, branched – chain polymer show a continuous series of rather broad and low-melting-point endotherms, whereas a high-molecular-weight, stereo regular, linear polymer reveals a single narrow and higher-melting-point endotherm. If a polymer has been incompletely cured, the heating cycle may reveal an exotherm at a

temperature close to the one used for the polymerization reaction. An exotherm just below the melting temperature indicates "cold crystallization," which results if a sample is quenched quickly after being melted. On reheating, crystallites form rapidly and exothermically just prior to remelting of the polymer. Annealing temperatures are similarly revealed as exotherms.

If the molecular weight or density of a polymer has been established by appropriate (often lengthy) methods, subsequent determination of its melt temperature (a 15-min process) can be related to molecular weight or density. Product quality is maintained subsequently by simply examining curves of polymer materials to obtain molecular weights or densities from an appropriate calibrated graph.

Instead of using the traditional method of preparing a derivative from the organic sample and a reagent, the sample is heated with a specific reagent at a programmed heating rate in a selected atmosphere. The DTA or DSC curve shows the derivative-forming reaction, the physical transitions of the sample or reagent (whichever is in excess), and the physical transitions of the intermediates and final products. When one reactant is volatile and in excess, a rerun usually shows only the derivative characteristics.

The area of exotherms or endotherms is used to calculate the heat of the reaction or the heat of a phase transition. Suitable calibration is necessary with DTA equipment, but the values are given directly with DSC instruments.

Example – 3

Polyethylene is a semi crystalline thermoplastic that when heated undergoes a process of melting. This melting destroys the crystal structure of the polymer and is an endothermic process. Although plastics usually melt over a temperature range, the melting point is defined as the temperature at which the melting is complete. The melting point of a plastic is an important property because it is minimum temperature for processing the plastic and the maximum temperature for applications where structural integrity is required.

A second important property for the characterization of semi crystalline thermoplastics is the percent crystallinity. Many physical properties that gives the plastic its useful attributes are dependent on the percent crystallinity.

Both the melting point and the percent crystallinity are obtained from a single differential scanning calorimetry scan (Figure 1.9). The melting point is taken as 133°C, where the melting is approximately complete. Since differential scanning calorimetry is directly quantitative, the peak area is equal to the heat of fusion, H_f , in units of calories per gram. The percent crystallinity is determined by assuming that the heat of fusion is proportional to the percent of crystallinity of the sample. Thus if the heat of fusion of 100% Polyethylene has been determined to be 68.4 cal/g and the measured heat for the sample is 54.5 cal/g the percent crystallinity is 79.7%, as shown in figure 1.9.

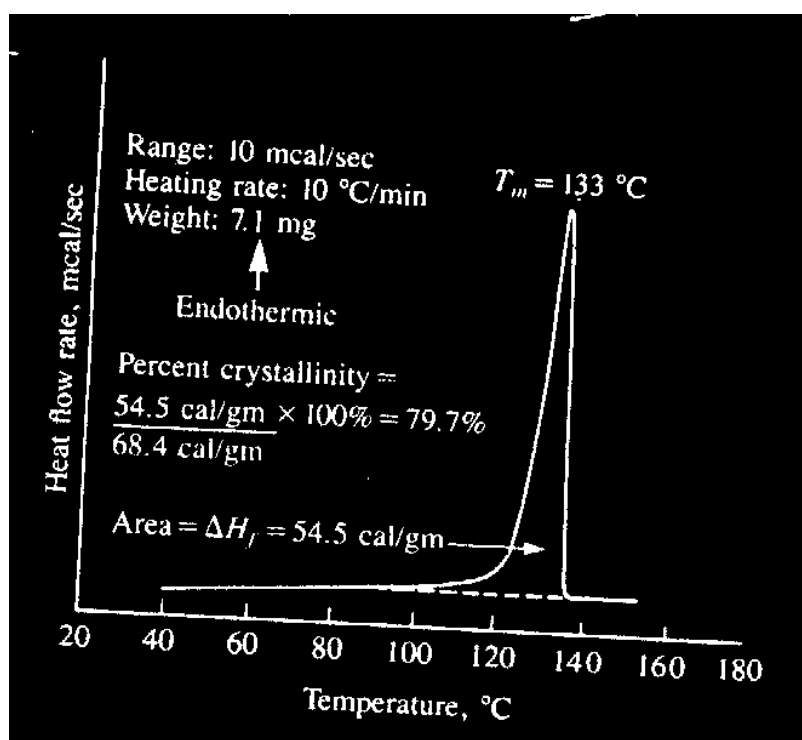


FIG -

Self Check Exercise - 1

1. What are the different thermal analysis techniques? give their applications in a few words.
2. What is the importance of microcomputer system in thermal analysis.
3. Explain the process of DTA.
4. Give any one disadvantage of DTA .

Self Check Exercise – 2

1. Describe thermogravimetry.
2. Discuss the thermogravimetric method with an example.
3. 20 Mg sample of crystalline calcium oxalate of molar mass 146, in a thermal study loses about 2.46mg H₂O above 150°C. Formulate the sample.

Activity:

Run a TGA and DTA for a known sample from the instrument available in the Chemistry Department of Bharathiyar University.

Model Answer

Self Check Exercise – 1

4. Although the area of a DTA peak is proportional to the heat of a reaction and the mass of the sample, it is inversely proportional to the sample thermal diffusivity which is a function of grain size and compactness. The inverse relation prevents, DTA peak areas from being used for direct calorimetric measurements. It is necessary to calibrate a DTA instrument for each type of sample and to carefully control experimental parameters to obtain useful thermodynamic data.

22.3 Let us Sum Up

i) Theories of TGA and DTA are discussed in detail ii) Experimental methods are illustrated iii) The applications of TGA and DTA techniques are illustrated using typical TG and DTA curves for a few compounds.

22.4 Points for Discussions:

- i) The different thermal methods and their application may be discussed.
- ii) Obtain TGA and DTA curves from a standard source and try to interpret the results.

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LESSON – 23

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- 23.2 AUGER ELECTRON SPECTROSCOPY (AES)
 - 23.2.1. Principle and experimental method
 - 23.2.2. Applications
- 23.3 LET US SUM UP
- 23.4 POINTS FOR DISCUSSION
- 23.5 REFERENCES

23.0 AIMS AND OBJECTIVES

The aim of the lesson is to study and understand the Auger emission phenomenon and to understand the importance of Auger emission spectroscopy in studying surfaces of solids. After studying this lesson you would be able to learn :

The principle of Auger effect

Auger effect effectively takes the fingerprint of the material.

23.1 INTRODUCTION

When an atom is excited by the removal of an electron from an inner energy level, it may return to its normal state by transferring an electron from some outer level to the vacant inner level. The energy of this transition either appears as X rays or is used to eject a second electron from the outer shell Fig. 2.1. This latter method is called the Auger emission process; observation of the energy of such an ejected electron leads to a method of

analysis known as Auger emission spectroscopy (AES). If X rays are emitted, their wavelengths are characteristic of that element and their intensities are proportional to the number of excited atoms. Thus, X-ray emission methods can be used for both qualitative and quantitative measurements.

Atoms are excited in several ways : by direct bombardment of the material with electrons (direct emission analysis, electron probe microanalysis, and Auger emission spectroscopy), by bombardment with protons or other particles (particle induced x-ray emission, PIXE), or by irradiation of the material with X rays of shorter wavelength. In the latter case, the exciting X radiation causes an inner electron to be ejected with subsequent emission of the characteristic X rays of the sample (fluorescence analysis). It is also possible to measure the energy of the electrons ejected from the sample, and this leads to a method of analysis known as electron spectroscopy for chemical analysis (ESCA)

Another method of X-ray analysis uses the differing absorption of X rays by different materials (absorption analysis). Major discontinuities in the absorption of X rays by an element occur when the energy of the X rays becomes sufficient to knock an electron out of an inner level of an atom.

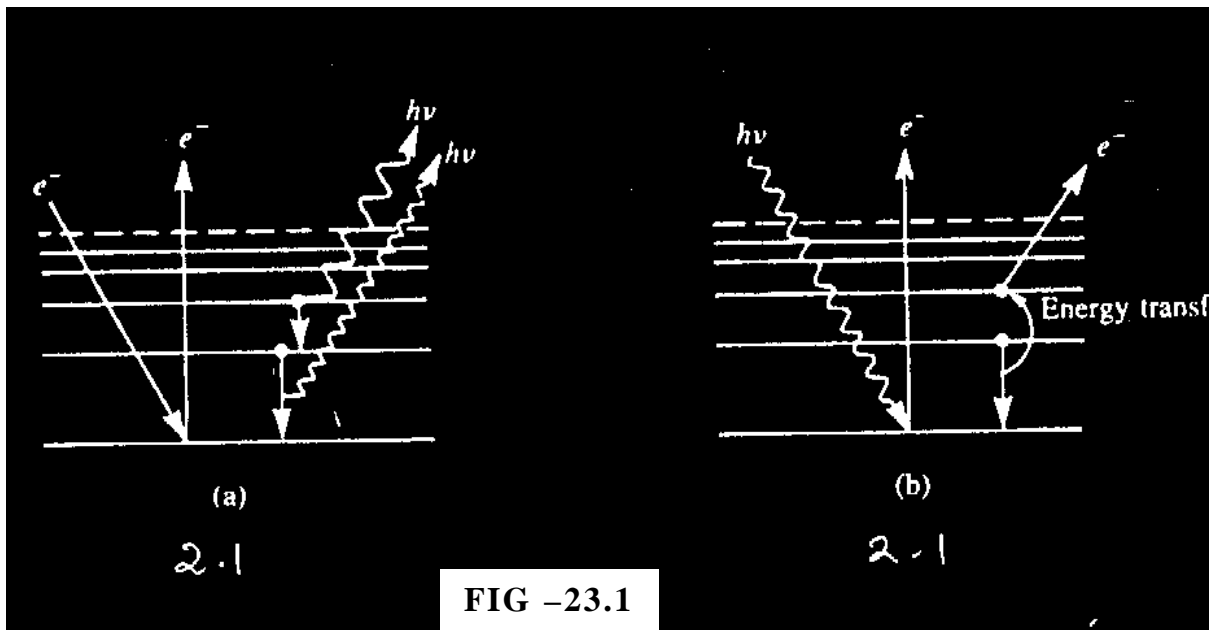
Still another method of using X rays in analytical work is the diffraction of X rays from the planes of a crystal (diffraction analysis). This method depends on the wave character of the X rays and the regular spacing of planes in a crystal. Although diffraction methods are used for quantitative analysis, they are most widely used for qualitative identification of crystalline phases.

Since electrons quickly lose their energy by colliding with molecules, methods that involve electron bombardment or detection of emitted electrons must be carried out in a vacuum. Furthermore, since electrons cannot penetrate deeply into solid materials or escape from any significant depth when generated in a solid, such methods characterize the surface layers of

solids and are useful for analyzing surfaces. Auger electron spectroscopy (AES) and electron spectroscopy for chemical analysis (ESCA), are carried out in a vacuum and usually characterize not more than the outer 2nm of the surface under investigation.

In 1913 Moseley first showed the extremely simple relationship between atomic number, Z , and the reciprocal of the wavelength, $1/\lambda$ for each spectral line that belongs to a particular series of emission lines for each element in the periodic table. This relationship is expressed as

$$\frac{c}{\lambda} = a(Z - \sigma)^2 \quad \dots (1)$$



23.2 AUGER EMISSION SPECTROSCOPY (AES)

23.2.1 AES measures electrons emitted from a surface, induced by electron bombardment (Fig. 2.1b). The first step is ionization of an inner atomic level by a primary electron. Once the atom is ionized, it must relax by emitting either a photon (an X ray) or an electron (the nonradiative Auger process). In most instances nature chooses the Auger process. For example, a KLL Auger transition means that the K-level electron undergoes the initial

ionization, An L-level electron moves in to fill the K-level vacancy and, at the same time, gives up the energy of that transition (L to K) to another L-level electron, which then becomes the ejected Auger electron. Other Auger electrons originate from LMM and MNN transitions. At this point the atom is doubly ionized. The energy of the ejected electron is a function only of the atomic energy levels involved in the Auger transition and is thus characteristic of the atom from which it came. A threshold energy, related to the transition energy, exists and a primary energy five to six times greater than the Auger energy maximizes the sensitivity to that particular transition. All elements except hydrogen and helium produce Auger peaks. Most elements have more than one intense Auger peak so that a recording of the spectrum of energies of Auger electrons released from any surface, compared with the known spectra of pure elements, enables a chemical analysis to be made.

Since an excited atom can lose energy by the X-ray emission process or by Auger electron emission, the relative sensitivities of these two techniques are complementary when considering the relative abundance of X rays and Auger electrons after ionization of a particular level. In the light elements ($Z < 30$), the Auger process dominates, which makes AES relatively more sensitive. For heavier elements, the electron microprobe becomes more sensitive for transitions following ionization of inner shells. The sensitivity of AES is maintained, however, by utilizing Auger transition between outer shells – for example, MNN – where the Auger process dominates.

Although the penetration of the primary electron beam may be as deep as 1 μm for high-energy electrons, the Auger electrons emitted are, on the average, of much lower energies. Electrons of such low energy must originate very close to the surface if they are to escape without being lost by inelastic scattering before reaching the surface. Typically, Auger electrons come from the first few atomic layers; the sampling depth is about 2 nm.

The sensitivity of the Auger technique is determined by the probability of the Auger transitions involved, the incident beam current and energy, and the collection efficiency of the energy analyzer. With a high-sensitivity cylindrical mirror analyzer (CMA), the detection limit for the elements varies between 0.1 and 1 atomic percent (or 10^{-3} of a monolayer). Because the electron beam can be focused to a small diameter (50 nm), it is possible to do spatial resolution or surface mapping of a sample. When operated in this manner, AES is usually referred to as the Auger microprobe. AES is traditionally run with high-intensity electron guns and low-resolution analyzers, resulting in fast analysis. Unfortunately, this limits one to primarily elemental information with little information on chemical bonding, such as one clearly obtains in the chemical shifts of electron scattering for chemical analysis (ESCA), or in the molecular fragments found in secondary ion mass spectrometry (SIMS). For example, hydrocarbon compounds appear in AES only as a C peak, since H is not observed.

Fig. 2.2 shows the Auger spectra of Ag, Cd, In and Sb, the (MNN transitions). The spectra are very similar; the only major difference is the shifts in energy from one element to the next. These shifts are of the order of 25eV and, since the peak positions can be measured to an accuracy of ± 1 eV, there is no ambiguity in the identification of adjacent elements in the periodic chart. Auger spectra of all the elements lie between 50 and 1000 eV. The KLL transitions correspond quite nicely with tabulated X-ray energies. There are, however, some minor differences due to the energy Auger electrons must lose in escaping from the sample. The Auger lines are relatively broad due to the double uncertainty of the exact origins and destinations within a sublevel of both the electrons that fall into inner levels and those being expelled from outer level. Lines due to LMM transitions tend to correlate with X-ray energies, but some lines begin to appear that the selection rules for photon emission forbid. As the atomic number increases, the Auger spectra become more complex and may overlap.

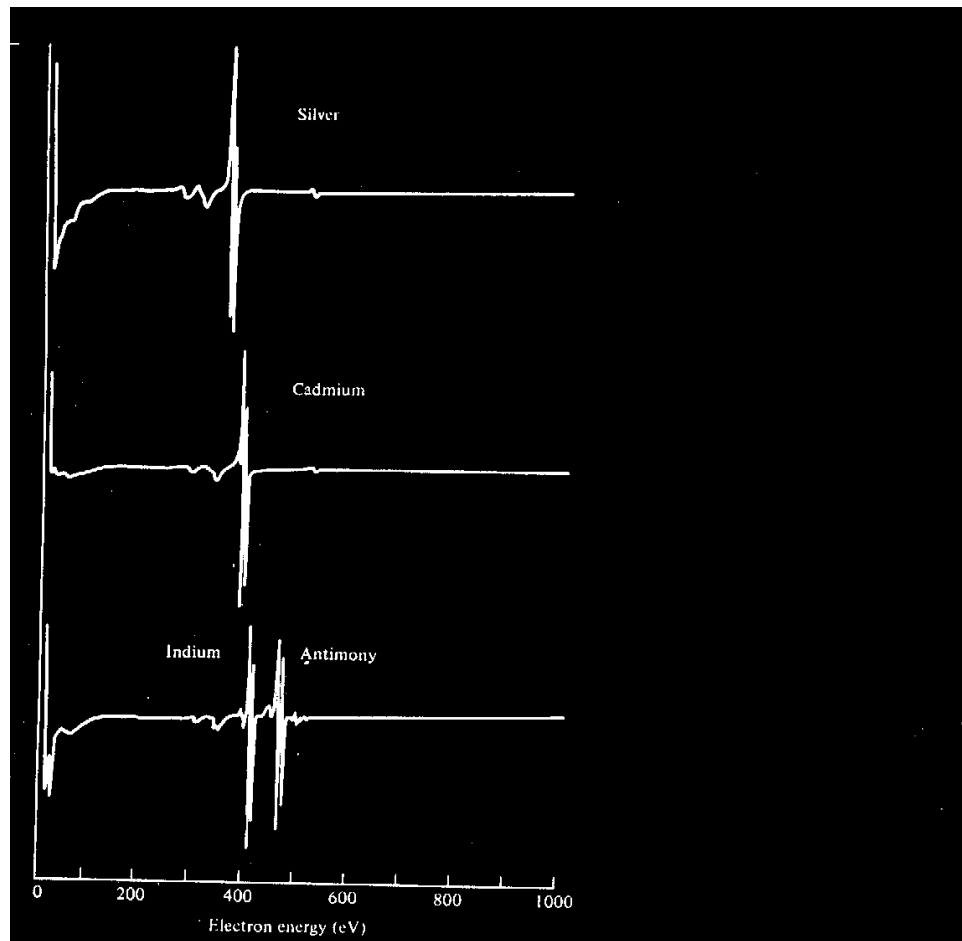


FIG –
222

The strength of AES is its ability to give both a qualitative and quantitative nondestructive analysis of the elements in the immediate surface atomic layers from a very small area of a solid. When combined with a controlled removal of surface layers by ion sputtering, AES provides the means to solve some very important problems, such as corrosion on metallic surfaces. To provide ion sputtering for surface cleaning and / or depth profiling, the sample chamber is backfilled with argon and an electron impact source is used.

AES Instrumentation

The Auger spectrometer consists of an ultra-high vacuum chamber console, a sample carousel and manipulator unit, and a combination electron

gun / energy analyzer unit. Auxiliary equipment often includes a grazing incidence electron gun and a sputter ion gun for cleaning surfaces and profiling studies. Auger spectrometers are available as large-beam ($\sim 25\text{-}\mu\text{m}$) depth-profiling instruments or as Auger microprobes with beam diameters of $5\mu\text{m}$. If an instrument is to be used as a high-sensitivity depth profiler and also as a high lateral resolution microprobe, two electron guns may be required to realize the optimum use of each operating mode.

The energy distribution of electrons emitted from the target, NE is evaluated by scanning the negative voltage applied to the outer cylinder of the cylindrical mirror analyzer (CMA) (Fig. 2.3). Thus as the voltage applied to the outer cylinder is scanned, the secondary electron distribution is measured by the current output of the analyzer. Because the Auger peaks are superimposed on a rather large continuous background of secondary electrons, it has become popular to differentiate electronically the N_E function.

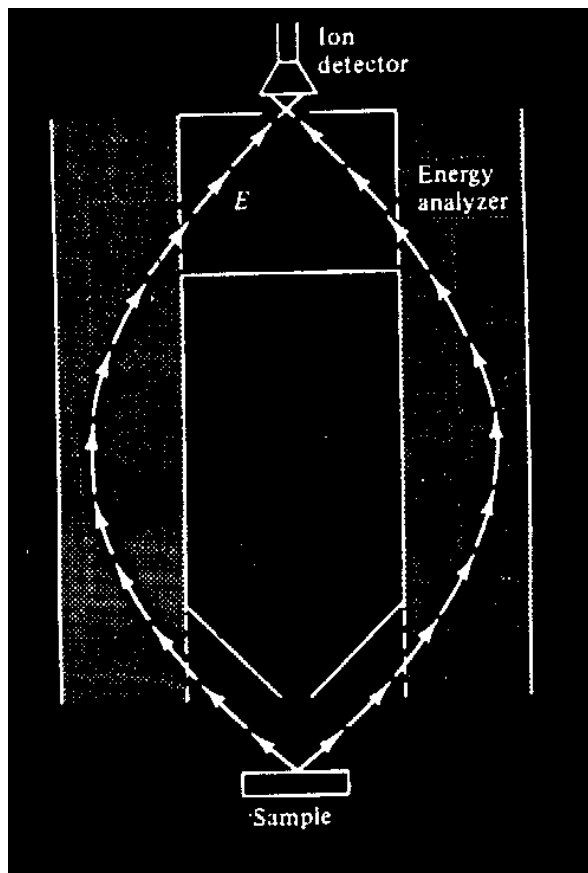


FIG -
2.3

23.2.2 Quantitative Analysis with AES — APPLICATIONS

Quantitative analysis is possible in principle. The relative intensities of peaks depend on the following variables: inner-level ionization cross sections, Auger transition rates, and inelastic scattering of the emitted Auger electrons. With careful calibration, quantitative analysis of a homogeneous sample should be achieved with an accuracy of about 10%. Thus, although quantitative Auger spectroscopy is not very exact, it is still of significant value in surface analysis.

The difficulties in the quantification of Auger data are illustrated in depth-profiling analysis. In this operation the change in peak shape of the differentiated spectra distorts the conventional peak-height estimates of concentration. Changes in peak shape occur because of changes in the oxidation state of the emitting atom. This is particularly severe in cases where bonding orbitals are involved in the Auger transitions. Peak shape changes also may be induced by matrix effects, since the energy loss mechanisms and their effect on peak shape may be different in different matrices. To provide accurate quantitative information within the normal quantitative limits of AES, it is necessary to use the total Auger current. This is expressed by the area under the curve for the peak of interest, with background subtracted. By using undifferentiated data and integrating over the total number of Auger electrons in the peak, one still has a choice of the limits of integration. Now chemical shifts may be observed and a depth profile can be realized with no artifacts.

Scanning Auger Microprobe (SAM)

The scanning Auger microprobe has a finely focused, scanning electron beam as the probe for AES analysis of a surface. For a surface area, the SAM provides an electron micrograph, an Auger image of selected elements on a cathode ray tube display for observation or photographing, and a depth composition profile. First, the cathode ray tube image is used to determine specific points or an area of interest on the sample surface. From the

micrograph obtained, points of interest or an area up to 200 μm can be chosen for compositional analysis.

The image mode is useful because the positions of various elements in the sample are delineated in a few minutes. An xy recording of a line scan across a selected region of the image for a given element gives a relative quantitative measure of its concentration.

The thin-film analyzer mode of the SAM simultaneously sputter-etches a relatively large surface area (several millimeters in diameter) and multiplexes the Auger signals from a smaller area about 15 μm in diameter. Up to six selected Auger peaks can be recorded as the surface is etched. Depth resolution is about 10% of the total etched thickness. Elements are detected when present in quantities down to 0.1% of a monolayer.

At best, the spatial resolving power of SAM is 500 nm with tungsten thermionic emitters as the electron source. The use of LaB_6 emitters extends the resolving power to 100-200 nm because of their high electron optical brightness. Field emitters, which provide even higher brightness, are expected to allow one to analyze smaller areas in less time when they come into use.

Many surface composition problems involve compositional inhomogeneity, both in depth and across a material surface. Scanning Auger microscopy offers high resolution in the form of scanning electron microscope-type images, combined with elemental mapping capabilities. For example, graphite present in spherical nodules indicates that a specimen of cast iron is ductile cast iron. Examination of the carbon Auger images shows carbon to be present not only in the graphite nodules but also, at lower concentration, in regions between nodules. Carbon is not evident in the circular regions around nodules. The iron Auger image shows iron to be present everywhere in the specimen surface except in the graphite regions.

Self Check exercise –1

- 1) Explain how Auger emission occurs?
- 2) Compare the Auger emissions with other X-ray methods
- 3) Explain the terms KLL and MNN transitions.

Model answers

Self check exercise –1

3) KLL Auger transition means that the K level electron undergoes initial ionisation, an L- level electron moves into fill the K-level vacancy and at the same time gives up the energy of that transition (L to K) to another L-level electron, which then becomes the ejected Auger electron. In MNN transitions the atom is doubly ionised.

Self Check exercise –2

- 1) Indicate the limitation in AES method.
- 2) Discuss the applications of the AES techniques.

23.3 Let us Sum Up

i) Auger emission is explained; ii) Auger emission is compared with other X-ray methods. Applications of AES are illustrated. The limitation of AES method is also indicated.

23.4 Points for discussion

- i) Comparison of various X-ray techniques
- ii) The importance of AES in the analysis of surfaces by SAM

23.5 References

- 1) ATKINS PHYSICAL CHEMISTRY – 7th Edn. OUP – INDIAN - 2002
- 2) Instrumental methods of analysis – Willard, Merritts Dean – 7th Edn
CBs New Delhi.

LESSON - 24

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24.0 AIMS AND OBJECTIVES

To understand the spectral methods such as ultraviolet photoelectron spectroscopy and X-ray photo electron spectroscopy.

The objective is to

- i) Learn the importance of these techniques in studying the surface characteristics of solids.
- ii) How UPS can be used to study the details of valence shell electrons.

24.1 INTRODUCTION

PHOTO ELECTRON SPECTROSCOPY

The technique of Photoelectron spectroscopy (PES) measures the ionization energies of molecules when electrons are ejected from different orbitals, and uses the information to infer the orbital energies. The technique is used to study solids and the important information that it gives about species at or on surfaces.

24.2.1 THE TECHNIQUE

Because energy is conserved when a photon ionizes a sample, the energy of the incident photon $h\nu$ must be equal to the sum of the ionization energy, I , of the sample and the kinetic energy of the photoelectron, the ejected electron (Fig.3.1)

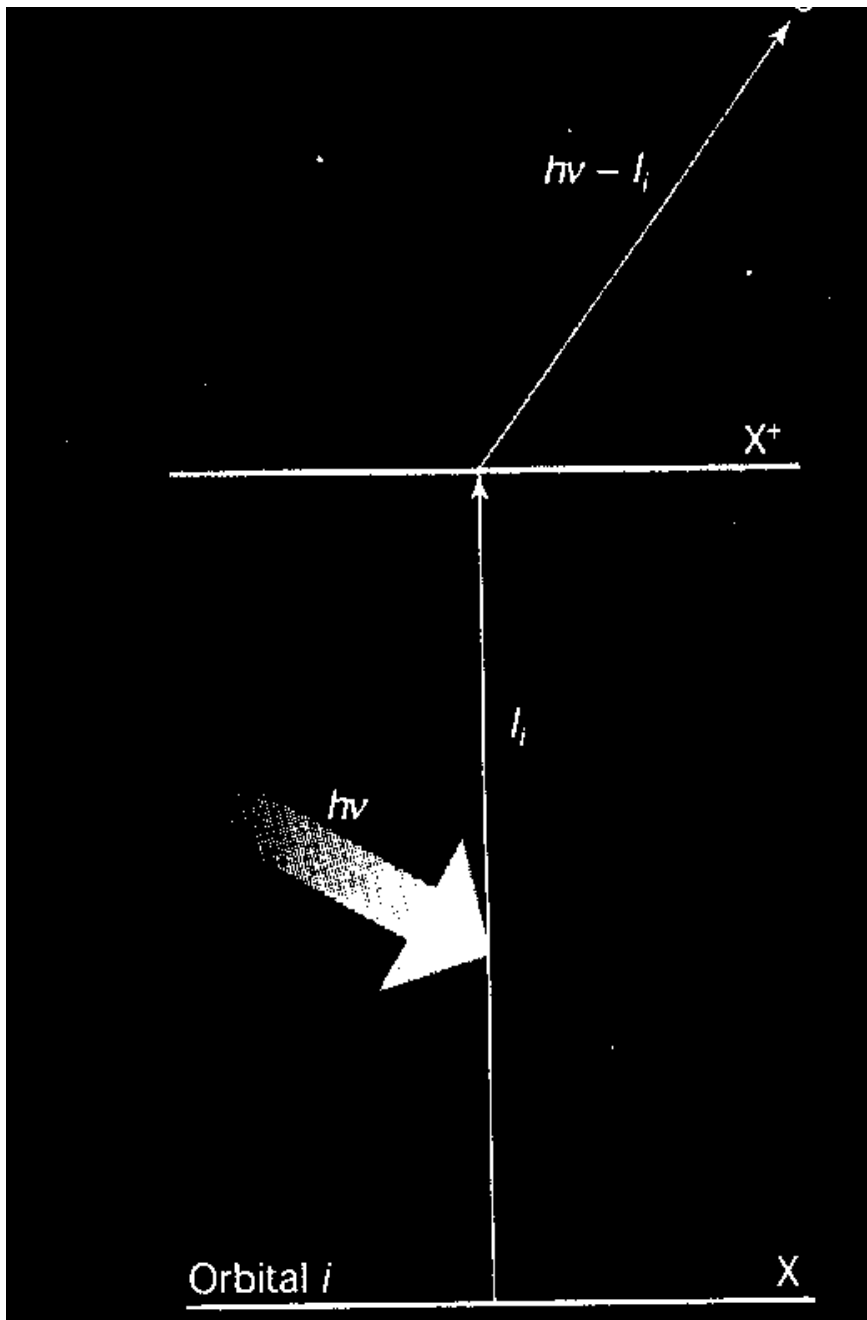


FIG - 24.1

$$\begin{array}{l}
 1 \\
 2
 \end{array}
 \quad
 \begin{array}{l}
 -h\nu = \quad m_e v^2 + 1 \\
 \quad \quad \quad \dots (1)
 \end{array}$$

This equation (which is like the one used for the photoelectric effect, can be refined in two ways. First, Photoelectrons may originate from one of a number of different orbitals, and each one has a different ionization energy. Hence a series of different kinetic energies of the photoelectrons will be obtained, each one satisfying

$$\begin{array}{l}
 1 \\
 2
 \end{array}
 \quad
 \begin{array}{l}
 -h\nu = \quad m_e v^2 + 1_i \\
 \quad \quad \quad \dots (2)
 \end{array}$$

where 1_i is the ionization energy for ejection of an electron from an orbital i . Therefore, by measuring the kinetic energies of the photoelectrons, and knowing ν these ionization energies can be determined. Photoelectron spectra are interpreted in terms of an approximation called Koopmans theorem. Which states that the ionization energy 1_i is equal to the orbital energy of the ejected electron (formally $1_i = -E_i$). That is, we can identify the ionization energy with the energy of the orbital from which it is ejected. The theorem is only an approximation because it ignores the fact that the remaining electrons adjust their distributions when ionization occurs.

The ejection of an electron may leave an ion in a vibrationally excited state. Then not all the excess energy of the photon appears as kinetic energy of the photo electron, and we should write.

$$\begin{array}{l}
 1 \\
 2
 \end{array}
 \quad
 \begin{array}{l}
 -h\nu = \quad m_e v^2 + 1_i + E^+_{\text{vib}} \\
 \quad \quad \quad \dots (3)
 \end{array}$$

where E^+_{vib} is the energy used to excite the ion into vibration. Each vibrational quantum that is excited leads to a different kinetic energy of the photoelectron, and gives rise to the vibrational structure in the photo electron spectrum.

The ionization energies of molecules are several electrovolts even for valence electrons, so it is essential to work in at least the ultraviolet region of the spectrum and with wavelengths of less than about 200nm. Much work has been done with radiation generated by a discharge through helium: the He(I) line ($1s^1 2p^1 \rightarrow 1s^2$) lies at 58.43nm, corresponding to a photon energy of 21.22 eV. Its use gives rise to the technique of ultraviolet photoelectron spectroscopy (UPS). When core electrons are being studied, photons of even higher energy are needed to expel them: X-rays are used, and the technique is denoted XPS. A modern version of PES makes use of synchrotron radiation, which may be continuously turned between UV and X-ray energies. The additional information that stems from the variation of the photoejection probability with wavelength is a valuable guide to the identity of the molecule and the orbital from which photo ionization occurs.

Example – 1

Photoelectrons ejected from N_2 with He (I) radiation had kinetic energies of 5.632eV ($1\text{eV} = 8065.5\text{cm}^{-1}$). Helium (I) radiation of wavelength 58.43nm has wavenumber $1.711 \times 10^5 \text{ cm}^{-1}$ and therefore corresponds to an energy of 21.22eV.

Then from eqn 21.2 $21.2 \text{ eV} = 5.63 \text{ eV} + I_i$ So $I_i = 15.59 \text{ eV}$. This ionization energy is the energy needed to remove an electron from the HOMO of the N_2 molecule, the $3\sigma_g$ bonding orbital.

Self Check Exercise – 1

Under the same circumstances, photoelectrons are also detected at 4.53eV. To what ionization energy does that correspond? Suggest an origin.

The kinetic energies of the photoelectrons are measured using an electrostatic deflector that produces different deflections in the

paths of the photoelectrons as they pass between charged plates (Fig.3.2). As the field strength is increased, electrons of different speeds, and therefore kinetic energies, reach the detector. The electron flux can be recorded and plotted against kinetic energy to obtain the photoelectron spectrum.

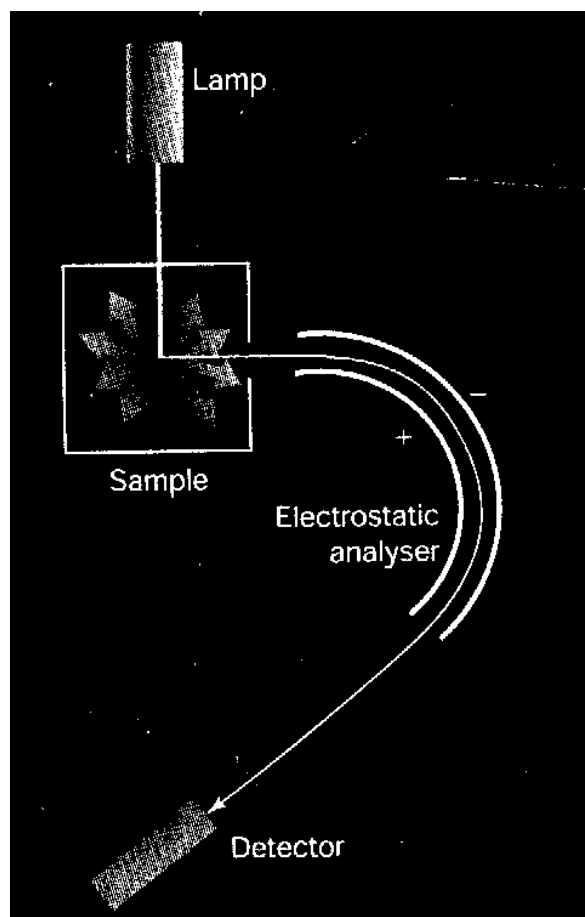


FIG – 24.2

24.2.2 Ultraviolet Photoelectron Spectroscopy

A typical photoelectron spectrum (of HBr) is shown in (ig.3.3). If we disregard the fine structure, we see that the HBr lines fall into two main groups. The least tightly bound electrons (with the lowest ionization energies and hence highest kinetic energies when ejected) are those in the nonbonding lone pairs of Br (with $I = 11.8$ eV). the

next ionization energy lies at 15.2 eV, and corresponds to the removal of an electron from the H-Br σ bond.

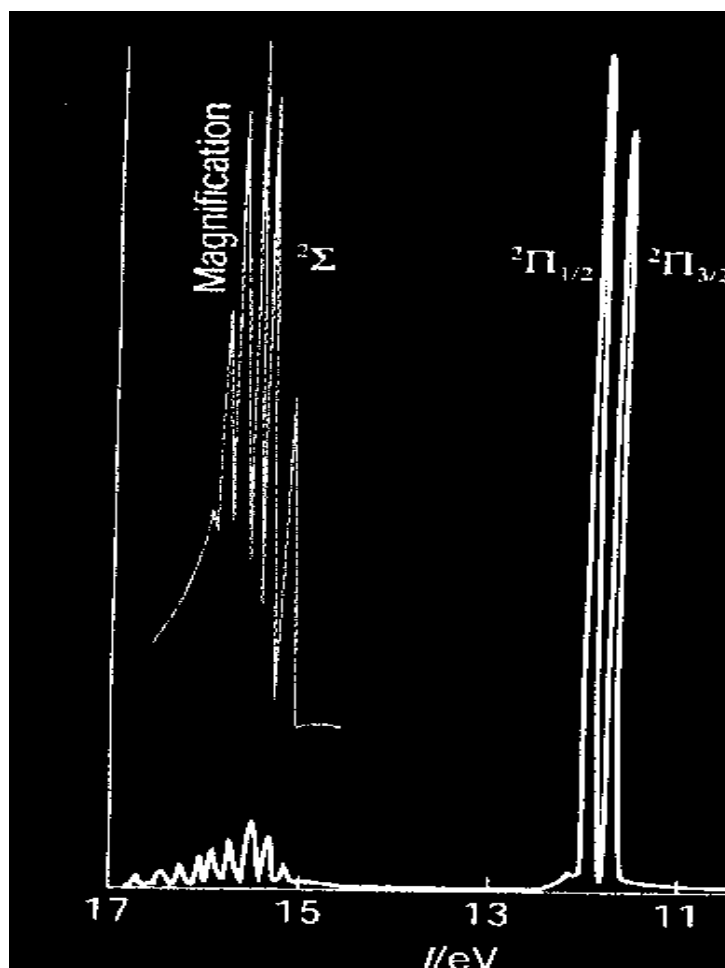


FIG - 24.3

The HBr spectrum shows that ejection of a σ electron is accompanied by a long vibrational progression. The Franck-Condon principle would account for this progression if ejection were accompanied by an appreciable change of equilibrium bond length between HBr and $(\text{HBr})^+$ because the ion is formed in a bond-compressed state, which is consistent with the important bonding effect of the σ electrons. The lack of much vibrational structure in the two

bands labeled $^2\Pi$ is consistent with the nonbonding role of the Br4p lone pair of electrons, for the equilibrium bond length is little changed when one is removed.

Example

The highest kinetic energy electron in the spectrum of H_2O using 21.22 eV. He radiation are at about 9 eV and show a large vibrational spacing of 0.41 eV (or 3310 cm^{-1}), which is similar to the vibrational wavenumber of the symmetric stretching mode of the neutral H_2O molecule (3652 cm^{-1}). Therefore, we can suspect that the electron is ejected from an orbital that has little influence on the bonding in the molecule. That is, photoejection is from a largely nonbonding orbital).

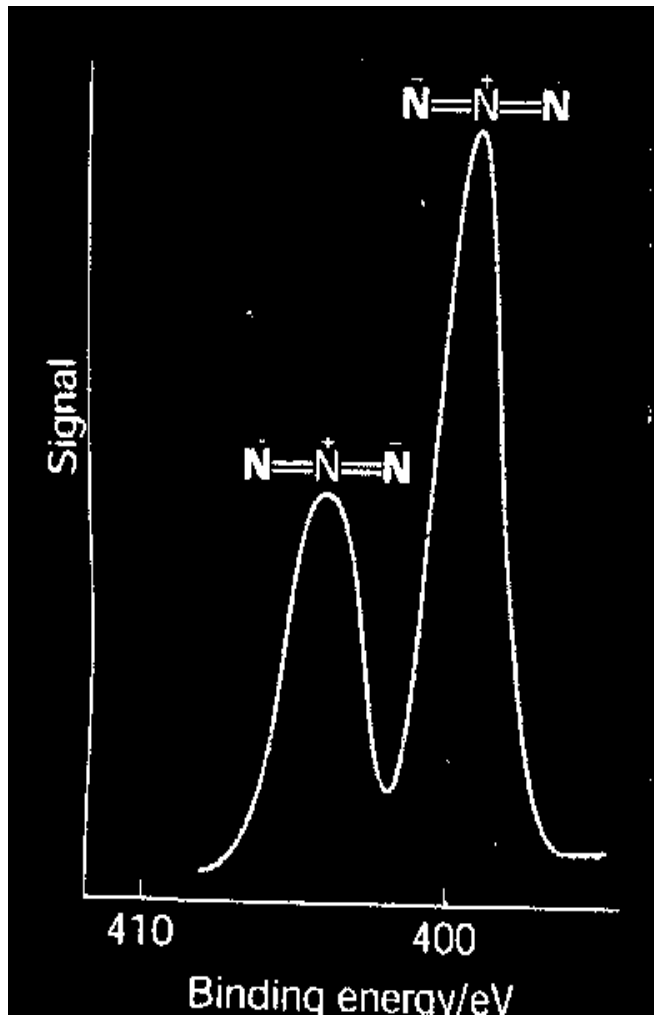
X-Ray Photoelectron Spectroscopy

In XPS, the energy of the incident photon is so great that electrons are ejected from inner cores of atoms. As a first approximation, core ionization energies are insensitive to the bonds between atoms because they are too tightly bound to be greatly affected by the changes that accompany bond formation, so core ionization energies are characteristics of the individual atom rather than the overall molecule. Consequently, XPS gives lines characteristics of the elements present in a compound or alloy. For instance, the K-shell ionization energies (eV) of the second-row elements are

Li	Be	B	C		N	O	F
50	110	190	280		400	530	
	690						

Detection of one of these values (and values corresponding to ejection from other inner shells) indicates the presence of the corresponding element. This application is responsible for the alternative name

electron spectroscopy for chemical analysis (ESCA). The technique is mainly limited to the study of surface layers because, even though X-rays may penetrate into the bulk sample, the ejected electrons cannot escape except from within a few nanometers of the surface. Despite (or because of) this limitation, the technique is very useful for studying



the surface state of heterogeneous catalysts, the differences between surface and bulk structures and the

FIG - 24.4

processes that can cause damage to high-temperature superconductors and semiconductor wafers.

Whereas it is largely true that core ionization energies are unaffected by bond formation, it is not entirely true, and small but detectable shifts can be detected and interpreted in terms of the environments of the atoms. For example, the azide ion, N_3^- , gives the spectrum shown in Fig.3.4. Although the spectrum lies in the region of 400 eV (and hence is typical of N1s electrons), it has a doublet structure with splitting 6 eV. This splitting can be understood by noting that the structure of the ion is $\text{N}^+ = \text{N}^- = \text{N}^-$, with more negative charges on the outer two 'N' atoms than on the inner, the formal charges are (-1, +1, -1). The presence of the negative charges on the terminal atoms lower the core ionisation energies, whereas the positive charge on the central atom rises it. This inequivalence of the atoms results in two lines in the spectrum with intensities in the ratio 2: 1 observations like this can be used to obtain valuable information about the presence of chemically inequivalent atoms, of the same element.

The other applications are give below : The XPS (X-ray photo electron spectroscopy) is able to finger print the materials present. The UPS which examines electron ejected from valence shells, is more suited to establishing the bonding characteristics and the details of valence shell electronic structures of the substances on the surfaces. Its usefulness is its ability to reveal which orbitals of the adsorbate are involved in the bond to the substrate. For example the photo emission spectroscopy studies indicate the differences in π electron energies of benzene in the free state and in the adsorbed state, on palladium. This difference is due to the fact that benzene molecules lie parallel to the surface and are attached to it by their π -orbital.

Self Check exercise –2

1. State Koopman's theorem. How is it useful?
2. Discuss the applications of PES & UPS – spectroscopies

Model answer – self check exercise-1

$$h\nu = \text{KE} + I_i$$

$$h\nu = 21.22 \text{ eV} \text{ and } \text{KE} = 4.53 \text{ eV}$$

Hence $I = 21.22 - 4.53$

16.7eV – this corresponds to the origin of the electron from $1\pi_u$.

24.3 Let us Sum Up

- i) Koopman's theorem is explained.
- ii) Applications of PES and UPS spectroscopies are discussed.
- iii) PES spectrum of HBr is illustrated.

24.4 Points for discussion

- 1) Analysis of Ionisation energies from photo electron spectroscopy provides evidence for the molecular orbital structures of molecules.
- 2) One can specify which is the HOMO of the molecule from the ionisation energy value.
- 3) Analysis of the photo electron spectrum of a molecule like HBr shows, that the lowest energy bands correspond to Bromine lone pair– and the highest energy band corresponds to removal of ' σ ' bond electron.

24.5 References

- 1) ATKINS PHYSICAL CHEMISTRY – 7th Edn. OUP – INDIAN - 2002
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