SOLID

Definition: Solids are characterised by incompressibility, rigidity and mechanical strength. The atoms molecules or ions in solids are closely-packed and they are held together by strong forces and can not move at random. Thus, in solids there is well ordered arrangement of molecules, atom or ions.

Types of Solids :

(a) Crystalline solids

(b)   Amorphous solids

(c)   Poly-crystalline or micro-crystalline solids.

SOLID

(a) CRYSTALLINE SOLIDS :

The solids in which atoms, ions or molecules are arranged in a definite pattern, constantly repeated, giving a definite geometrical shape, characteristic of substance and independent of the sources from which they have been obtained are called crystals. A crystalline solid is an aggregate of minute crystals, packed together in a well-defined order.

Properties of crystalline solids : (i) In a crystal, there is perfect and well-ordered arrangement of molecules throughout the entire body, each molecule is surrounded by a set of other molecules in a definite symmetrical way.

SOLID

(ii) A crystalline solid has a sharp and definite melting point.

(iii) A crystal when melted expands only about 10% in volume or about 3% in inter-molecular spacing.

(iv) The crystals are bounded by surfaces which are planar and are arranged according to a definite plan.

(v) The crystals have a rigorous geometrical order. Thermal motions cause disorder. It is clear that if a small region of disorder is introduced into a crystal, it would cause disturbance in the long range and destroy the crystalline arrangement. This explains the reason of sharp melting point of crystalline substances.

SOLID

(vi) When subjected to a mechanical stress, a crystal tends to fracture along a petfectly definite direction.

(vii) The important feature of a crystal is the periodicity of arrangement along with regularity.

(viii) A crystalline substance is anisotropic, i.e., its physical properties like mechanical, electrical and optical properties are different in different directions. For example, the velocity of light passing through a crystal changes with the direction in which it is measured. Moreover, in silver iodide crystal, the coefficient of thermal expansion is positive in one direction and negative in another direction. Anisotropy offers a strong evidence for the presence of well ordered molecular arrangement in crystals.

SOLID

(b) AMORPHOUS SOLIDS

The solids which do not have any definite geometrical shape are called amorphous solids, e.g glass, rubber, plastic etc.

Properties of amorphous solids: (i) Amorphous solids are considered to be super-cooled liquids in which the force of attraction holding the molecules together is so great that the substance is rigid and there is no regularity of structure.

(ii) Amorphous solids do not have sharp melting points. They gradually soften on heating. Absence of sharp melting point suggests the absence of long-range order in amorphous solids.

SOLID

(iii) On increasing the temperature, the viscosity of amorphous substances decreases and gradually changes into the liquid state.

(iv) In amorphous solids, there is non-periodicity of the arrangement alongwith no regularity.

(v) Amorphous solids are isotropic, i.e., their physical properties like mechanical, thermal, electrical properties are same in all directions. In amorphous substances, the particles are randomly arranged and disordered. Due to this, all directions are equivalent and so all the propelties remain the same in all directions.

SOLID

(c) MICRO-CRYSTALLINE OR POLY-CRYSTALLINE SOLIDS

In many solids, the shape of the crystals is not clearly seen, because several smaller micro-sized crystals are tightly packed together without any specific order. Therefore, a substance, which in fact is crystalline, but is superfine to be seen as a crystal, is called a micro-crystalline or poly-crystalline solid, e.g., many metals and alloys.

Properties of Micro-crystalline or Poly-crystalline Solids:

In micro-crystalline solids, the micro-crystals are randomly oriented, so the former will appear to be isotropic, even when each single crystal is anisotropic.

CRYSTAL

**Definition:** 1. A crystal is a solid which is composed of atoms arranged in an orderly repetitive array.

2. A homogeneous anisotropic substance (substance whose physical properties such as refractive index, electrical conductivity, magnetic susceptibility etc. are different in different directions) having a definite geometrical shape with surfaces that are usually plane and having sharp edges.

External Features of a Crystal :

The external features of a crystal are as follows:

1. Faces: The crystals are bounded by surfaces which are usually planar and arranged in a definite pattern. These surfaces are called faces of the crystal.

CRYSTAL
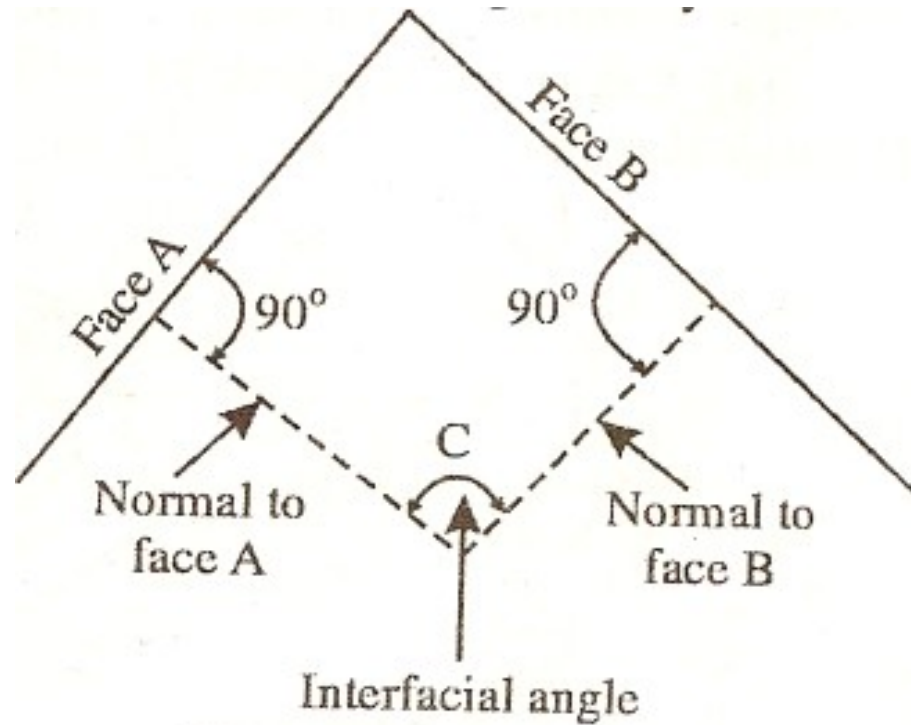
CRYSTAL

2. Edge: When two adjacent faces intersect, we get an edge.

3. Solid angle : When three or more edges intersect, we get a solid angle.

4. Interfacial angle : The angle between the normals to the two intersecting faces is called an interfacial angle.

5. Relationship between faces, edges and interfacial angles: A crystal is bounded by three external elements which are plane faces, straight edges and interfacial angles. These are inter-related by the following equation,   f + c = e + 2
where   f = Number of faces.   c = Number of interfacial angles   e = Number of edges.   ,

CRYSTAL

SPACE LATTICE : Every solid substance possesses a definite shape which is characteristic an distinctive for particular substance. In other words, a solid forms crystals. A crystal is a homogeneous portion of a solid substance made up of regular pattern, of structural units (atoms, molecules or ions) bounded by plane surfaces making definite angles with each other resulting in a definite and distinctive geometric form. The regul pattern of points which describe the three dimentional arrangement of particles in a crystal structure, is called the space lattice or crystal lattice.

A crystal can be imagined to be generated from the repetition of some basic unit of pattern. But rather than draw out the entire unit of pattern, it is much more convenient to represent the unit of pattern by a point.

CRYSTAL

Simple space lattice
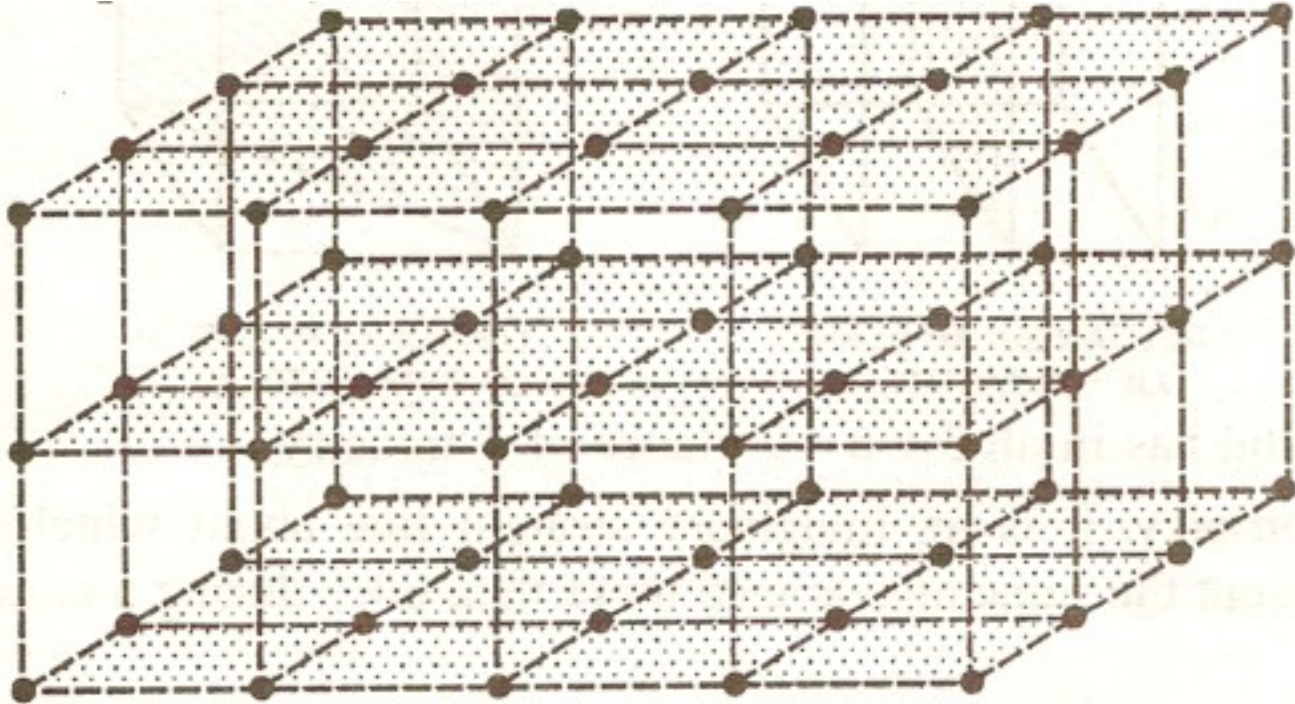
UNIT CELL

Definition: It is defined as the smallest geometrical portion of the crystal, which, when repeated in three dimensions, would generate the complete crystal. Each unit cell, in turn, must be constituted of atoms, molecules or ions, as the case may be, and arranged to give the particular geometrical configuration of the crystal.

Types of Unit cell:

1. **Simple or primitive type:** It is that arrangement in which the atoms, ions or molecules are present only at the corner of the unit cell. It is labelled as P, This unit cell consists of one atom at each of the eight corners. Since each atom at the corner is shared by 8 unit cells, therefore only $1/8^{th}$ of the atom is within the unit cell. Thus the number of atoms per unit cell in primitive or simple lattice is 8 x 1/8 = 1.
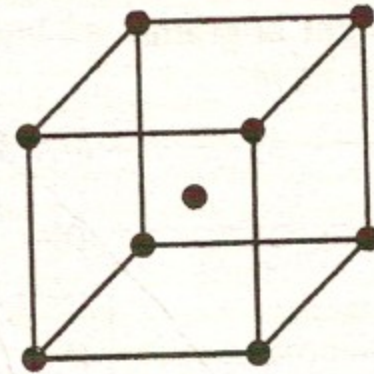
UNIT CELL

2. Body centered : In this arrangement in addition to the points at the corners, there is one point at the centre within the body of the unit cell. It is labelled as I. In a body centered cubic unit cell , there are eight atoms at the comers (each shared by 8 unit cells) and one at the centre (belonging to only one unit cell). Therefore, the number of atoms per unit cell is

8 x 1/8 + 1 = 2.
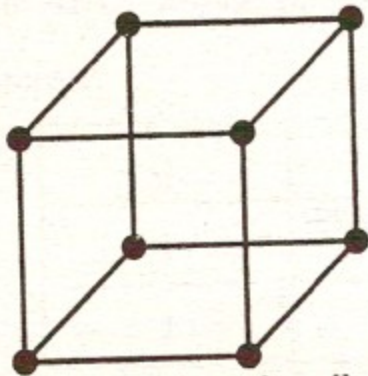
a) Primitive (P) cubic unit cell

(b) Body centered (I) cubic unit cell.

UNIT CELL

3. **Face-centred :** When in the unit cell, besides the points at the corners there is one point present in the centre of each face, it is called face-centred arrangement. It is labelled as F. In a face centred cubic unit cell , there are eight atoms at the corners (each shared by 8 unit cells) and six at the faces (each shared by two unit cells).

Therefore, the number of atoms per unit cell is

8 x 1/8 + 6 x 1/2 = 4.

4. **End-centered :** In this type there are points at the corners and at the centres of two end faces. It is labelled as C. In an end-centred orthorhombic cell (there is no end-centred cubic unit cell), there are eight atoms at the comers and two at the end faces so that the number of atoms per unit cell is 8 x 1/8 + 2 x ½ = 2.
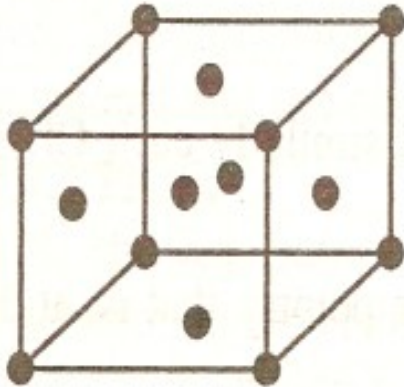
UNIT CELL

(c) Face-centred (F) cubic unit cell.
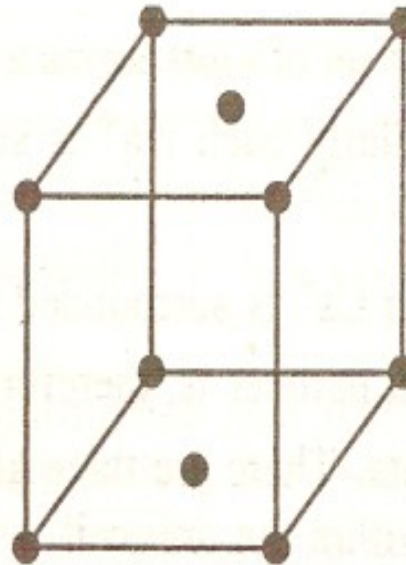
(d) End-centred (C) orthorhomic unit cell

Density of Unit Cell

Knowledge of the volume density and molecular weight of the constituent atoms of the cell also give information about the number of atoms or lattice per cell.

Consider a unit cell with volume V (in cm3) which can be calculated from the unit cell dimensions.

Let p (gm/cm2) be the density of the crystal. Then the weight of the matter in the unit cell = Volume x density =Vxp.

If n = number of atoms or molecules per unit cell.

m = atomic (molecular) weight of one atom or molecule.

Then, the weight of the matter in a unit cell
= n x m x 1.66 x 10^{-24} gm = n X M

where, 1.66 x 10^{-24} is the weight of an hydrogen atom in grams used in converting molecular weight in grams.

Density of Unit Cell

Thus

$$n \times M = V \times \rho$$

$$\rho = \frac{n \times M}{V} = \frac{n \times M}{V \times 6.023 \times 10^{23}}$$

$$\rho = \frac{n \times M}{V \times N}$$

where N = 6.023 x 10^{23} is the Avogadro's number.
The volume of unit cell for different lattice is given below:
Cubic v = a^3;   Hexagonal = abc sin 60°

Orthorhombic v = abc; Rhombohedral = $\frac{1}{2} a^3 \sin^2 \alpha / \cos \alpha / 2$

The Bragg's equation.

 W.H. Bragg pointed out that scattering of X-rays by crystal
 could be considered as reflection from successive
 planes of atoms in the crystals. However, unlike reflection
 ordinary light, the reflection of X-rays can take place only
 at certain angles which are determined by the wavelength
 of the X-rays and the distance between the planes in the
 crystal. The fundamental equation which gives a simple
 relation between the waveleng of the X-rays the interplanar
 distance in the crystal and the angle of reflection, is known as
 the Bragg's equation.

Derivation of the Bragg's equation.

.
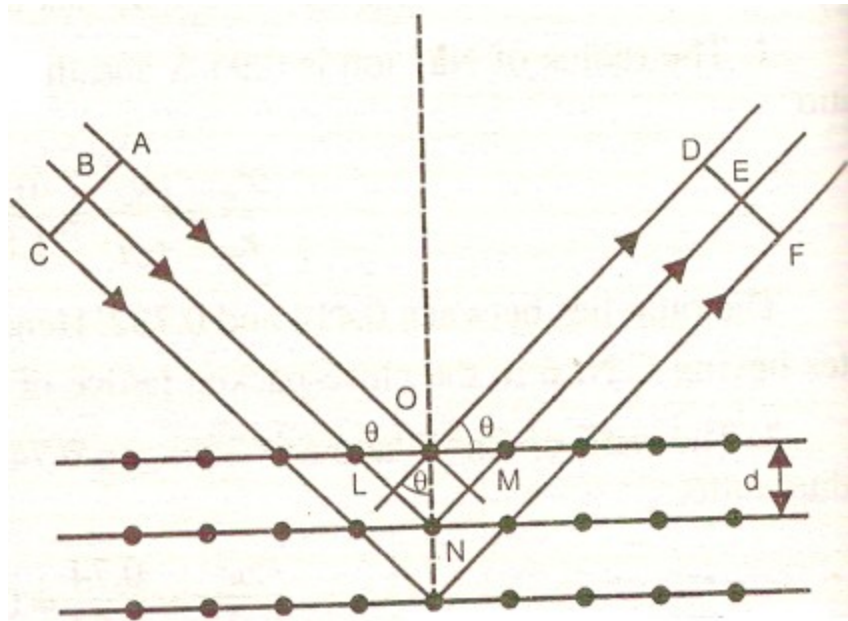
The horizontal lines represent parallel planes in the crystal structure separated from one another by the distance *d.* Suppose a beam of X-rays falls on the crystal at glancing angle θ Some of these rays will be reflected from the upper plane at the same angle θ while some others will be absorbed and set reflected from the successive layers.

Derivation of the Bragg's equation.

Let the planes *ABC* and *DEF* be drawn perpendicular to the incident and reflected beams. The waves reflected by different layer planes will be in phase with one another only if the differencein the path lengths of the waves reflected from the successive planes is equal to an integral number of wave lengths. Drawing *OL* and *OM* perpendicular to the incident and reflect beams, it will be seen that the difference in the path lengths of the waves reflected from the first two planes is:

$$\delta = LN + NM$$

This should be equal to a whole number multiple of wavelength λ,

$$LN + NH = n\lambda$$

Since the triangles *OLN* and *OMN* are congruent hence *LN = NM*

$$2\,LN = n\lambda$$

$$\boxed{2d\sin\theta = n\lambda}$$

Derivation of the Bragg's equation.

This is the Bragg's equation. This gives the condition which must be satisfied for the reflection of *X-rays* from a set of atomic planes. Knowing , θ *n* and λ, *d* be can be calculated.

Graphite

Structure : Each carbon atom is covalently bonded to three others involving sp2 hybrid orbitals instead of four as in diamond. Thus, all atoms in a single plane are linked to give flat hexagons as in benzene. The hexagons are held together in sheet like structures, parallel to one another. The C - C covalent bond distance is 1.42 A. The distance between the sheets or layers, however is comparatively large being about 3.35 A. This rules out the possibility of covalent bonding between the layers. Such crystals in which the various sheets of atoms are separated from one another by a distance larger than the maximum permissible for the formation of chemical bond are said to have layer lattices.

Graphite
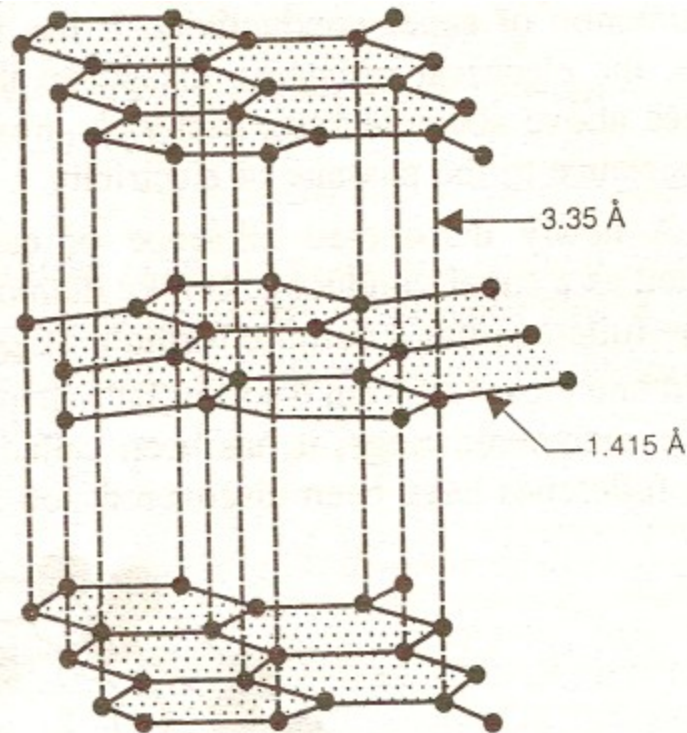
Graphite is a good conductor : In graphite, each carbon atom is connected only to three other carbon atoms ; while the fourth valency is unsatisfied. In other words, these delocalised electrons are free to move within the layer itself. This accounts for the fact that graphite is good conductor of electricity.
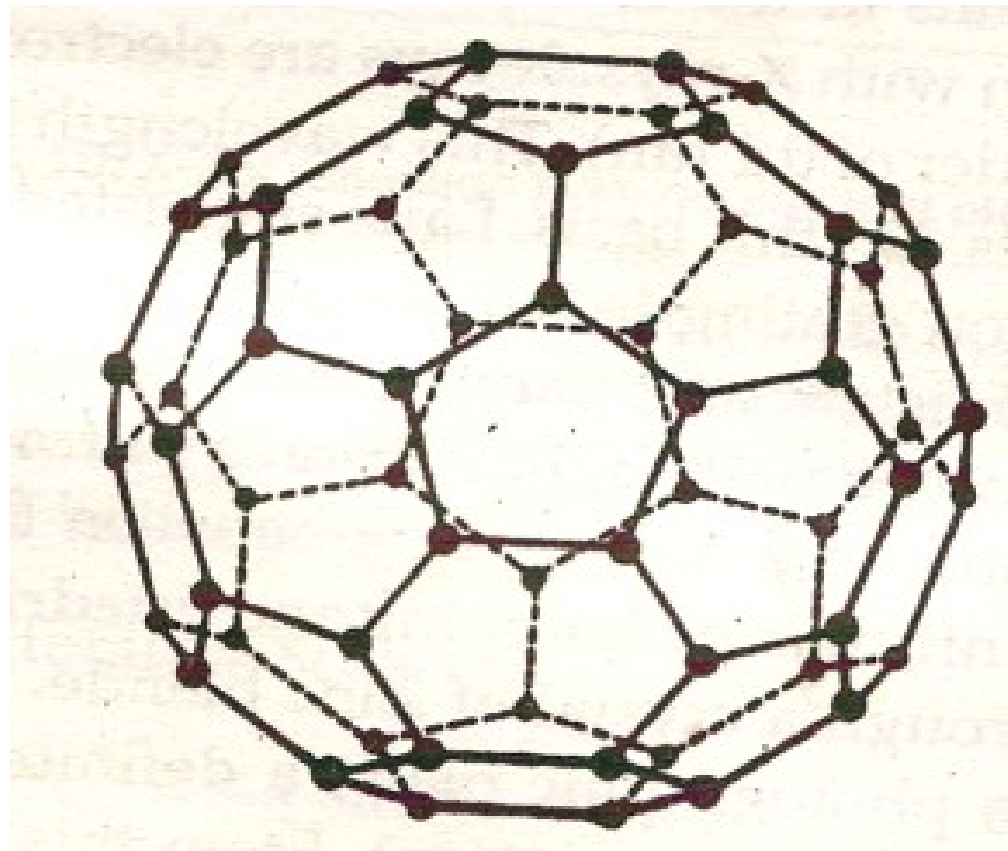
FULLERENES

Introduction : Fullerene is an allotrope of carbon. It is a molecule of formula C_{60}. It is popularly known as Buckminster fullerene in honour of the american architect Buckminster Fuller, who designed dome structures based on hexagons & pentagons.

Preparation : Fullerenes are prepared by vaporizing a graphite rod in a helium atmosphere. Mixture of fullerenes like C_{60}, C_{70} etc., are formed which are separated by solvent extraction. Pure C_{60} is isolated from this mixture by column chromatography.

Structure : The C_{60} molecule has a truncated icosahedron structure. An icosahedron is a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. A carbon atom is present at each vertex of this structure. The molecule is aromatic and has several resonance structures. The valencies of each carbon atom are satisfied by two single and one double bond. C_{60} is also known as buckyball as it is a spherical cluster of carbon atoms arranged in series of 5and 6, membered rings to form a soccer ball shape.

FULLERENES

FULLERENES

Properties of Fullerenes *:

1. Fullerene is a black powdery material.

2. It forms deep magenta solution, when dissolved in benzene.

3. It is very tough and thermally stable.

4. It exists as a discrete molecule, unlike the other two allotropes of carbon (viz. diamond and graphite).

5. It can be compressed to lose 30% of its volume without destroying its carbon cage structure.

Applications of fullerenes :

1. It is suitable for use as a lubricant due to its spherical structure. The bucky balls would act as molecular ball bearings.

FULLERENES

2. It can be used as a superconductor when mixed with alkali metals.

3. It can also be used as soft ferromagnet.

4. Other possible areas of uses are:

(i) Electronic and Microelectronic devices.

(ii) Non-linear optical devices.