

## Solid State

Solids can be classified as crystalline or amorphous on the basis of the nature of order present in the arrangement of their constituent particles.

| Property                                      | Crystalline solids   | Amorphous solids   |
|---|--|--|
| Shape   | Definite characteristic geometrical shape  | Irregular shape  |
| Melting point                                 | Melt at a sharp and characteristic temperature   | Gradually soften over a range of temperature                                       |
| Cleavage property                             | When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth | When cut with a sharp edged tool, they cut into two pieces with irregular surfaces |
| Heat of fusion                                | They have a definite and characteristic heat of fusion   | They do not have definite heat of fusion   |
| Anisotropy                                    | Anisotropic in nature  | Isotropic in nature  |
| Nature  | True solids  | Pseudo solids or super cooled liquids  |
| Order in arrangement of constituent particles | Long range order   | Only short range order.  |

Molecular solids are classified into:

- 1) Non polar molecular solids: non polar covalent bonds

Held by weak dispersion forces/London forces

Soft and non conductors of electricity

Low melting point

Exist in liquid or gaseous state at room temperature

2) Polar molecular solids: relatively stronger dipole-dipole interactions.

Soft and non-conductors of electricity

Higher melting point than non polar molecular solids

3) Hydrogen bonded: polar covalent bonds

Non-conductor of electricity

Volatile liquids or soft solids at room temperature

Ionic solids: ions are the constituent particles.

1) Cations and anions are bound by strong coulombic forces

2) Hard and brittle in nature

3) High melting and boiling points

4) Non-conductors of electricity at solid state while in molten state conduct electricity.

Metals: they contribute free and mobile electrons. This is the reason for the high electrical and thermal conductivity of metals. Also this attributes to the lusture and colour of the metal.

Non-metals: they have covalent bonds which are strong and directional. They are hard and brittle in nature. Eg: diamond. They are usually insulators (do not conduct electricity)

Crystalline solids: regular and repeating pattern of the constituent particles.

Crystal lattice: regular 3D arrangement of points in space.

There are 14 possible 3D lattices known as Bravais lattices.

Characteristics of a crystal lattice:

(a) Each point in a lattice is called lattice point or lattice site.

(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

Unit cell: smallest portion of a crystal lattice which when repeated in different direction generates the entire lattice.

Characteristics of a unit cell:

- (i) Its dimensions along the three edges,  $a$ ,  $b$  and  $c$ . These edges may or may not be mutually perpendicular.
- (ii) Angles between the edges,  $\alpha$  (between  $b$  and  $c$ )  $\beta$  (between  $a$  and  $c$ ) and  $\gamma$  (between  $a$  and  $b$ ). Thus, a unit cell is characterised by six parameters,  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$  and  $\gamma$ .

Unit cells are of 2 types:

- 1) primitive and
- 2) centred

centred unit cells are further classified into:

- (i) body centred unit cells
- (ii) face centred unit cells and
- (iii) end centred unit cells

| Crystal system           | Possible variations                                | Axial distances or edge lengths | Axial angles  | Examples   |
|--------------------------|--|---------------------------------|---|--|
| Cubic                    | Primitive, Body-centred, Face-centred              | $a = b = c$                     | $\alpha = \beta = \gamma = 90^\circ$                | NaCl, Zinc blende, Cu  |
| Tetragonal               | Primitive, Body-centred                            | $a = b \neq c$                  | $\alpha = \beta = \gamma = 90^\circ$                | White tin, SnO <sub>2</sub> , TiO <sub>2</sub> , CaSO <sub>4</sub> |
| Orthorhombic             | Primitive, Body-centred, Face-centred, End-centred | $a \neq b \neq c$               | $\alpha = \beta = \gamma = 90^\circ$                | Rhombic sulphur, KNO <sub>3</sub> , BaSO <sub>4</sub>              |
| Hexagonal                | Primitive  | $a = b \neq c$                  | $\alpha = \beta = 90^\circ$<br>$\gamma = 120^\circ$ | Graphite, ZnO, CdS.  |
| Rhombohedral or Trigonal | Primitive  | $a = b = c$                     | $\alpha = \beta = \gamma \neq 90^\circ$             | Calcite (CaCO <sub>3</sub> ), HgS (cinnabar)                       |

Calculation of the total number of atoms in a unit structure:

- 1) the open structure: there are 8 atoms on its corners, hence the total number of atoms in 1 unit cell=  $8 * \left(\frac{1}{8}\right) = 1$
- 2) body centred cell:
  - (i) 8 corners \* (1/8) atom per corner = 1 atom.
  - (ii) 1 body centre atom=1\*1= 1 atom

Hence 2 atoms per unit cell.

3) Face centred cell: atoms at all corners and centre of all faces

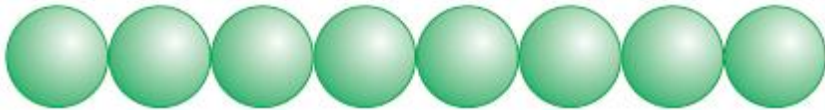
- (i)  $8 \text{ corners} * (1/8) \text{ atom per corner} = 1 \text{ atom}$
- (ii)  $6 \text{ (face centre)} * (1/2) \text{ atom per face} = 3 \text{ atoms}$

Hence 4 atoms per unit cell.

Packing in solid structures are close, ie close packing. Close packing can be classified in 3 ways:

a) One dimension: There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange them in a row and touching each other.

The number of nearest neighbours of a particle is called its coordination number.

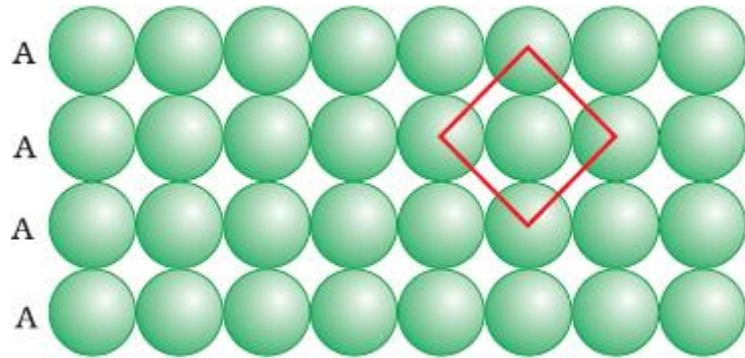


b) Two dimension: Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres.

2 types:

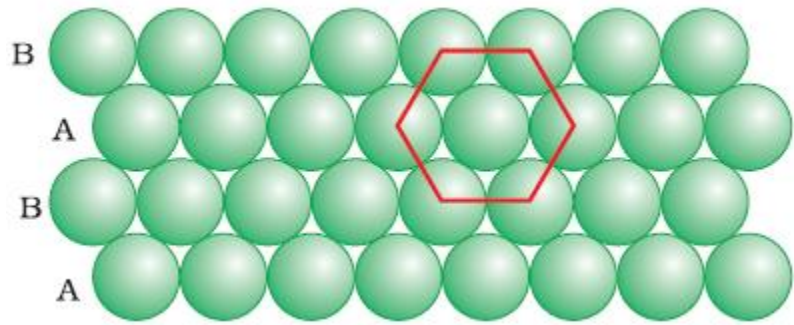
1) AAA type: coordination number= 4

Also known as square close packing in 2D



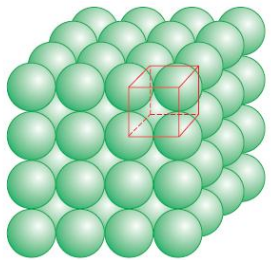
2) ABAB type: coordination number=6.

Also known as 2 dimensional hexagonal close packing.



c) Three dimensional close packing:

1) Square/cube arrangement: AAA type



2) Hexagonal 3 D packing can be made in 2 ways



There are different types of imperfections or defects in molecular structures.

Point defects and line defects are common types of defects.

Point defects are of three types –

Stoichiometric defects,

Impurity defects and

Non-stoichiometric defects.

Vacancy defects and interstitial defects are the two basic types of stoichiometric point defects.

In ionic solids, these defects are present as Frenkel and Schottky defects.

Impurity defects are caused by the presence of an impurity in the crystal.

In ionic solids, when the ionic impurity has a different valence than the main compound, some vacancies are created.

Nonstoichiometric defects are of metal excess type and metal deficient type.

Sometimes calculated amounts of impurities are introduced by doping in semiconductors that change their electrical properties.

When a group 13 element is added to Germanium or Silicon, it forms a p type semiconductor and when group 15 element is added, it forms an n-type semiconductor. Such materials are widely used in electronics industry.

Solids show many types of magnetic properties like paramagnetism, diamagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. These properties are used in audio, video and other recording devices. All these properties can be correlated with their electronic configurations or structures

Formulae:

- 1) The faces, edges and interfacial angles are related as  $f + c = e + 2$ , Where  $f$  = no. of faces,  $e$  = no. of edges,  $c$  = no. of interfacial angles.
- 2) The law of symmetry states that all crystals of same substances possess the same elements of symmetry.
- 3) Density of unit cell = Mass of the unit cell / Volume of the unit cell
- 4) Number of unit cell ( $Z$ ):  $n_c/8 + n_f/2 + n_i/1$ , where,  $n_c$  = no of atoms at the corners of the cube,  $n_f$  = number of atoms at six faces of the cube,  $n_i$  = no of atoms inside the cube.
- 5) The size of trigonal void is 0.115 times of the radius of the bigger sphere involved.

## Sample Examples

1) An element has a body-centred cubic (*bcc*) structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm<sup>3</sup>. How many atoms are present in 208 g of the element?

Ans: Volume of the unit cell = (288 pm)<sup>3</sup>

$$= (288 \times 10^{-12} \text{ m}) = (288 \times 10^{-10} \text{ cm})^3$$

$$= 2.39 \times 10^{-23} \text{ cm}^3$$

Volume of 208 g of the element: Mass/density =  $208/7.2 = 28.88 \text{ cm}^3$

Number of unit cells in this volume =  $28.88/2.39 \times 10^{-23}$

$$= 12.08 \times 10^{23} \text{ unit cells}$$

Since each *bcc* cubic unit cell contains 2 atoms, therefore, the total number of atoms in 208 g = 2 (atoms/unit cell)  $\times 12.08 \times 10^{23}$  unit cells

$$= 24.16 \times 10^{23} \text{ atoms}$$