

**XII**  
**Chemistry**  
**Ch. 1: The Solid State**  
**Points to remember**

1. Solid: Solid is a state of matter in which the constituting particles are arranged very closely. The constituent particles can be atoms, molecules or ions.
2. Properties of solids:
  - a. They have definite mass, volume and shape.
  - b. Intermolecular distances are short and hence the intermolecular forces are strong.
  - c. Their constituent particles have fixed positions and can only oscillate about their mean positions.
  - d. They are incompressible and rigid.
3. Classification of on the basis of the arrangement of constituent particles:
  - a. Crystalline solids: The arrangement of constituent particles is a regular orderly arrangement. Example: iron, copper, diamond, graphite
  - b. Amorphous solids: The arrangement of constituent particles is an irregular arrangement. Example: Glass, plastics, rubber
4. Properties of crystalline solids:
  - a. They have a definite characteristic geometrical shape
  - b. They have a long range order.
  - c. They have a sharp melting point.
  - d. They are anisotropic in nature i.e. their physical properties show different values when measured along different directions in the same crystal.
  - e. When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth.
  - f. They have a definite and characteristic heat of fusion
  - g. They are called true solids
5. Polymorphic forms or polymorphs: The different crystalline forms of a substance are known as polymorphic forms or polymorphs. For example: graphite and diamond.
6. Types of crystalline solids:

Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical nature	Electrical conductivity	Melting point
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Molecular solids	Molecules					
1. Non polar		Dispersion or London forces	Ar, CCl <sub>4</sub> , H <sub>2</sub> , I <sub>2</sub> , CO <sub>2</sub>	Soft	Insulator	Very low
2. Polar		Dipole-dipole interactions	HCl, solid SO <sub>2</sub> , solid NH <sub>3</sub>	Soft	Insulator	Low
3. Hydrogen bonded		Hydrogen bonding	H <sub>2</sub> O (ice)	Hard	Insulator	Low
Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF <sub>2</sub>	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
Covalent or network solids	Atoms	Covalent bonding	SiO <sub>2</sub> (quartz), SiC, C (diamond), AlN  C(graphite)	Hard  Soft	Insulators  Conductor (exception)	Very high

### 7. Characteristics of amorphous solids:

- a. They have an irregular shape.
  - b. They have a short range order.
  - c. They gradually soften over a range of temperature
  - d. They are isotropic in nature i.e. their physical properties are the same in all directions.
  - e. When cut with a sharp edged tool, they cut into two pieces with irregular surfaces.
  - f. They do not have definite heat of fusion
  - g. They are called pseudo solids or super cooled liquids. This is because they have a tendency to flow, though very slowly.
8. Crystal lattice: A regular ordered arrangement of constituent particles in three dimensions is called crystal lattice.
9. Lattice points or lattice sites: The fixed positions on which the constituent particles are present are called lattice points or lattice sites. A group of lattice points which when repeated over and over again in 3 dimensions give the complete crystal lattice.
10. Unit cell: The unit cell is defined as the smallest repeating unit in space lattice which when repeated over and over again generates the complete crystal lattice. The crystal can consist of an infinite number of unit cells.
11. Parameters which characterize a unit cell:
- a. Dimensions of the unit cell along the three edges,  $a$ ,  $b$  and  $c$ : These edges may or may not be mutually perpendicular.
  - b. Inclination of the edges to each other: This is denoted by the angle between the edges  $\alpha$ ,  $\beta$ , and  $\gamma$  respectively.  $\alpha$  is the angle between the edges  $b$  and  $c$ ,  $\beta$  is the angle between the edges  $a$  and  $c$ , and  $\gamma$  is the angle between  $a$  and  $b$ .
12. Seven crystal systems:
- a. Cubic:  $\alpha = \beta = \gamma = 90^\circ$ ,  $a = b = c$
  - b. Tetragonal:  $\alpha = \beta = \gamma = 90^\circ$ ;  $a = b \neq c$
  - c. Orthorhombic:  $\alpha = \beta = \gamma = 90^\circ$ ;  $a \neq b \neq c$
  - d. Monoclinic:  $\alpha = \gamma = 90^\circ$ ,  $\beta \neq 90^\circ$ ;  $a \neq b \neq c$
  - e. Hexagonal:  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ;  $a = b \neq c$
  - f. Rhombohedral or trigonal:  $\alpha = \beta = \gamma \neq 90^\circ$ ;  $a = b = c$
  - g. Triclinic:  $\alpha \neq \beta \neq \gamma \neq 90^\circ$ ;  $a \neq b \neq c$
13. Types of unit cells:
- a. Primitive or simple unit cells have constituent particles only at its corners.

- b. Centred unit cells are those unit cells in which one or more constituent particles are present at positions in addition to those present at the corners.

The centred unit cells are of three types:

- i. Face centred unit cell: A face centred unit cell consists of one constituent particle present at the centre of each face in addition to those present at the corners.
- ii. Body centred unit cell: A body centred unit cell consists of a one constituent particle is present at its body centre in addition to those present at the corners.
- iii. End centred unit cell: An end centred unit cells consists of one constituent particle present at the centre of any two opposite faces in addition to those present at the corners.

14. Number of particles at different lattice positions:

- a. Corner: If an atom is present at any one corner, it is shared by eight unit cells. So, only one eighth of an atom actually belongs to the unit cell.
- b. Face centre: If an atom is present at the centre of the face, it is shared by two unit cells. So, only half of the atom actually belongs to the unit cell.
- c. Body centre: If an atom is present at the body centre, it is not shared by any other unit cell. So, that one atom completely belongs to the same unit cell.
- d. End centre: If an atom is present at the edge centre, it is shared by four unit cells. So, only one fourth of an atom belongs to the unit cell.

15. Number of atoms in different unit cells:

- a. Primitive unit cell: 1 atom
- b. Face centred unit cell: 3 atoms
- c. Body centred unit cell: 2 atoms

16. Coordination number is the number of nearest neighbours of a particle.

17. Close packed structures:

- a. Close packing in one dimension: Each sphere is in contact with two of its neighbours. Coordination number is two.
- b. Close packing in two dimensions: It is generated by stacking the rows of close packed spheres in two ways:
  - i. Square close packing: When the spheres of the second row are placed exactly above those of the first row. This way the spheres are aligned horizontally as well as vertically. The arrangement is AAA type. Coordination number is 4.
  - ii. Hexagonal close packing: When the spheres of the second row are placed above the first one in a staggered manner in such a

- way that its spheres fit in the depression of the first row. The arrangement is ABAB type. Coordination number is 6.
- c. Close packing in three dimensions: They can be obtained by stacking the two dimensional layers one above the other. It can be obtained in two ways:
    - i. Three dimensional close packing from two dimensional square close packed layers: Here, The spheres of the upper layer are placed exactly over the first layer such the spheres of the layers are perfectly aligned horizontally and vertically. It has a AAAA.. type pattern. The lattice is simple cubic lattice.
    - ii. Three dimensional close packing from two dimensional hexagonal close packed layers: There are two steps involved as:
      - i. Placing the second layer over the first layer: if a two dimensional layer is considered as A, the second layer which is placed above the first layer in such a way that the spheres of the second layer (considered as B) are placed in the depressions of the first layer. This gives rise to two types of voids: tetrahedral voids and octahedral voids.
      - ii. Placing the third layer over the third layer: There are two possibilities:
        - a. Covering the tetrahedral voids: Here, tetrahedral voids of the second layer may be covered by the spheres of the third layer. It gives rise to ABABAB... type pattern. The three dimensional structure is called hexagonal close packed structure. Coordination number is 12. Example: Mg, Zn
        - b. Covering the octahedral voids: Here, octahedral voids of the second layer may be covered by the spheres of the third layer. It gives rise to ABCABCABC... type pattern. The three dimensional structure is called cubic close packed structure or face centred cubic structure. Coordination number is 12. Example: Cu, Ag

#### 18. Types of voids:

- a. Tetrahedral voids: This type of void is formed at the centre when four spheres are joined in the form of a tetrahedron.
- b. Octahedral void: This type of void is surrounded by six spheres.

19. In hcp or ccp arrangement, octahedral and tetrahedral voids are present. The number of octahedral voids present in a lattice is equal to the number of close packed particles. The number of tetrahedral voids is twice the number of octahedral voids.

- Example: If the number of close packed particles =  $n$   
 Number of particles present in octahedral voids =  $n$   
 Number of particles present in tetrahedral voids =  $2n$

20. Packing efficiency is the percentage of total space occupied by constituent particles (atoms, molecules or ions)

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

- Packing efficiency for face centred unit cell = 74%
- Packing efficiency for body centred cubic unit cell = 68%
- Packing efficiency for simple cubic unit cell = 52.4%

21. Radius ratio in an octahedral void: For an atom to occupy an octahedral void, its radius must be 0.414 times the radius of the sphere.

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

22. Radius ratio for tetrahedral void: For an atom to occupy a tetrahedral void, its radius must be 0.225 times the radius of the sphere.

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

23. Density of a unit cell is same as the density of the substance.

24. Relationship between radius of constituent particle (r) and edge length (a):

- Simple cubic unit cell:  $a = 2r$
- Face centred unit cell:  $a = 2\sqrt{2}r$
- Body centred unit cell:  $a = \frac{4r}{\sqrt{3}}$

25. Volume of a unit cell = (edge length)<sup>3</sup> = a<sup>3</sup>

- Simple cubic unit cell: Volume =  $(2r)^3$
- Face centred unit cell: Volume =  $(2\sqrt{2}r)^3$
- Body centred unit cell: Volume =  $\left(\frac{4r}{\sqrt{3}}\right)^3$

26. Number of atoms in a unit cell (z):

- Simple cubic unit cell:  $z = 1$
- Face centred unit cell:  $z = 4$
- Body centred unit cell:  $z = 2$

27. Density of unit cell:

$$\text{Density of unit cell} = \frac{zM}{a^3 \cdot N_A}$$

28. Crystal defects are basically irregularities in the arrangement of constituent particles.

29. Defects are of two types:

- Point defects - Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.
- Line defects - Line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points.

30. Point defects are of three types:

- Stoichiometric or intrinsic or thermodynamic defects: These are the point defects that do not disturb the stoichiometry of the solid.
- Non - stoichiometric defects: These are the point defects that disturb the stoichiometry of the solid.
- Impurity defects: These are the defects in ionic solids due to the presence of impurities present in them.

31. Stoichiometric defects for non- ionic solids are of two types:

Vacancy defect	Interstitial defect
A crystal is said to have vacancy defect when some of the lattice sites are vacant.	A crystal is said to have interstitial defect when some constituent particles (atoms or molecules) occupy an interstitial site.
This results in decrease in density of the substance.	This results in increase in density of the substance.

32. Stoichiometric defects for ionic solids are of two types:

Schottky defect	Frenkel or dislocation defect
In this defect equal number of cations and anions are missing.	In this defect, the smaller ion (usually cation) is dislocated from its normal site to an interstitial site.
It is basically a vacancy defect in ionic solids.	It creates a vacancy defect at its original site and an interstitial defect at its new location.
It decreases the density of a solid	It does not change the density of the solid
Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes.	Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions.
For example: NaCl, KCl, CsCl and AgBr	For example: ZnS, AgCl, AgBr and AgI

33. Non-stoichiometric defects are of two types:

- a. Metal excess – This type of defect is due to excess of metal cations. These may be due to:
  - i. Anionic vacancies: A compound may have an extra metal ion if the negative ion is absent from its lattice site. This empty lattice site is called a hole. To maintain electrical neutrality this site is occupied by an electron. The hole occupied by an electron is called f-centre or Farbenzenter centre . F- centre is responsible for the colour of the compound.
  - ii. Presence of extra cations: A compound is said to have extra cations if a cation is present in the interstitial site. An electron is present in the interstitial site to maintain the electrical neutrality.
- b. Metal deficiency: This defect arises because of absence of metal ions from its lattice sites. The electrical neutrality is maintained by an adjacent ion having a higher positive charge.

34. Solids can also be classified into three types based on their electrical conductivities:

- a. Conductors-The solids with conductivities ranging between  $10^4$  to  $10^7 \text{ ohm}^{-1}\text{m}^{-1}$  are called conductors.
- b. Insulators - These are the solids with very low conductivities ranging between  $10^{-20}$  to  $10^{-10} \text{ ohm}^{-1}\text{m}^{-1}$ .
- a. Semi- conductors - These are the solids with conductivities in the intermediate range from  $10^{-6}$  to  $10^4 \text{ ohm}^{-1}\text{m}^{-1}$ .

35. Band theory – A metal is characterized by a band structure. The highest filled band is called valence band and the lowest unoccupied band is called conduction band. The gap between the two bands is called forbidden band.

- a. In case of conductors, the valence band and conduction band overlap
- b. In case of insulators, the forbidden gap is very large and the electrons are unable to excite to the conduction band.
- c. In case of semiconductors, forbidden gap is small. Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band.

36. Types of semiconductors:

- a. Intrinsic: These are those semiconductors in which the forbidden gap is small. Only some electrons may jump to conduction band and show some conductivity. They have very low electrical conductivity. Example: Silicon, germanium
- b. Extrinsic: When an appropriate impurity is added to an intrinsic semiconductor. Their electrical conductivity is high.



37. Doping: The process of adding an appropriate amount of suitable impurity to increase the conductivity of semiconductors.

38. Types of extrinsic semi conductors:

n-type semiconductors	p -type semiconductors
They are formed when silicon is doped with electron rich impurity like group 15 elements.	They are formed when silicon is doped with electron deficient impurity like group 13 elements.
The increase in conductivity is due to the negatively charged electrons.	The increase in conductivity is due to the positively charged holes.

39. Diode: It is a combination of n-type and p-type semiconductors and is used as a rectifier.

40. Transistors: They are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. npn and pnp type of transistors are used to detect or amplify radio or audio signals.

41. 12- 16 compounds – These compounds are formed by the combination of group 12 and group 16 compounds. They possess an average valency of 4. Example: ZnS, CdS, CdSe and HgTe

42. 13- 15 compounds – These compounds are formed by the combination of group 13 and group 15 compounds. They possess an average valency of 4. Example: InSb, AlP and GaAs

43. Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis.

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

- Paramagnetic: These are those substances which are weakly attracted by the magnetic field. It is due to presence of one or more unpaired electrons.
- Diamagnetic: Diamagnetic substances are weakly repelled by a magnetic field. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons.

- c. Ferromagnetic: These are those substances which are attracted very strongly by a magnetic field.
- d. Antiferromagnetic: They have equal number of parallel and anti parallel magnetic dipoles resulting in a zero net dipole moment.
- e. Ferrimagnetic: They have unequal number of parallel and anti parallel magnetic dipoles resulting in a net dipole moment.