

# Solid State

## Introduction: -

Solid, Liquid and gases are three physical state of matter, By rising of temperature solid melt into liquid, and liquid into gas. The physical state of matter is the result of interplay of intermolecular force of attraction like dipole-dipole interaction, dipole-induced dipole interaction, London force, hydrogen bonding etc. Food, shelter and cloth are solid matter, almost all metal like gold, platinum, silver, aluminum etc are solid. Most of the pharmaceutical drugs are also solid and liquid.



## Characteristics of Solid State: -

Followings are the important characteristics of solid state -

1. Solid of fixed composition has fixed mass, volume, shape and density.
2. Solid state are higher denser than liquid and gaseous state.
3. Most of the solid are hard, incompressible and rigid.
4. Intermolecular forces of constituent particles in solid are stronger than liquid and gaseous state.
5. Solid state has high melting and boiling point.
6. The particles of solid remain stationary at one position.

## Classification of solid: -

The presence or absence of orderly arrangement of the constituent particles, solid divided into 2 types

**1) Crystalline Solid** :- A crystalline solid is a homogeneous solid in which the constituents particles, atom, ions or molecules are arranged in a definite repeating pattern.

Eg- NaCl, CsCl, KCl etc.

The crystalline solid are aggregates of many small, tiny crystals called unit cell. There are 2 form of substances.

**a) Isomorphous** :- Two or more substances having the same crystal structure called isomorphous. They shows the same atomic ratio (Iso- Same, Morphous – Form).

Eg- NaF and MgO (1:1), NaNO<sub>3</sub> and CaCO<sub>3</sub> (1:1:3)

NaCl and KCl have almost all the properties identical but the crystal structures are different.

**b) Polymorphous** :- A single substance that crystallizes in two or more form under different condition (Poly-many, Morphous –form).

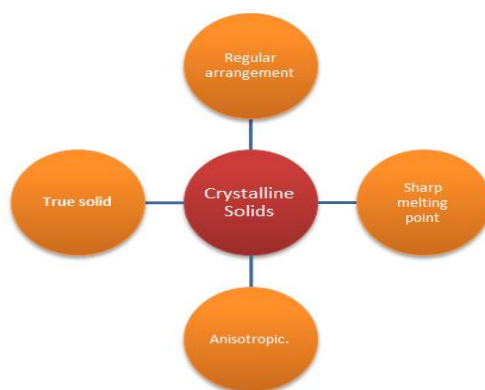
Eg-Carbon has two allotropic form i.e. diamond, graphite. Sulphur has two allotropic form i.e. rhombic and monoclinic.

**c) Anisotropy**:-The ability of crystalline solid to change values of physical properties, when measured in different direction called anisotropy.

## 2) Amorphous solid:-

The substance that appears like solids but do not have well developed perfectly ordered crystalline structure are called amorphous solids. eg- Tar, Glass, Plastics, Rubber, Butter etc.

- 1) Amorphous solid do not have ordered identical internal structure.
- 2) They do not melt at definite sharp melting point.
- 3) They do not solid in real sense, they are called super cooled liquid .
- 4) The structure of amorphous solid is similar to the structure of liquid
- 5) It behaves as fluids and very slowly floats under gravity
- 6) Amorphous solid are also called pseudo solid or super cooled liquids.



#### FLOW CHART OF CRYSTALLINE SOLID

#### Classification of solids:-

#### Crystalline and Amorphous solids:

| S.No. | Crystalline Solids                        | Amorphous solids                                  |
|-------|-------------------------------------------|---------------------------------------------------|
| 1     | Regular internal arrangement of particles | Irregular internal arrangement of particles       |
| 2     | Sharp melting point                       | Melt over a range of temperature                  |
| 3     | Regarded as true solids                   | Regarded as super cooled liquids or pseudo solids |
| 4     | Undergo regular cut                       | Undergo irregular cut.                            |
| 5     | Anisotropic in nature                     | Isotropic in nature                               |

**Glass :-** Glass is an optically transparent materials produced by fusing Silicon dioxide , Sodium oxide , boron oxide and a small amount of transition metal oxide for giving color to the glass.

Eg- 1. Quartz glass – It is obtained from only silicon dioxide

2. Pyrex glass – It is by fusing 60 to 80 %  $\text{SiO}_2$ , 10 to 20 %  $\text{B}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ .

3. Soda Lime – It is obtained by fusing 75%  $\text{SiO}_2$ , 15%  $\text{Na}_2\text{O}$  and 10%  $\text{CaO}$  .

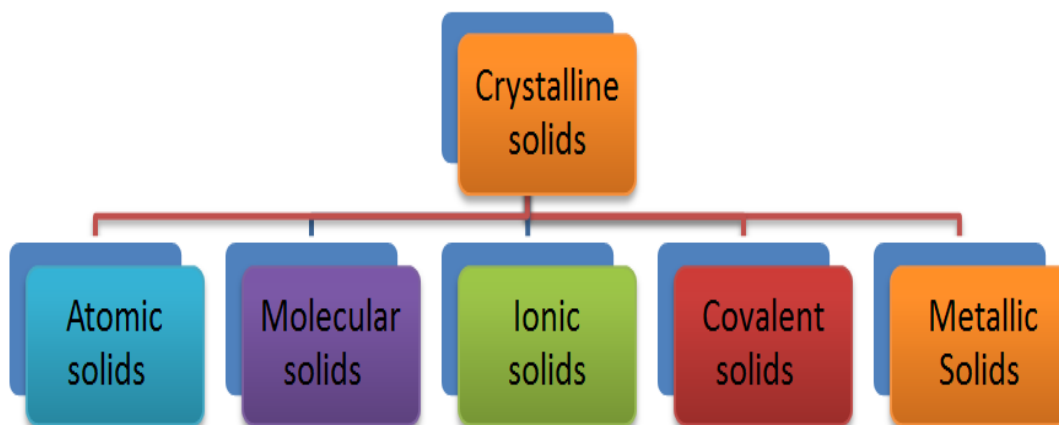
4. Red glass – It contain traces of Gold and Copper.

5. Yellow glass – It contain  $\text{UO}_2$  6. Blue glass – It contain  $\text{CoO}$  or  $\text{CuO}$

7. It contain  $\text{Fe}_2\text{O}_3$  or  $\text{CuO}$  .

## Classification of Crystalline Solids based on Different Binding Forces :-

Crystalline solids can be classified into different categories depending upon the type of constituent particles and the nature of attractive forces operating between them.



### 1) Atomic Solids:-

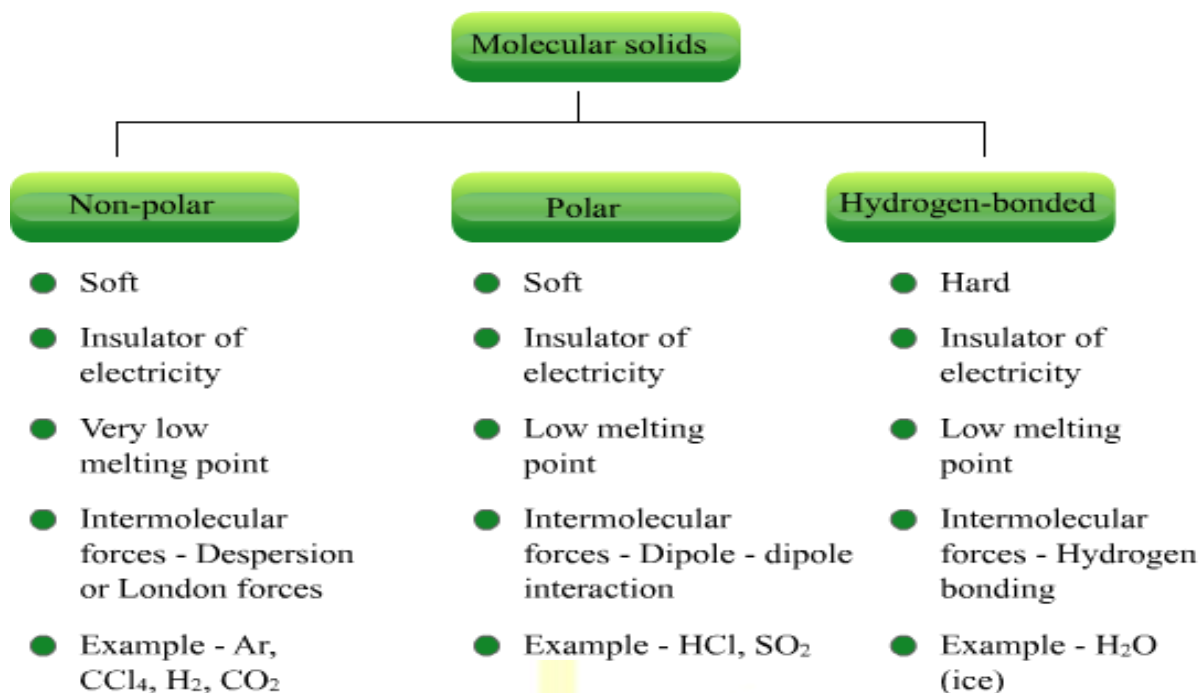
In these solids the constituent particles are atoms. These closely packed atoms are held up by London dispersion forces. Some examples are crystals of noble gases. Such solids are very soft; possess very low melting points and poor conductors of heat and electricity.

### 2) Molecular Solids:-

In these solids, the constituent particles which pack up together are molecules of the substance. These molecules may be non – polar (dipole moment = 0) such as etc. or they may be polar (dipole moment > 0) like etc.

In case of non – polar molecules, the attractive forces operating between the molecules are Vander Waal forces (also called dispersion forces). The example of such solids are : dry ice (Solid, iodine (crystals)).

In case of polar molecules, the attractive forces operating between the molecules in solid state are dipole – dipole forces. The examples of such solids are : solid, solid HCl. However, in some solids with polar molecules, the interparticle forces are hydrogen bonds. The examples of such solids are ice; solid hydrogen fluoride (HF); solid ammonia, etc.

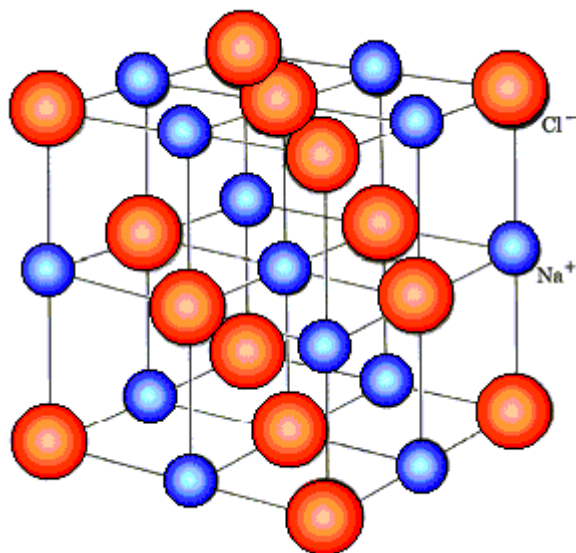


### Characteristics of Molecular Solids

- Some of the general characteristics of molecular solids are :
- They are generally soft.
- Their melting points are low to moderately high. The melting points of solids with non – polar molecules are relatively low whereas solids with polar molecules have moderately high melting points.
- They are generally bad conductors of heat and electricity.
- They have generally low density.

### 3) Ionic Solids

In ionic solids, the constituent particles are ions of opposite charges. Each ion is surrounded by a definite number of ions of opposite charge.





## Ionic structure of NaCl

The numbers of ions that surround a particular ion of opposite charge is called co-ordination number of the ion. For example, in sodium chloride crystal each sodium ion is surrounded by six chloride ions. Hence coordination number of  $\text{Na}^+$  is 6. At the same time each chloride ion is surrounded by six  $\text{Na}^+$  ions. Therefore the co-ordination number of  $\text{Cl}^-$  is also 6. However, in calcium fluoride crystal each  $\text{Ca}^{2+}$  ion is surrounded by eight  $\text{F}^-$  ions and each  $\text{F}^-$  ion is surrounded by four  $\text{Ca}^{2+}$  ions.

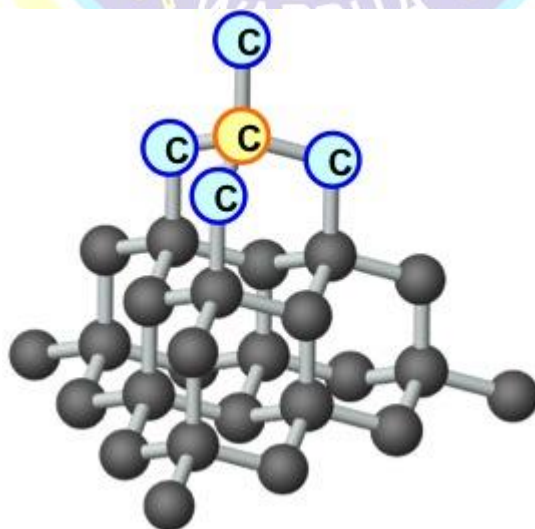
Thus, in crystal co-ordination numbers of  $\text{Ca}^{2+}$  and  $\text{F}^-$  ions are respectively 4 and 8. The interparticle forces in ionic solids are ionic bonds operating between the ions of opposite charges some examples of ionic solids are : sodium chloride ( $\text{NaCl}$ ) ; cesium chloride ( $\text{CsCl}$ ), zinc sulphide ( $\text{ZnS}$ ), calcium fluoride, etc.

### Characteristics of Ionic Solids

- Some common characteristics of ionic solids are as follows:
- They are hard, brittle and have low volatility.
- They have high melting points.
- They are poor conductors of electricity in solid state, however they become good conductors of electricity in molten state or in dissolved state.
- They are generally soluble in polar solvents like water.

### 4) Covalent Solids:-

In these types of solids the constituent particles are atoms of same or different elements connected to each other by **covalent bond network**.



**Diamond structure**

For example, in diamond only carbon atoms constitute the covalent network while carborundum covalent bond network is constituted by silicon and carbon atoms. Obviously, the interparticle forces operating in these solids are covalent bonds.

These solids are also called network solids because the covalent bonds extend in three dimensions forming a giant interlocking structure. Some examples of covalent solids are :

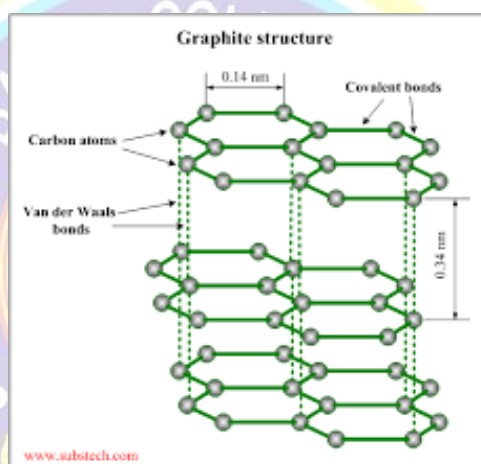
Diamond, silicon carbide, aluminium nitride etc.

**1) Diamond :-** a) Diamond is allotropic form of carbon ,All carbon atoms show  $sp^3$  hybridisation

b) All carbon atom, binding continues in all direction to form a big giant network of covalent solid.

c) It is a very strong and hard. d) It melts at  $3550^\circ\text{C}$

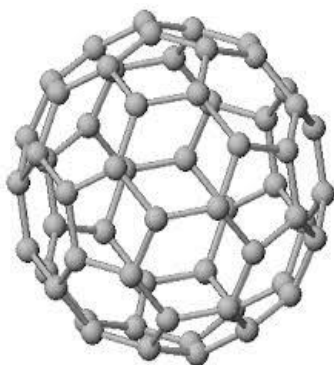
**2) Graphite :-** a) Graphite is a another allotropic form of carbon, all carbon atom of  
b) Each carbon atom bonded to three other  $sp^2$  hybrid carbon and formed interlinked six membered ring of carbon atom .  
c) The remaining half filled unhybridised  $2p_z$  orbital is used for  $\Pi$ - bonding.  
d) The delocalized electron free to move, So graphite is a good conductor of electricity.



**Graphite Structure**

**3) Buckminster Fullerene or Buckball or fullerene:-**

In 1985. A new allotrope of carbon was discovered, when a high power laser focused on carbon. It has  $C_{60}$  formula and had a shape of soccer ball .like graphite all carbon atoms are  $sp^2$  hybridized.The structure of fullerene is similar to soccer ball structure formed by arranging carbon hexagon and carbon pentagon.Fullerene are observed in carbon s



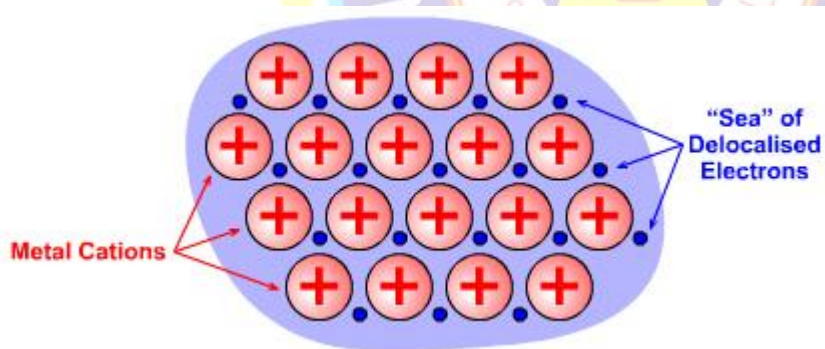
### Characteristics of Covalent Solids

Some common characteristics of covalent solids are:

- They are very hard. Diamond is the hardest naturally occurring substance.
- They have very high melting points.
- They are poor conductors of heat and electricity.
- They have high heats of fusion.

### 5) Metallic Solids

In these types of solids, the constituent particles are metal atoms. The interparticle forces in these solids are metallic bonds. In the metallic crystals the metal atoms occupy the fixed positions but their valence electrons are mobile.



The close packed assembly of metal kernels (part of metal atom without valence electrons) remains immersed in the sea of mobile valence electrons. The attractive force between the kernels and mobile valence electrons is termed as metallic bond.

### Characteristics of Metallic Solids

- The common characteristics of metallic solids are as follows:
- They generally range from soft to very hard.
- They are malleable and ductile.
- They are good conductors of heat and electricity.

- They possess bright luster.
- They have high melting and boiling points.
- They have moderate heats of fusion.

### Classification of Solids on the Basis of Binding Forces:-

| Crystal Classification | Unit Particles                                    | Binding Forces                                                                  | Properties                                                                                                             | Examples                                       |
|------------------------|---------------------------------------------------|---------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|
| Atomic                 | Atoms                                             | London dispersion forces                                                        | Soft, very low melting, poor thermal and electrical conductors                                                         | Noble gases                                    |
| Molecular              | Polar or non – polar molecules                    | Vander Waal's forces (London dispersion, dipole – dipole forces hydrogen bonds) | Fairly soft, low to moderately high melting points, poor thermal and electrical conductors                             | Dry ice (solid, methane)                       |
| Ionic                  | Positive and negative ions                        | Ionic bonds                                                                     | Hard and brittle, high melting points, high heats of fusion, poor thermal and electrical conductors                    | NaCl, ZnS                                      |
| Covalent               | Atoms that are connected in covalent bond network | Covalent bonds                                                                  | Very hard, very high melting points, poor thermal and electrical conductors                                            | Diamond, quartz, silicon                       |
| Metallic               | Cations in electron cloud                         | Metallic bonds                                                                  | Soft to very hard, low to very high melting points, excellent thermal and electrical conductors, malleable and ductile | All metallic elements, for example, Cu, Fe, Zn |

**Lattice Point:** - The constituent's particles, atom, ions or molecules of solid represented by a point called lattice point.

**Lattice line:** - The lattice points linked by a line called lattice line .

**Space lattice:** - The collection of all the points in the crystal having similar environment is called space lattice.

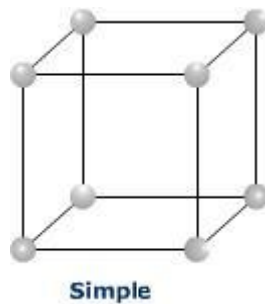
**Unit cell :-** The smallest repeating structural unit of a crystalline solid is called unit cell.

**Bravais lattice:** - The collection of all points in the crystal having similar environment

The shape of any crystal lattice depends upon the shape of a unit cell which is depends upon following two factor.



- A) The length of three edges of the unit cell .The three edges denoted by a ,b and c  
 B)The angle  $\alpha$  , $\beta$  and  $\gamma$  between three edges of the unit cell .



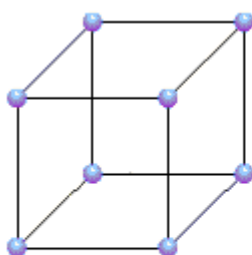
Bravais has established fourteen different types of lattices called Bravais lattices according to the arrangement of the points in the different unit cells involved.

These are listed below:

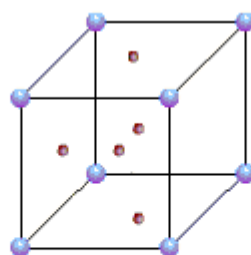
| Crystal System | Types of Lattices                                  |
|----------------|----------------------------------------------------|
| Cubic          | Simple, Face centered, Body centered               |
| Tetragonal     | Simple, Body centered                              |
| Orthorhombic   | Simple, Face centered, Body centered, End centered |
| Monoclinic     | Simple, End centered                               |
| Rhombohedral   | Simple                                             |
| Triclinic      | Simple                                             |
| Hexagonal      | Simple                                             |

Thus, there are seven crystal types for which fourteen different types of lattices (7 primitive or simple, 3 body centered, 2 face centered and 2 end centered are possible).The following fourteen different types of lattices are known as Bravais lattices.

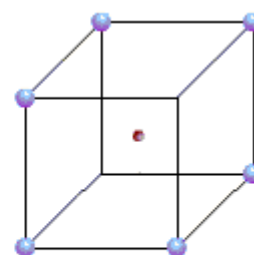
### 1) Cubic Lattice :-



**Simple cube**



**Face centred cube (fcc)**

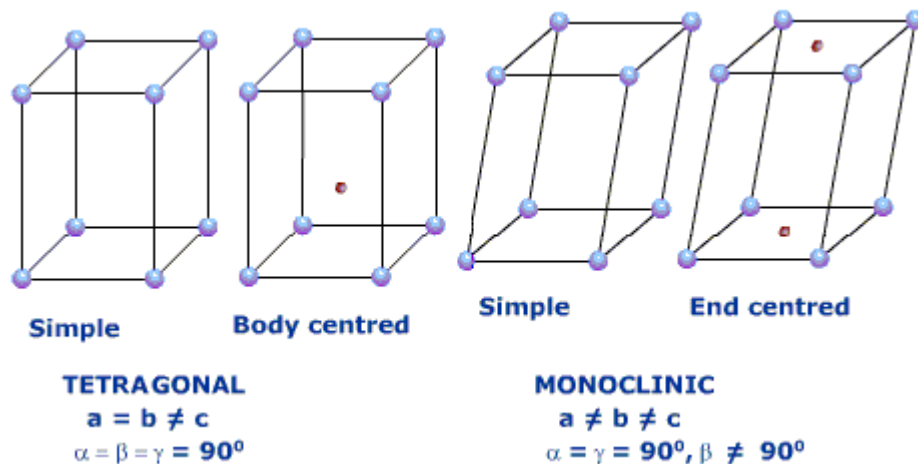


**Body centred cube (bcc)**

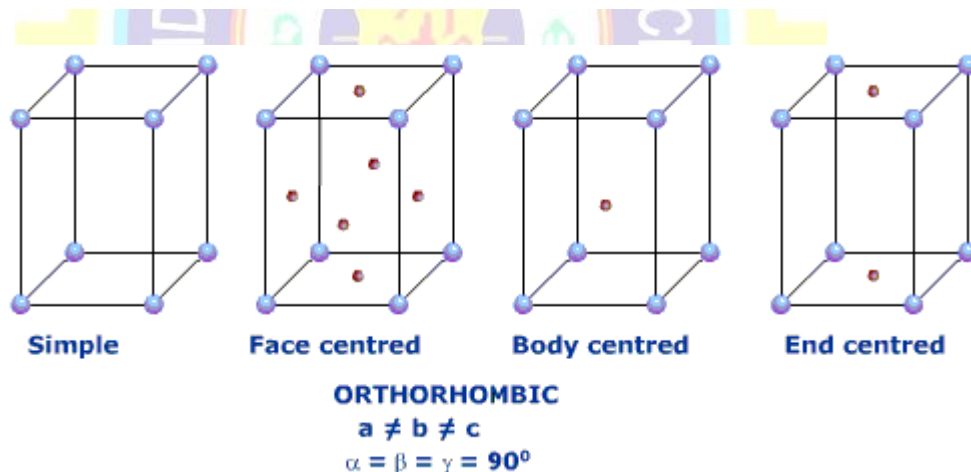
**CUBIC ( $a = b = c$ ;  $\alpha = \beta = \gamma = 90^\circ$ )**

- 1) In this lattice, all sides are equal  $a = b = c$ , all angles of  $90^\circ$ ,  $\alpha = \beta = \gamma = 90^\circ$   
 2) There are 3 types of cubic cell a) SCC b) BCC c) FCC

**2) Tetragonal Lattice:** - In this lattice, unit cell has 2 sides equal and third side with different length  $a = b \neq c$ . All angle of  $90^\circ$ ,  $\alpha = \beta = \gamma = 90^\circ$ . There are 2 types of unit cell  
 a) Primitive or Simple tetragonal b) Body centered tetragonal.

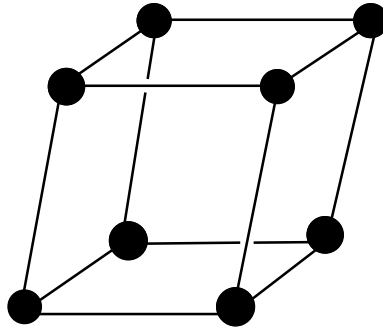


**3) Monoclinic Lattice :-** In this unit cell, all sides of different length  $a \neq b \neq c$ . Two angles are  $90^\circ$  and third angle is different  $\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$ . There are two types of monoclinic unit cell i.e. Simple or primitive monoclinic unit cell and End centered monoclinic unit cell



**4) Orthorhombic lattice :-** In this unit cell, all the three sides different  $a \neq b \neq c$ . All the three angles equal  $\alpha = \beta = \gamma = 90^\circ$ . There are four types i.e. Simple, Face centred, Body centred and face centred orthorhombic.

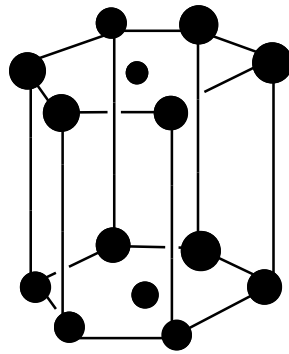
**5) Triclinic Lattice :-** In this unit cell, all the three sides of different length  $a \neq b \neq c$ . All the three angles different and not  $90^\circ$ ,  $\alpha \neq \beta \neq \gamma \neq 90^\circ$ . This lattice, unit cell exist in only one type i.e. primitive.



**Triclinic lattice**

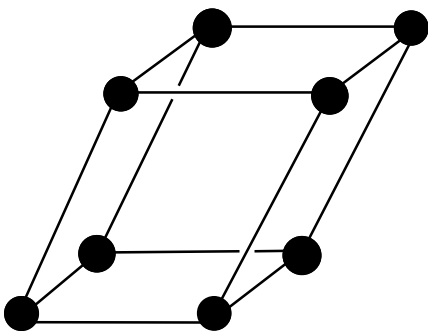
$$a \neq b \neq c$$

**6) Hexagonal Lattice:-** In this cell, two sides are equal and third side is of different length  $a = b \neq c$ . Two angles are equal to  $90^\circ$  and third is  $120^\circ$ ,  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$ .



**Primitive Hexagonal Lattice**

**7) Rhombohedra Lattice: -** In this unit cell, all sides are equal in length  $a = b = c$ . Two axial angles are equal to  $90^\circ$  and third angle is not equal to  $90^\circ$ ,  $\alpha = \beta = \gamma \neq 90^\circ$ . Rhombohedral unit cell exists in only one type.



**Rhomohedral Lattice**

**Types of unit cell with example:-**

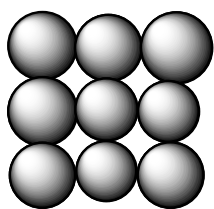
| S.No | Crystal System | Types        | Example              |
|------|----------------|--------------|----------------------|
| 1    | Cubic          | Simple       | Polonium             |
| 2    | Cubic          | Body Centred | Fe, Rb, Na, Ti, W, U |

|    |              |              |                                                     |
|----|--------------|--------------|-----------------------------------------------------|
| 3  | Cubic        | Face Centred | Cu,Al,Ni,Au,Pt                                      |
| 4  | Tetragonal   | Primitive    | SnO <sub>2</sub>                                    |
| 5  | Tetragonal   | Body centred | TiO <sub>2</sub> ,CaSO <sub>4</sub>                 |
| 6  | Orthorhombic | Primitive    | Rhombic sulphur                                     |
| 7  | Orthorhombic | Body centred | KNO <sub>3</sub>                                    |
| 8  | Orthorhombic | Face centred | BaSO <sub>4</sub>                                   |
| 9  | Orthorhombic | End centred  | MgSO <sub>4</sub> .7H <sub>2</sub> O                |
| 10 | Monoclinic   | Primitive    | Monoclinic sulphur                                  |
| 11 | Monoclinic   | End centred  | Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O |
| 12 | Triclinic    | Primitive    | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>       |
| 13 | Hexagonal    | Primitive    | ZnO,BeO,CoS,SnS                                     |
| 14 | Rhombohedral | Primitive    | Calcite ,NaNO <sub>3</sub> ,<br>FeCO <sub>3</sub>   |

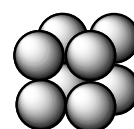
Some of the commonly occurring unit cells are discussed below :-

### A) Simple Cubic unit cell :-

- 1) In case of simple cubic unit cell, there are 8 particles at eight corners of unit cell.
- 2) The complete crystal is formed by repetition of unit cell in all three directions and particles at the corners are shared between neighbouring unit cells.
- 3) Every particle at the corner of unit cell is shared by eight neighbouring unit cells.
- 4) Each unit cell contains only  $\frac{1}{8}$  of the particles at the corners.
- 5) Hence, total no. of particles i.e. atom, ion or compound present in one simple cubic unit is equal to  $\frac{1}{8} \times 8 = 1$  particle.



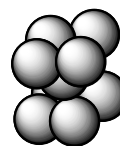
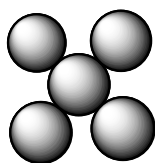
**Two dimensional arrangement  
of Simple cubic cell**



**Simple cubic structure**

### B) Body centred cubic unit cell :-

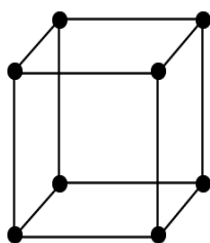
- 1) Body centred cubic unit cell is a modification of simple cubic unit cell.
- 2) In this cell, one particle is present at each corner and one additional particle is present at the centre of the body of unit cell.
- 3) Hence, total no. of spheres in body centred cubic unit cell =  $\frac{1}{8} \times 8 = 1$  sphere.
- 4) In this cell, structure is formed by fitting second layers of spheres into the depression of the first layer and third layer spheres in the depression of the second layer and so on.
- 5) Each sphere is surrounded by eight spheres, 4 in the layer above and 4 in the layer below.



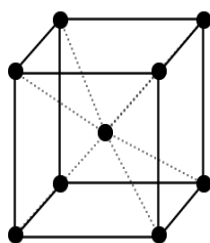
### Body centered cubic unit cell in one dimension

#### C) Face centred cubic unit cell :-

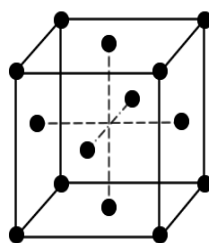
- 1) Face centred cubic unit cell is also modification of simple cubic unit cell.
- 2) There are 8 spheres at eight corners of the cube and one additional at the center of each face.
- 3) The no. of atoms situated at eight corners of unit cell of FCC type  $\frac{1}{8} \times 8 = 1$
- 4) There are total six faces of a cube, Hence  $\frac{1}{2} \times 6 = 3$ .
- 5) So, total spheres present in fcc type unit cell  $= 1 + 3 = 4$ .



P (Primitive)



I (Body)



F (Face)

#### Packing in Solids:-

| S.No | Crystal Lattice | Occupied Space | Empty Space |
|------|-----------------|----------------|-------------|
| 1    | SCC             | 52.4%          | 47.6%       |
| 2    | BCC             | 68%            | 32%         |
| 3    | FCC             | 74%            | 26%         |

#### Arrangement of particles:-

##### 1) Stage –I (Linear packing in One direction )

- a) The linear arrangement of spheres in one dimension can be made by arranging the spheres in one row touching one another.
- b) Each sphere except terminal is surrounded by two spheres hence coordination number is 2



- 2) **Stage –II:-** Planar packing arrangement of spheres this difference of rows can be done in two different ways-

##### a) AAAA type arrangement:-

- 1) In this arrangement, one sphere is placed one over the other and shows a horizontal as well as vertical.
- 2) Each sphere is surrounded by another 4 spheres, Hence C.N is 4.
- 3) In this arrangement square voids are formed.



4) In the formation of crystals, the constituent particles (atoms, ions or molecules) get closely packed together. The closely packed arrangement is that in which maximum available space is occupied. This corresponds to a state of maximum density. The closer the packing, the greater is the stability of the packed system.

3) (1) **Close packing in two dimensions:** The two possible arrangements of close packing in two dimensions.

4) (i) **Square close packing:** In which the spheres in the adjacent row lie just one over the other and show a horizontal as well as vertical alignment and form a square. In this arrangement each sphere is in contact with four spheres. (fig 5.6)

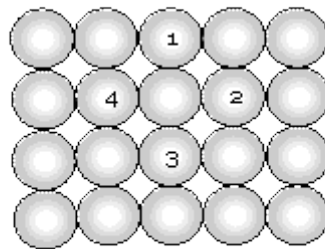


Fig. 5.6. Square close packing

(ii) **Hexagonal close packing:** In which the spheres in every second row are seated in the depression between the spheres of the first row. The spheres in the third row are vertically aligned with spheres in the first row. The similar pattern is noticed throughout the crystal structure. In this arrangement each sphere is in contact with six other spheres. (fig 5.7)

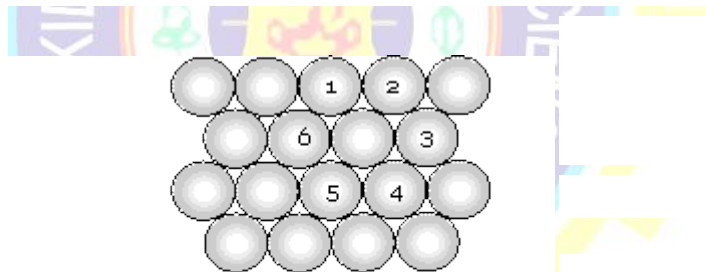


Fig. 5.7. Hexagonal close packing

### Hexagonal Close Packing in three dimension

The third layer lies vertically above the first and the spheres in the third layer rest in one set of hollows on the top of the second layer. This arrangement is called ABAB .... type and 74% of the available space is occupied by spheres. This arrangement is found in Be, Mg, Zn, Cd, Sc, Y, Ti, Zr, Tc, Ru. (Fig 5.9)

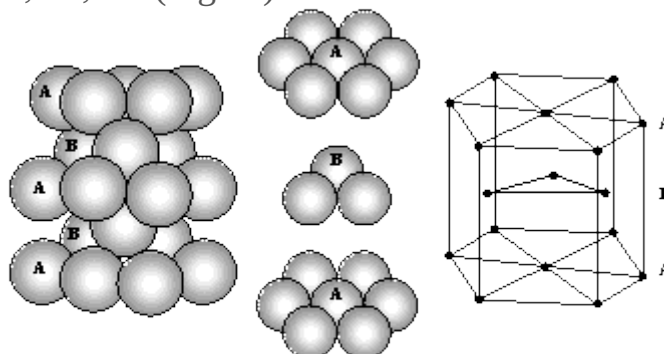


Fig. 5.9. Hexagonal close packing (hcp) in three dimensions

## Cubic Close Packing

The third layer is different from the first and the spheres in the third layer lie on the other set of hollows marked 'C' in the first layer. This arrangement is called ABCABC.....type and in this also 74% of the available space is occupied by spheres. The cubic close packing has face centered cubic (fcc) unit cell. This arrangement is found in Cu, Ag, Au, Ni, Pt, Pd, Co, Rh, Ca, Sr.(fig5.10)

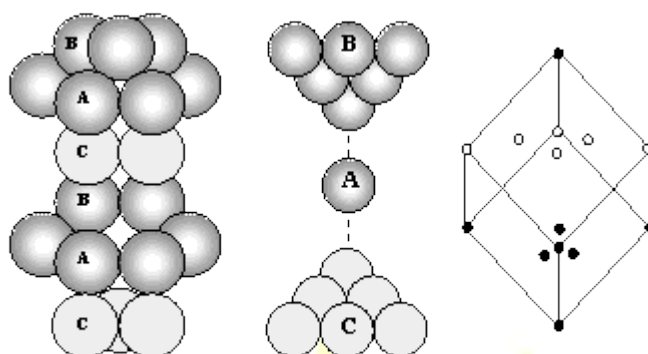


Fig. 5.10. Cubic close packing (ccp or fcc) in three

## Radius Ratio

Ionic compounds occur in crystalline forms. Ionic compounds are made of cations and anions. These ions are arranged in three dimensional array to form an aggregate of the type  $(A^+B^-)_n$ . Since, the Coulombic forces are non-directional, hence the structures of such crystals are mainly governed by the ratio of the radius of cation ( $r_+$ ) to that of anion ( $r_-$ ). The ratio  $r_+$  to  $r_-$  ( $r_+/r_-$ ) is called as radius ratio.

$$\text{Radius ratio} = \frac{r_+}{r_-}$$

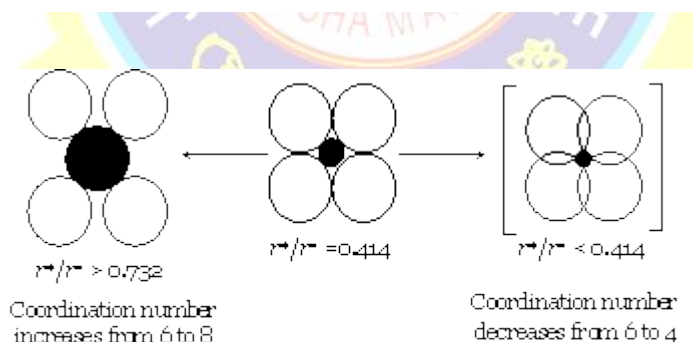


Fig. 5.17. Effect of radius ratio on co-ordination number

**Table: Limiting Radius ratios and Structure**

| Limiting radius ratio ( $r^+/r^-$ ) | C.N. | Shape               |
|-------------------------------------|------|---------------------|
| < 0.155                             | 2    | Linear              |
| 0.155 – 0.225                       | 3    | Planar triangle     |
| 0.225 – 0.414                       | 4    | Tetrahedral         |
| 0.414 – 0.732                       | 6    | Octahedral          |
| 0.732 – 0.999 or 1                  | 8    | Body-centered cubic |

## Interstitial Sites in Close Packing

Even in the close packing of spheres, there is left some empty space between the spheres. This empty space in the crystal lattice is called site or void or hole. Voids are of following types,

(1) **Trigonal void:** This site is formed when three spheres lie at the vertices of an equilateral triangle. Size of the trigonal site is given by the following relation,

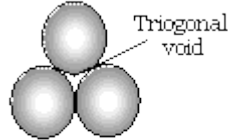


Fig. 5.12

$$r = 0.155 R$$

$r$  = Radius of the spherical trigonal void

$R$  = Radius of closely packed spheres

(2) **Tetrahedral void:** A tetrahedral void is developed when triangular voids (made by three spheres in one layer touching each other) have contact with one sphere either in the upper layer or in the lower layer.

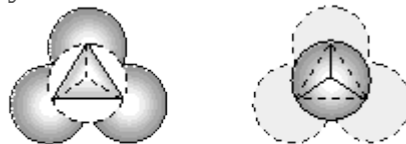


Fig. 5.13. Tetrahedral void

**The number of tetrahedral voids is double the number of spheres in the crystal structure.**

$$\frac{r}{R} = 0.225$$

Where,  $r$  is the radius of the tetrahedral void or atom occupying tetrahedral void.

$R$  is the radius of spheres forming tetrahedral void.

(3) **Octahedral void:** This type of void is surrounded by six closely packed spheres, i.e. it is formed by six spheres.

The number of octahedral voids is equal to the number of spheres.

$$\frac{r}{R} = 0.414$$

(4) **Cubic void:** This type of void is formed between 8 closely packed spheres which occupy all the eight corner of cube.

$$\frac{r}{R} = 0.732$$

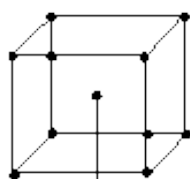


Fig. 5.15. Cubic void

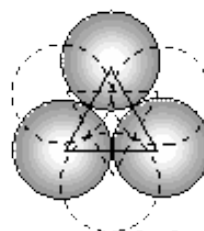


Fig. 5.14. Octahedral void

## Stoichiometric Defects

The compounds in which the number of positive and negative ions is exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) are called stoichiometric defects. These are of following types,

**(a) Interstitial defect:** This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystals.

**(b) Schottky defect:** This type of defect when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This type of defect occurs in highly ionic compounds which have high co-ordination number and cations and anions of similar sizes. e.g., NaCl, KCl, CsCl and KBr etc.

**(c) Frenkel defect:** This type of defect arises when an ion is missing from its lattice site and occupies an interstitial position. The crystal as a whole remains electrically neutral because the number of anions and cations remain same. Since cations are usually smaller than anions, they occupy interstitial sites. This type of defect occurs in the compounds which have low co-ordination number and cations and anions of different sizes. e.g., ZnS, AgCl and AgI etc. Frenkel defect are not found in pure alkali metal halides because the cations due to larger size cannot get into the interstitial sites. In **AgBr both Schottky and Frenkel defects occur simultaneously.**



Presence of large number of Schottky defect lowers the density of the crystal. When Frenkel defect alone is present, there is no decrease in density. The closeness of the charge brought about by Frenkel defect tends to increase the dielectric constant of the crystal. Compounds having such defect conduct electricity to a small extent. When electric field is applied, an ion moves from its lattice site to occupy a hole, it creates a new hole. In this way, a hole moves from one end to the other. Thus, it conducts electricity across the crystal. Due to the presence of holes, stability (or the lattice energy) of the crystal decreases.

**(ii) Non-stoichiometric defects:** The defects which disturb the stoichiometry of the compounds are called non-stoichiometry defects. These defects are either due to the presence of excess metal ions or deficiency of metal ions.

(a) **Metal excess defects due to anion vacancies:** A compound may have excess metal anion if a negative ion is absent from its lattice site, leaving a 'hole', which is occupied by electron to maintain electrical neutrality. This type of defects are found in crystals which are likely to possess Schottky defects. Anion vacancies in alkali metal halides are reduced by heating the alkali metal halides crystals in an atmosphere of alkali metal vapours. The 'holes' occupy by electrons are called F-centres (or colour centres).

(b) **Metal excess defects due to interstitial cations:** Another way in which metal excess defects may occur is, if an extra positive ion is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in the interstitial site. This type of defects are exhibit by the crystals which are likely to exhibit Frenkel defects e.g., when ZnO is heated, it loses oxygen reversibly. The excess is accommodated in interstitial sites, with electrons trapped in the neighborhood. The yellow colour and the electrical conductivity of the non-stoichiometric ZnO is due to these trapped electrons.

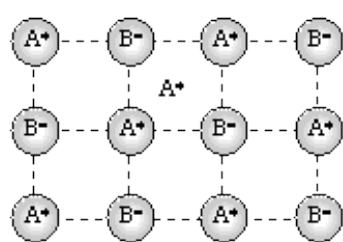


Fig. 5.20. Metal excess defect due to extra cation

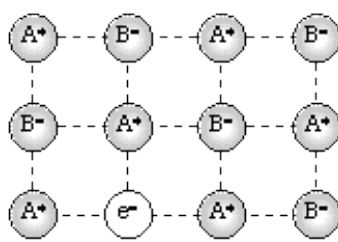


Fig. 5.21. Metal excess defect due to anion vacancy

## Impurity Defect

These defects arise when foreign atoms are present at the lattice site (in place of host atoms) or at the vacant interstitial sites. In the former case, we get substitutional solid solutions while in the latter case, we get interstitial solid solution. The formation of the former depends upon the electronic structure of the impurity while that of the later on the size of the impurity.

## Consequences of metal deficiency defects

Due to the movement of electron, an ion  $A^+$  changes to  $A^{+2}$  ions. Thus, the movement of an electron from  $A^+$  ion is an apparent of positive hole and the substances are called p-type semiconductor.

## Properties of Solids

Some of the properties of solids which are useful in electronic and magnetic devices such as, transistor, computers, and telephones etc., are summarized below,

(1) **Electrical properties:** Solids are classified into following classes depending on the extent of conducting nature.

(i) **Conductors:** The solids which allow the electric current to pass through them are called conductors. These are further of two types; Metallic conductors and electrolytic conductors. The electrical conductivity of these solids is high in the range  $10^4 - 10^7 \text{ ohm}^{-1} \text{ cm}^{-1}$ . Their conductance decrease with increase in temperature.

(ii) **Insulators:** The solids which do not allow the current to pass through them are called insulators. e.g., rubber, wood and plastic etc. the electrical conductivity of these solids is very low i.e.,  $10^{-12} - 10^{-22} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

(iii) **Semiconductors:** The solids whose electrical conductivity lies between those of conductors and insulators are called semiconductors. The conductivity of these solid is due to the presence of impurities. e.g. Silicon and Germanium. Their conductance increase with increase in temperature. The electrical conductivity of these solids is increased by adding impurity. This is called Doping. When silicon is doped with P (or As, group 5<sup>th</sup> elements), we get n-type semiconductor. This is because P has five valence electrons. It forms 4 covalent bonds with silicon and the fifth electron remains free and is loosely bound. This give rise to n-type semiconductor because current is carried by electrons when silicon is doped with Ga (or in in/Al, group 3<sup>rd</sup> elements) we get p-type semiconductors.

**Magnetic Properties of Solids:** Every substance around us has some magnetic properties in it. Different types of materials show different properties in the presence of magnetic field. The magnetic properties of a substance originate from the electrons present in the atoms or molecules. Every electron in an atom behaves like a small magnet. Electrons can also be referred to as small loops of current which retain their magnetic moment. These magnetic moments come from two types of motion of electrons:

1. The orbital movement around the nucleus of an atom.
2. When the electron spins around its own axis.

On the basis of the magnetic properties solids can be classified as follows:

| Properties    | Description                                       | Alignment of magnetic dipoles                                           | Examples                               | Application                |
|---------------|---------------------------------------------------|-------------------------------------------------------------------------|----------------------------------------|----------------------------|
| Diamagnetic   | They are weakly repelled by the magnetic fields   | All the electrons in the orbitals are paired and are completely filled. | NaCl, Benzene                          | Behaves like an insulator. |
| Paramagnetic  | They are weakly attracted by the magnetic fields. | Contains at least one unpaired electron in the orbital.                 | O <sub>2</sub> , Cu <sup>2+</sup> etc. | Electronic appliances      |
| Ferromagnetic | Strongly attracted by                             | Consists of                                                             | Cobalt,                                | CrO <sub>2</sub> is        |



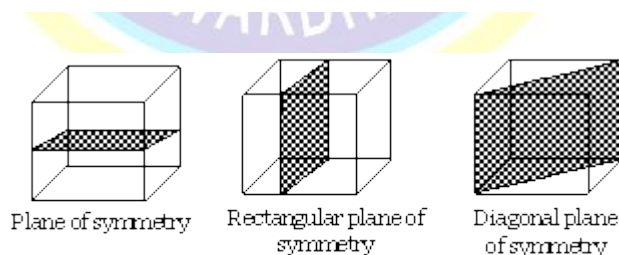
|                   |                                                          |                                                                             |                                                           |                                            |
|-------------------|----------------------------------------------------------|-----------------------------------------------------------------------------|-----------------------------------------------------------|--------------------------------------------|
|                   | the magnetic field.<br>The can be magnetised permanently | unpaired electrons, all having the same direction                           | nickel, $\text{CrO}_2$ etc.                               | commonly used in making cassette recorder. |
| Antiferromagnetic | Net magnetic moment is zero.                             | Dipole moments are arranged in a compensatory way                           | $\text{NiO}$ , $\text{MnO}$ , $\text{V}_2\text{O}_3$ etc. | —                                          |
| Ferrimagnetic     | Possess small net magnetic moments                       | Unequal number of parallel and antiparallel arrangement of magnetic moments | $\text{Fe}_3\text{O}_4$                                   | —                                          |

## Crystallography

“The branch of science that deals with the study of structure, geometry and properties of crystals is called crystallography”.

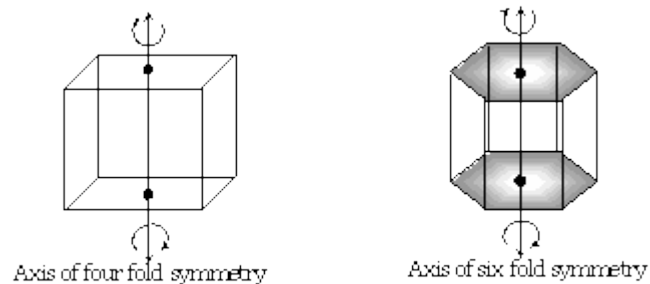
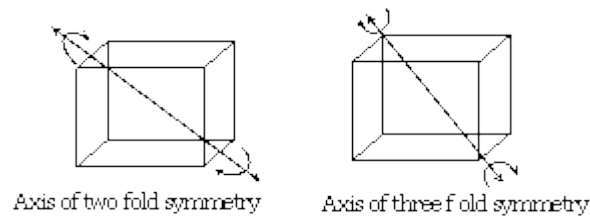
(1) **Symmetry in Crystal:** A crystal possess following three types of symmetry,

(i) **Plane of symmetry:** It is an imaginary plane which passes through the centre of a crystal can divides it into two equal portions which are exactly the mirror images of each other.

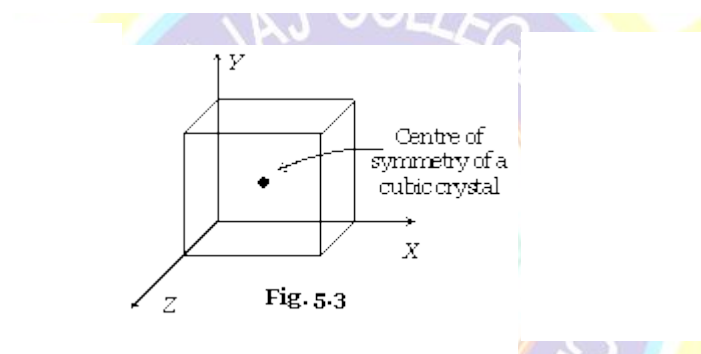


**Fig. 5.1**

(ii) **Axis of symmetry :** An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete revolution i.e., in a rotation through  $360^\circ$ . Suppose, the same appearance of crystal is repeated, on rotating it through an angle of  $360^\circ/n$ , around an imaginary axis, is called an n-fold axis where, n is known as the order of axis. By order is meant the value of n in  $2\pi/n$  so that rotation through  $2\pi/n$ , gives an equivalent configuration.



(iii) **Centre of symmetry:** It is an imaginary point in the crystal that any line drawn through it intersects the surface of the crystal at equal distance on either side.



Only simple cubic system has one centre of symmetry. Other system do not have centre of symmetry.

The total number of planes, axes and centre of symmetries possessed by a crystal is termed as elements of symmetry.

A cubic crystal possesses total 23 elements of symmetry.

Plane of symmetry  $(3 + 6) = 9$

Axes of symmetry  $(3 + 4 + 6) = 13$

Centre of symmetry (1)  $= 1$

Total symmetry = 23

## CHEMISTRY IN EVERY DAY LIFE

### **Introduction: -**

The principal of chemistry have been used for the benefit of human being. Every one use some materials like soap, detergents, bleaches, and tooth paste etc. Uses of cloth recently uses of synthetic fiber for the cloth ,chemical uses to give color to the cloth, many number of chemicals are uses for the disease as a medicine .Explosive, fuels, rocket propellants , electronic machine and materials etc are used. By chemistry the life becomes more suitable and easy. In this chapter we are discuss about –medicines, food preservatives and cleansing agents.

### **Drugs: -**

When the biological response is therapeutic and useful , these chemicals are called medicine and are used in diagnosis ,prevention and treatment of disease.

If medicine taken in higher dose are potential poisons .Use of chemicals for therapeutic effect are called chemotherapy . Erlich Paul is the father of chemotherapy .

**Classification of Drugs :-** Drugs are classified mainly as follows:

#### **A) *On the basis of pharmacological effect -***

It is useful for doctor because it provides them the whole range of drugs available for the treatment of particular types of problem. for example analgesics have pain killer , antiseptic kill or controlled the growth of microorganism .

#### **B) *On the basis of drug action -***

It is based on the action of a drug on a biochemical process .like all antihistamines inhibit the action of the compound, histamine which causes inflammation in the body .

#### **C) *On the basis of chemical structure -***

Drugs classified in this way have structural feature and often have similar pharmacological activity .like sulphonamide have common structural feature .

#### **D) *On the basis of molecular target -***

Drugs interact with biomolecules like carbohydrates ,lipids ,proteins and nucleic acid.These are called target molecules or drug targets .Those drugs have similar structure shows same function .

### **Drugs –Target Interaction:-**

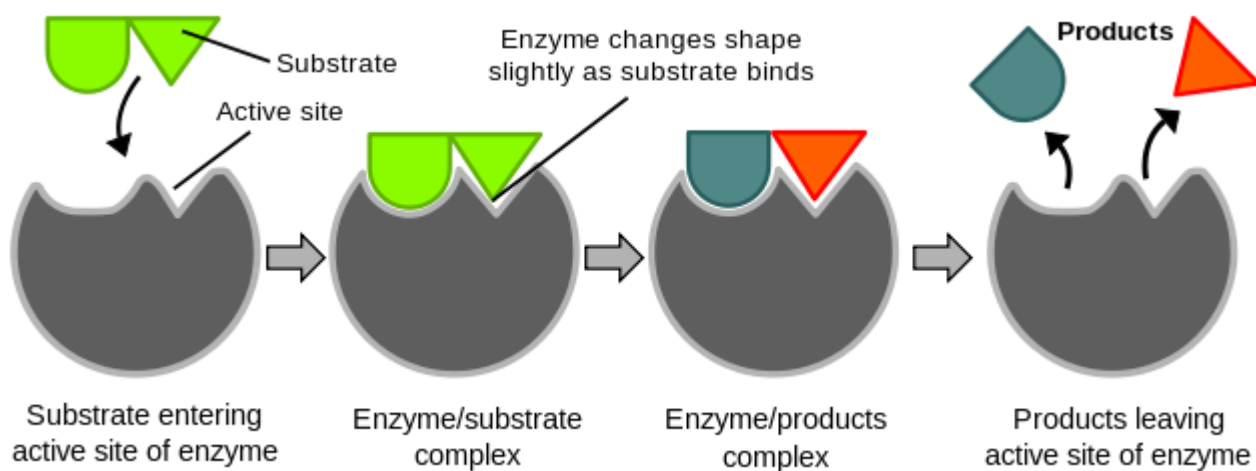
Proteins which perform the role of biological catalyst in the body are called

enzymes , those which are crucial to communication system in the body are called receptors. We shall explain the drug-target interaction with the example of enzymes of receptor.

#### a) *Catalytical action of enzymes*

Enzymes shows catalytical activity, it shows two major functions:

i)The first function of an enzymes is to hold the substrate for a chemical reaction.Active site of enzymes hold the substrate molecule in a suitable position .



Substrate binds the active site of the enzymes by ionic bonding, hydrogen bonding, van der Waals interaction or dipole-dipole interaction.

ii) The second function of enzymes is to provide functional groups that will attack the substrate and carry out chemical reaction.

#### b) *Drug –enzymes interaction*

Drug stop any of the above activity of enzymes .These can block the binding site of the enzymes and prevent the binding of substrate or can stop the catalytical activity of enzymes ,such drugs are called enzymes inhibitors.

Drugs stop the bonding of substrate on active site of enzymes in 2 ways

i) Drug compete with substrate for their attachment on the active sites of enzymes,such drugs are called **competitive inhibitors** .

ii)Some drugs do not bind to the enzymes active site ,these bind on a different sites of enzymes are called allosteric site .This binding of inhibitor at allosteric site change the shape of the active site in such a way that substrate do not identify it.

If the bond formed between an enzymes and an inhibitor is a strong covalent bond and

**Antacids:**

Antacids are commonly taken to relieve heartburn, which is a common symptom of gastritis or acidity. The stomach produces gastric acid to aid digestion. This acid is mainly composed of hydrochloric acid. Excessive secretion of the acid can lead to stomach disorders such as gastritis, gastric ulcers and peptic acid disease. These disorders can be treated by antacids, which reduce the amount of acid in the stomach. Antacids contain weak bases that neutralize the acid in the stomach by reacting with them chemically to produce salt and water.

Ex: Sodium hydrogen carbonate reacts with hydrochloric acid to give sodium chloride and water. However, antacids provide only temporary relief as they act on the symptoms alone and not on the cause of gastritis. Hence, their effect can wear off quickly and they have to be taken continually to obtain relief.

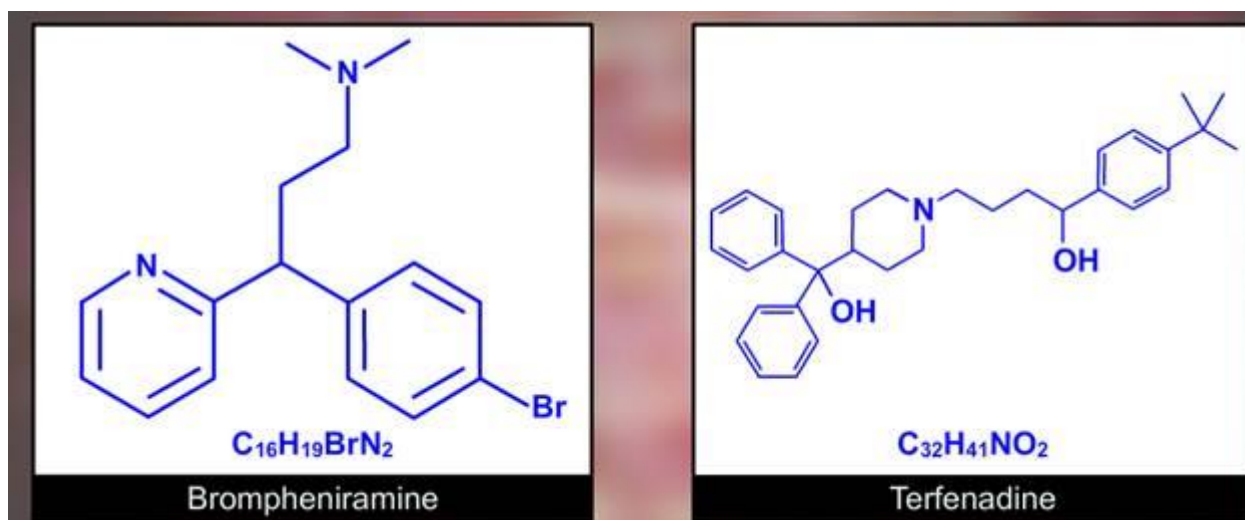
eg- Histamine , Cimetidine , Ranitidine etc .

**Antihistamines:**

The body's immune system consists of mast cells, which have antibodies attached to them. When antigens come into contact with the antibodies, the mast cells get stimulated and they release chemicals known as histamines and heparins into their surroundings, causing inflammation and irritation. In case of gastritis, the histamines bind to the receptors in the stomach wall and promote acidity.

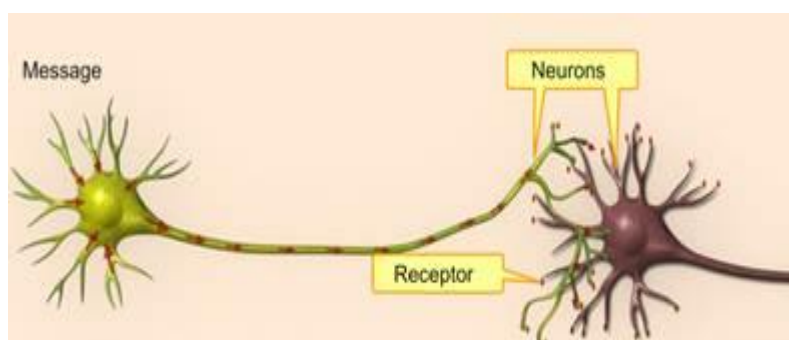
In case of allergies such as the common cold, the histamines bind to the receptors in the nasal cavity and cause blood vessels to swell and secrete excess fluid, causing sneezing and a running nose. Antihistamine drugs provide relief from the allergic effects of histamines by attaching themselves to the receptors and thus preventing histamines from binding to receptors. Thus, the histamines are prevented from causing chemical reactions and producing allergic symptoms.

Ex: Brompheniramine , Terfenadine etc



## Tranquilizers

Neurologically active drugs affect the message transfer mechanism between nerves and receptors.



Neurologically active drugs are commonly classified as tranquilisers and analgesics. A tranquiliser is a drug that acts on the central nervous system and is used to calm, lessen hypertension, subside depression (or) put a person to sleep. Tranquilisers ought to be taken in prescribed doses for short periods of time to avoid causing dependence and tolerance.

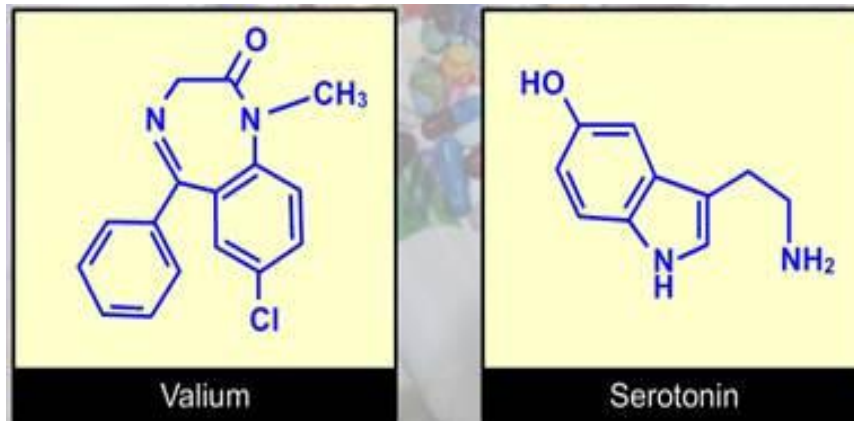
There are two types of tranquilisers: Major tranquilisers and Minor tranquilisers.

Major tranquilisers are commonly called anti-psychotic drugs, while minor tranquilisers are considered anti-anxiety drugs. Anti-psychotic drugs are used to treat patients with severe mental illnesses such as schizophrenia.

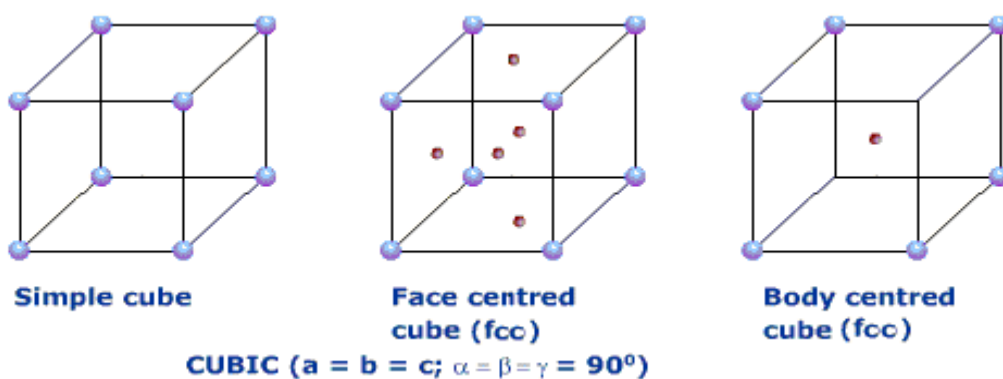
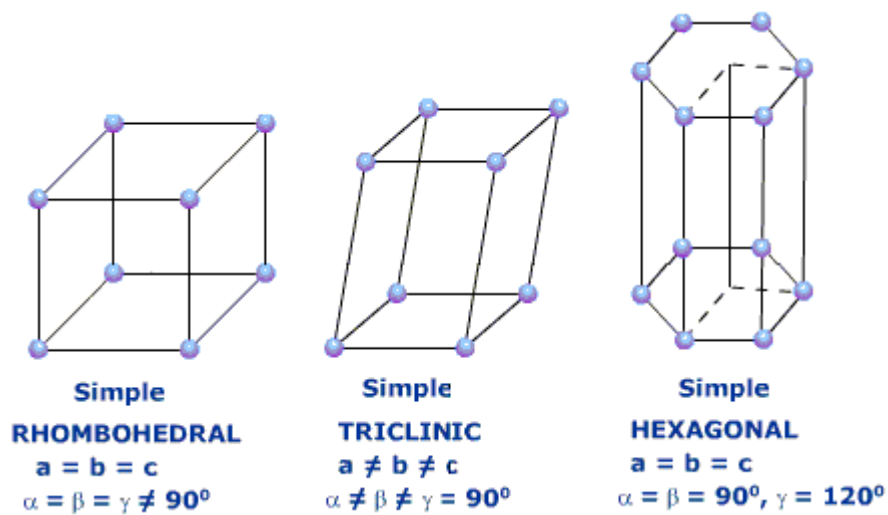
Ex: Haldol, Thorazine and Prolixin.

Anti-anxiety drugs are commonly used to treat emotional problems such as anxiety, depression and sleep disorders.

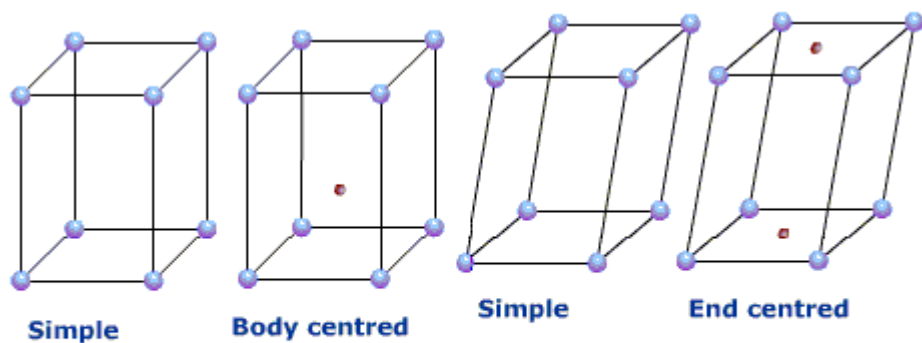
Ex: Valium, Librium and Xanax



Iproniazid , Phenelzine (Nardil) , Chlrodiazepoxide ,Equanil , Veronal ,Serotonin is a best tranquiliser medicine .







**TETRAGONAL**

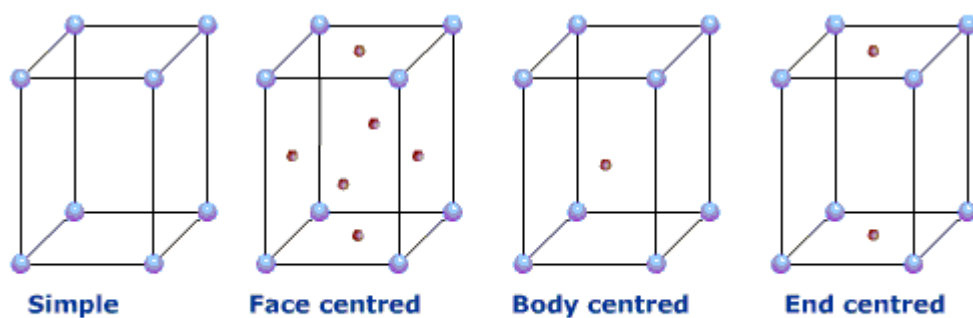
$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

**MONOCLINIC**

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$$

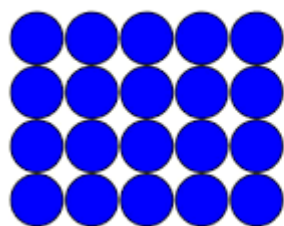


**ORTHORHOMBIC**

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

*square packing*



*hexagonal packing*

