The Solid State

General characteristics of solid state:

- Definite mass, volume and shape
- Short intermolecular distances
- Strong intermolecular forces
- Fixed lattice positions of the constituent particles
- Incompressibility and rigidity

Classification of the solid state:

- Crystalline
- Amorphous (sometimes called pseudo solids or super-cooled liquids)

Differences between the crystalline and amorphous solids

Crystalline	Amorphous
Have definite characteristic geometrical shape	Have irregular shape
Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
When cut with a sharp edged tool, the newly generated pieces are plain and smooth	When cut with a sharp edged tool, the newly generated pieces are with irregular surfaces
Have definite and characteristic heat of fusion	Do not have definite heat of fusion
Are true solids	Are pseudo solids
Anisotropic in nature	Isotropic in nature
Have long-range order	Have only short-range order

Classification of crystalline solids (On the basis of the nature of intermolecular forces)

Molecular solids

- Non-polar molecular solids →These consist either atoms or the molecules formed by non-polar covalent bonds. Example: H_2, Cl_2, I_2

- Polar molecular solids → The molecules ion these types of solids are held together by strong dipole-dipole interactions. Example: Solid SO_2, solid NH_3

- Hydrogen-bonded molecular solids → The molecules of such solids contain polar covalent bonds between H and f, O or N atoms. Example: Ice (H_2O)

Ionic solids

Ions are the constituent particles; e.g., NaCl, KNO_3

Metallic solids

Each metal atom is surrounded by electrons; e.g., Fe, Cu

Covalent or network solids

Formed by covalent bonds; e.g., diamond, silicon carbide

Crystal lattice: A regular three-dimensional arrangement of points in space.

- There are 14 Bravais lattices

  Unit cells: There are two categories of unit cells –

- **Primitive unit cells:** There are seven types of primitive unit cells –

- Cubic ($a = b = c$, $\alpha = \beta = \gamma = 90°$); e.g., NaCl

- Tetragonal ($a = b \neq c$, $\alpha = \beta = \gamma = 90°$); e.g., $CaSO_4$

- Orthorhombic ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$); e.g., KNO_3

- Hexagonal ($a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$); e.g., ZnO

- Rhombohedral or Trigonal ($a = b = c$, $\alpha = \beta = \gamma \neq 90°$); e.g., $CaCO_3$

- Monoclinic ($a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 120°$)

- Triclinic ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$); e.g., $Na_2SO_4.10H_2O$

- **Centred unit cells:** There are three types of centred unit cells –

- Body-centred unit cells: Contain one constituent particle at its body centre along with the ones present at corners

- Face-centred unit cells: Contain one constituent particle at the centre of each face along with the ones present at corners

- End-centred unit cells: Contain one constituent particle at the centre of any two faces along with the ones present at corners

Number of atoms in a unit cell:

- Total number of atoms in one primitive cubic unit cell = 1
- Total number of atoms in one body-centred cubic unit cell = 2
- Total number of atoms in one face-centred cubic unit cell = 4

Close-packed structures:

- **Coordination number:** The number of the nearest neighbours of a particle
- **Packing efficiency:** The percentage of total space filled by the particles

Close-Packing in One dimension

Only one way of arrangement, i.e., the particles are arranged in a row, touching each other

Close-Packing in Two Dimensions

Square close-packing in two dimensions

Close-Packing in Three Dimensions

Three-dimensional close-packing is obtained by stacking two-dimensional layers (square close-packed or hexagonal close-packed) one above the other.
- There are two highly efficient lattices of close-packing –
- Hexagonal close-packed (*hcp*)
- Cubic close-packed (*ccp*) [also called face-centred cubic (*fcc*) lattice]
- In *hcp* and *ccp,* 74% space is filled, i.e., packing efficiency = 74%.
  The remaining space is present in the form of voids.

There are two types of voids –

- Octahedral voids
- Tetrahedral voids

The packings other than *hcp* and *ccp* are not close packings as they have less packing efficiency.

- Packing efficiency in bcc = 68%

- Packing efficiency in simple cubic lattice = 52.4%

Number of octahedral voids = Number of close-packed particles
Number of tetrahedral voids = 2 × Number of close-packed particles
In ionic solids, the bigger ions (usually anions) form the close-packed structure and the smaller ions (usually cations) occupy the voids.

The fraction of the octahedral or tetrahedral voids that are occupied depends on the chemical formula of the compound.

Packing Efficiency

Percentage of total space filled by particles

packing efficiency $= \dfrac{\text{Volume of one particle}}{\text{Volume of cubic unit cell}} \times 100\%$

Calculations involving dimensions of unit cells:

Density of a unit cell $= \dfrac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$

$$\Rightarrow d = \dfrac{zM}{a^3 N_A}$$

Where,
$d \rightarrow$ Density
$z \rightarrow$ Number of atoms present in one unit cell
$M \rightarrow$ Molar mass
$a \rightarrow$ Edge length
$N_A \rightarrow$ Avogadro's number

Imperfections in solids:

- **Line defects**

    -These arise due to irregularities in the arrangement of constituent particles in entire rows of a lattice point

- **Point defects**

   -These arise due to irregularities in the arrangement of constituent particles around a point or an atom
   -There are three types of point defects: Stoichiometric, Impurity and Non-stoichiometric

    Stoichiometric defects (intrinsic or thermodynamic defects)

- Vacancy defect

    -Developed when a substance is heated
    -Decreases the density of the substance

- Interstitial defect

    -Increases the density of the substance
- In ionic solids, the vacancy and interstitial defects exist as Frenkel and Schottky defects.

-Frenkel defect (also called dislocation defect): It occurs when there is a large difference in the size of ions.
-Schottky defect: It is a vacancy defect and it decreases the density of the substance.

Impurity defects:

These defects arise when foreign atoms are present at the lattice site (in place of the host atoms).

Non-stoichiometric defects:

- Metal excess defect
  -Metal excess defect due to anionic vacancies
  -Metal excess defect due to the presence of extra cations

- Metal deficiency defect: Occurs when the metals show variable valency, i.e., the transition metals

Classification of solids on the bases of conductivities:

- Conductors
- Insulators
- Semiconductors
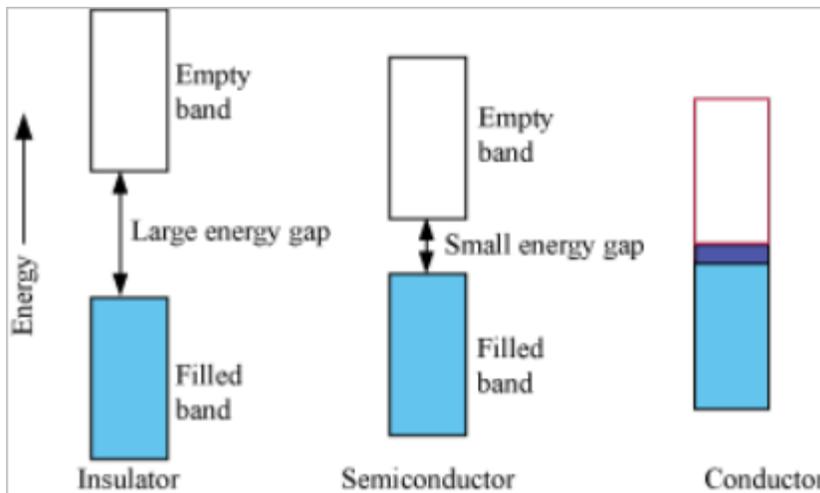
Doping: Adding an appropriate amount of suitable impurity to increase conductivity

- ***n*-type semiconductor**

  -Doped with electron-rich impurities

- ***p*-type semiconductor**

-Doped with electron-deficient impurities

- Semiconductors are widely used in electronic industries.

  Magnetic properties:
  Magnetic properties of substances originate because each electron in an atom behaves like a tiny magnet.

  -Classification of substances on the basis of magnetic properties:

- Paramagnetic: e.g., O_2
- Diamagnetic: e.g., H_2O
- Ferromagnetic: e.g., CrO_2
- Anti-ferromagnetic: e.g., MnO
- Ferrimagnetic: e.g., Fe_3O_4
  Ferromagnetic substances can be made permanent magnets.
  These magnetic properties are used in audio, video and other recording devices.