CHAPTER 01

SOLID STATE

1. Existence of matter as solid, liquid or gas depends upon the net effect of intermolecular forces and thermal energy. Solid state have definite mass, volume and shape. They are incompressible, rigid and intermolecular forces are strong.
2. **Solids** can be classified into two categories, *viz.* crystalline and amorphous depending upon the arrangement of constituent particles.
3. **Crystalline solids** (or true solids) have long range order of arrangement of constituent particles and are *anisotropic* in nature, i.e. Cu, Ag etc. They melt at a sharp and have characteristic temperature. They have a definite and characteristic enthalpy of fusion.

   On the basis of nature of intermolecular forces operating in them the crystalline solids have been classified into following four types :

   (i) **Molecular solids** Constituent particles are molecules which are bonded through dipole-dipole interaction/ van der Waals' forces. e.g. solid NH_3, CO_2 etc.

   (ii) **Metallic solids** Constituent particles are positively charged metal ions (kernels) surrounded by sea of free electrons. The oppositely charge kernels and electrons hold ions together and is called metallic-bond. e.g. Fe, Cu, Ag etc.

   (iii) **Covalent or network solids** Constituent particles are non-metal atoms bonded with each other through covalent bonds. e.g. diamond, silicon carbide (SiC), graphite etc.

   (iv) **Ionic solids** Constituent particles are positively and negatively charged ions bonded through strong electrostatic or coloumbic forces. e.g. NaCl, MgO, ZnS etc.
4. **Amorphous solids** or **pseudo solids** (also called supercooled liquids) have short range order of arrangement of constituent particles and are *isotropic* in nature, e.g. glass, rubber, plastic.

   They have a tendency to flow, though very slowly. Glass panes fixed to windows or doors of buildings are found to become thicker at the bottom because the glass flows down slowly and makes the bottom portion thicker.
5. **Crystal lattice** The geometrical form consisting only of a regular array of points in space is called a **lattice** or **space lattice.**
   - The scaffolding is a space lattice on which two dimensional pattern has been developed by placing structural units on its set of points. The structural unit is called **basis** or **motif**.
   - A **crystal lattice** (space lattice) is the pattern of points representing the locations of these motifs.
6. **Unit cell** is the smallest portion of a crystal lattice which repeated in different directions, generates the entire lattice.
7. **Types of unit cells** Based upon the parameters of the unit cells (i.e. lengths *a*, *b* and *c* and the angles α, β and γ), there are seven types of unit cells. These are called **crystal systems** because any crystalline solid must belong to any one of these unit cells.
8. There are fourteen lattices corresponding to seven crystal systems, known as **Bravais lattices**.

9. **Seven primitive unit cells and their possible variations as centred unit cell**

Crystal system	Possible variations	Axial distance or edge lengths	Axial angles	Examples
Cubic	Primitive, face-centred, body-centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, zinc blende (ZnS) and Cu
Tetragonal	Primitive, body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2, TiO_2 and $CaSO_4$
Orthorhombic	Primative, face-centred, body-centred, end-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3 and $BaSO_4$
Monoclinic	Primitive, end-centred	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	Monoclinic sulphur and $Na_2SO_4 \cdot 10H_2O$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Graphite, ZnO and CdS
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$) and HgS (Cinnabar)
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, H_3BO_3 and $K_2Cr_2O_7$

10. Types of cubic unit cells and number of atoms per unit cell are tabulated below :

Type of cell	Number of atoms at corners	Number of atoms on faces	Number of atoms in the body of cube	Total number of atoms present in the unit cell
Simple or Primitive cubic unit cell	$\frac{1}{8} \times 8 = 1$	0	0	1
Body centred cubic unit cell	$\frac{1}{8} \times 8 = 1$	0	$1 \times 1 = 1$	2
Face centred cubic unit cell	$\frac{1}{8} \times 8 = 1$	$\frac{1}{2} \times 6 = 3$	0	4

11. Constituent particles in a crystal lattice can be packed in following three steps :

(i) **One dimension** Simple close packing (or linear) (C.N. 2)
(ii) **Two dimension** Square close packing (scp) (C.N. 4) and hexagonal close packing (hcp) (C.N. 6)
(iii) **Three dimension** From 3*D* scp layers or from 3 hcp layers. (C.N. = 12)

12. Number of voids In close packed structure, there are two main type of voids present in lattice, i.e. tetrahedral and octahedral voids. It is found that.

(i) Number of octahedral voids = Number of particles present in close packing (N)
(ii) Number of tetrahedral voids $= 2 \times$ Number of particles present in close packing (N)
or, Tetrahedral voids $= 2 \times$ octahedral voids

13. Packing efficiency It is the fraction or percentage of total space filled by the particles, i.e.

$$\text{Packing efficiency} = \frac{\text{Volume occupied by spheres in the unit cell}}{\text{Total volume of unit cell}} \times 100$$

Type of unit cell	Number of atoms per unit cell	Radius (r)	Coordination number	Packing efficiency
Simple cubic unit cell	1	$\frac{1}{2}a$	6	52.4%
Body centred cubic unit cell	2	$\frac{\sqrt{3}}{4}a$	8	68%
Face centred cubic unit cell	4	$\frac{1}{2\sqrt{2}}a$	12	74%

(a = edge length)

14. Density (d) of the unit cell is calculated by using the given expression,

$$d = ZM/a^3N_A \quad \text{(for cubic crystal)}$$

where, Z = Number of atoms per unit cell, M = Molar mass or atomic mass
a = Edge length, a^3 = Volume of the unit cell and N_A = Avogadro's constant

15. Imperfections in solids A solid consist of an aggregate of large number of small crystals. These crystals have defect in them. These defects are of two types: Point defect and line defect.

16. Line defects are the irregularities from ideal arrangement in entire rows of lattice points. Where as **point defects** are the irregularities or deviation from ideal arrangement around a point in a crystalline solid.

These are further classified as stoichiometric defects, impurity defects and non-stoichiometric defects.

(i) **Stoichiometric defects** Point defect that do not disturb the stoichiometry of the solid are called stoichiometric defects (Intrinsic or thermodynamic defect) e.g.

(ii) **Non-stoichiometric defects** Those imperfections in the crystals, which lead to change in the composition of solids are called non-stoichiometric defects.

(iii) **Impurity defects** Arise when foreign atoms are present in the lattice site or in the interstitial site. e.g. solid solution of $CdCl_2$, AgCl.

17. Schottky defect A stoichiometric or vacancy defect, arises due to missing of equal number of cations and anions from the lattice and is shown by crystals having cation and anion of comparable size. e.g. CsCl, NaCl, AgBr etc. It decreases density of a substance.

18. Frenkel defect A stoichiometric or interstitial defect, arises when the smaller ion (usually cation) is dislocated from its normal site to an interstitial site. It results increase in conductivity but density of the crystal remains the same.

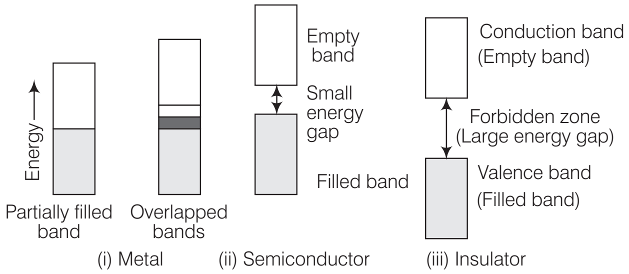
19. Metal excess defect can be due to anionic vacancies, e.g. on heating crystals of NaCl in presence of Na vapour, some anions leave lattice sites which are occupied by electrons called *F*-centres giving colour to crystals. These defects can also be generated due to presence of extra cations at interstitial sites, e.g. on heating, white ZnO it turns yellow as it loses oxygen and Zn^{2+} ions.

20. Electrical Properties Solids are classified into three groups on the basis of conduction power. These are as follows :

Types of solid	Conductivity	Reason of conductivity	Examples
Conductors	10^4-10^7 (very high)	Motion of electrons	Metals like Ag, Al
Insulators	10^{-20}- 10^{-10} (Very low)	Do not permit electricity to pass	Wood, rubber, bakelite
Semiconductors	10^{-6}-10^4 (Moderate)	Motion of interstitial electrons or holes or both	Si, Ge, etc.

21. Conduction of Electricity in Metallic Conductors

- Metals conduct electricity in solid as well as in fusion (molten) state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms form molecular orbitals which are too close in terms of energy to each other such that it forms a **band**.
- The distinction between conductors (metals), semiconductor and insulator is shown below :



Distinction among (i) metals (ii) semiconductors and (iii) insulators

22. Conduction of Electricity by Semiconductors

- Electrical conductivity of semiconductors increases with rise in temperature because more electrons can jump from valence band to the conduction band. Pure substances like silicon and germanium exhibit this type of conducting behaviour and are called **intrinsic semiconductors**. The conductivity of the intrinsic semiconductors is very low at room temperature.
- The process by which impurity is introduced in semiconductors to enhance their conductivity is called **doping**.

23. *n*-type Semiconductor

- Silicon and germanium of group 14 doped with electron rich impurity like phosphorus or arsenic of group 15 is called *n*-type semiconductors.
- Increase in conductivity is due to negatively charged electron.

24. *p*-type Semiconductor Silicon or germanium of group 14 doped with electron deficit impurities like B, Al or Ga of group 13 is called *p*-type semiconductor.

25. Applications of *n*-type and *p*-type Semiconductors

- Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components.
- Diode is a combination of *n*-type and *p*-type semiconductors and used as a rectifier.
- *n-p-n* and *p-n-p* type of transistors are used to detect or amplify radio or audio signals.
- A large variety of solid state materials have been prepared by combination of groups 13 and 15 or 12 and 16 to stimulate average valence of four as in Ge or Si.
- Typical compounds of group 13-15 are InSb, AlP and GaAs. The examples of group 12-16 compounds are CdS, CdSe and HgTe.

26. Magnetic Properties Motions of electron generates magnetic field. It behaves like a tiny bar magnet and possess magnetic moment. Magnitude of this magnetic moment is very small and its unit is **Bohr magneton** μ_B, which is equal to 9.27×10^{-24} A m^2.

On the basis of magnetic properties, substances can be classified into five categories :

27. Paramagnetic Substances Paramagnetic substances are weakly attracted by the external magnetic field and this property is called **paramagnetism**. These are magnetised in a magnetic field in the same direction and they lose their magnetism in the absence of magnetic field. They have one or more unpaired electrons, e.g. O_2, Fe^{3+}, Cr^{3+}, Cu^{2+}, etc.

28. Diamagnetic Substances Diamagnetic substances are weakly repelled by an external magnetic field and this property is called **diamagnetism.** These are weakly magnetised in a magnetic field in opposite direction. Such substances possesses all the paired electrons. e.g. NaCl, H_2O, TiO_2, C_6H_6, etc.

29. Ferromagnetic Substances Ferromagnetic substances are strongly attracted by the external magnetic field and this property is called **ferromagnetism.** These substances can be permanently magnetised. When such a substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced. e.g. Fe, Co, Ni, Gd, CrO_2, etc.

30. Anti-ferromagnetic These substances have domain structure similar to ferromagnetic substances but almost half number of domains is oppositely oriented and thus cancel out each others magnetic moment. e.g. MnO.

31. Ferrimagnetic Substances In ferrimagnetic substances, the magnetic moments of the domains are aligned in parallel and antiparallel directions in unequal number, the net magnetic moment is small. Thus, ferrimagnetic substances are weakly attracted by magnetic field than ferromagnetic substances and this property is called **ferrimagnetism.** They also lose ferrimagnetism on heating and become paramagnetic. e.g. Fe_3O_4 and ferrites like $ZnFe_2O_4$ and $MgFe_2O_4$.