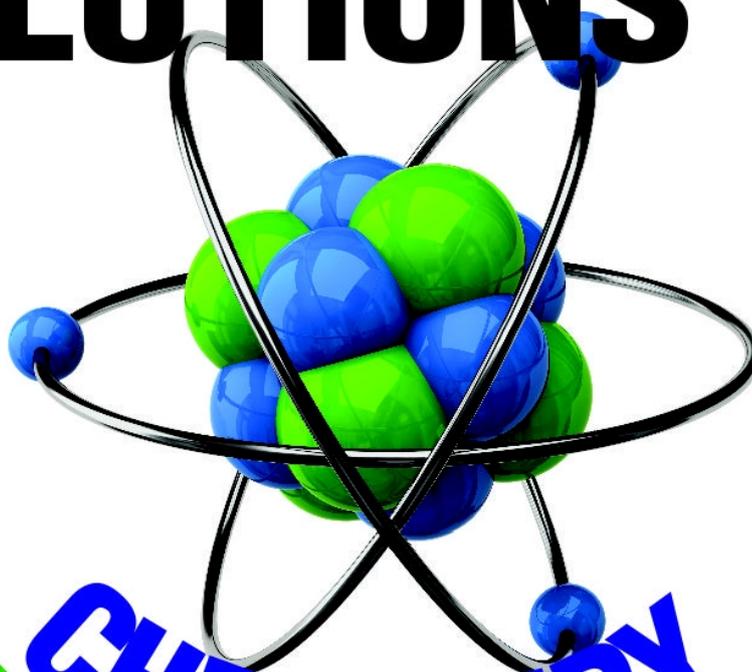


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CHAPTER

1

THE SOLID STATE

KEY CONCEPTS

- Solids are substances which have fixed shape and volume. They are characterised by rigidity, incompressibility, slow diffusion and mechanical strength. They are classified as:
 - Crystalline solids
 - Amorphous solids
- The crystalline solids are further classified as:
 - Metallic solids
 - Ionic solids
 - Covalent solids
 - Molecular solids
- A regular three dimensional arrangement of points in space is called a **space lattice** or **crystal lattice**. There are only 14 three-dimensional lattices known as **Bravais lattices**. The basic difference between the 14 Bravais lattices are the angles between the faces and the relative proportion of the sides.
- A unit cell is the smallest unit of the crystal which when repeated again and again gives the crystal of the given substance.
- There are three types of unit cells based on the cube. These are:
 - Primitive** or **simple cube** which has one constituent at each corner.
 - Body-centred cube** in which one constituent at the centre of the cube as well as one at each corner.
 - Face-centred cube** in which there is one constituent at the centre of each face as well as one at each corner.
- A pure metal in the solid crystalline state is composed of atoms that are identical in shape and size. The identical spheres can be packed in a number of ways.
 - The number of nearest neighbours of an atom, ion or a molecule is called its **coordination number**.
 - In the *hcp* and *ccp* structures, about 74 percent of the available space is occupied by the spheres. In *bcc* arrangement, about 68 percent of the available space is filled up. In simple cubic structures, about 52.4 percent of the available space is occupied by the spheres.
 - The density of the unit cell, $d = \frac{ZM}{a^3 N_A}$
 - Any departure from perfectly ordered arrangement of atoms or ions in crystals is called **imperfection** or **defects**. These are of two types:
 - Point defects
 - Line defects
 - Schottky defects** occurs when a pair of ions of opposite charge, *i.e.*, cations and anions are missing from the ideal lattice. The presence of a large number of schottky defects lowers the density of a crystal, *e.g.*, AgBr.
 - The atoms or ions which occupy the normally vacant interstitial sites in a crystal are known as **interstitials**. It results in increase in density of crystal.
 - Frenkel defects** is a combination of schottky defects and interstitials. It occurs when an ion leaves its position in the lattice and occupies an interstitial site leaving a gap in the crystal.
 - Non-stoichiometric defects** are a large number of inorganic solids in which the ratio of the number of atoms of one kind to the number of atoms of the other kind does not correspond to the ideal whole number ratio. Such compounds are called **non-stoichiometric compounds**.

15. When there is an excess of metal ions in non-stoichiometric compounds, the crystal lattice has vacant anion sites. These sites are occupied by electrons. The anion sites occupied by electrons are called **F-centres**.
16. Based on their electrical conductivity, solids are classified as:
 (a) Conductors
 (b) Insulators
 (c) Semi conductors
17. Pure substances that show conducting behaviour like that of silicon and germanium are called **intrinsic semiconductors**.
18. When solid substances are placed in a magnetic field, they do not show the same behaviour. Depending on their response to magnetic field, the substances are classified as:
- (a) Diamagnetic substances:
 (i) These substances are weakly repelled by a magnetic field.
 (ii) The electrons are paired.
- (b) Paramagnetic substances:
 (i) These substances are weakly attracted by the magnetic field.
 (ii) These substances have permanent magnetic dipoles due to the presence of atoms, molecules or ions containing unpaired electrons.
19. Substances having unpaired electrons are classified as:
 (a) Ferromagnetic substances ↑↑↑↑↑↑↑↑
 (b) Antiferromagnetic substances ↑↓↑↓↑↓↑↓
 (c) Ferrimagnetic substances ↑↑↓↑↑↓↑↓

NCERT Intext Questions

1.1. Why are solids rigid?

Ans. The constituent particles in solids have fixed positions and can oscillate about their mean positions. Hence, they are rigid.

1.2. Why do solids have a definite volume?

Ans. The constituent particles of a solid have fixed positions and are not free to move about, i.e., they possess rigidity. That is why they have definite volume.

1.3. Classify the following as amorphous or crystalline solids: Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper

Ans. Crystalline solids: Benzoic acid, potassium nitrate, copper

Amorphous solids: Polyurethane, teflon, cellophane, polyvinylchloride, fibre glass

1.4. Why is glass considered a super cooled liquid?

Ans. Glass is an amorphous solid. Like liquids, it has a tendency to flow, though very slowly. This can be seen from the glass panes of windows or doors of very old buildings which are thicker at the bottom than at the top. Therefore, glass is considered as a super cooled liquid.

1.5. Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property?

Ans. As the solid has same value of refractive index along all directions, it is isotropic in nature and hence amorphous. Being amorphous solid, it will not show a clean cleavage and when cut, it will break into pieces with irregular surfaces.

1.6. Classify the following solids in different categories based on the nature of intermolecular forces operating in them:

Potassium sulphate, tin, benzene, urea, ammonia, water, zinc sulphide, graphite, rubidium, argon, silicon carbide

Ans. Potassium sulphate = Ionic

Tin = Metallic

Benzene = Molecular (non-polar)

Urea = Molecular (polar)

Ammonia = Molecular (H-bonded)

Water = Molecular (H-bonded)

Zinc sulphide = Ionic

Graphite = Covalent

Rubidium = Metallic

Argon = Molecular (non-polar)

Silicon Carbide = Covalent

1.7. Solid A is a very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?

Ans. It is a covalent or network solid.

1.8. Ionic solids conduct electricity in molten state but not in solid state. Explain

Ans. In solid state, the ions cannot move, they are held by strong electrostatic forces of attraction. So, ionic solids do not conduct electricity in solid state. However, in the molten state, they dissociate to give free ions and hence conduct electricity.

1.9. What type of solids are electrical conductors, malleable and ductile?

Ans. Metallic solids

1.10. Give the significance of a 'lattice point'.

Ans. Each lattice point represents one constituent particle of the solid. This constituent particle may be an atom, a molecule or an ion.

1.11. Name the parameters that characterise a unit cell.

Ans. A unit cell is characterized by following parameters :

- (i) the dimensions of unit cell along three edges: a, b and c.
- (ii) the angles between the edges: α (between b and c); β (between a and c) and γ (between a and b)

1.12. Distinguish between

- (i) Hexagonal and monoclinic unit cells
- (ii) Face-centred and end-centred unit cells.

<i>Ans.</i> (i) Hexagonal unit cell	Monoclinic unit cell
$a = b \neq c$	$a \neq b \neq c$
$\alpha = \beta = 90^\circ$	$\alpha = \gamma = 90^\circ$
$\gamma = 120^\circ$	$\beta \neq 90^\circ$

(ii) Face-centred unit cell	End-centred unit cell
has particles at the corners and one particle at the centre of each face.	has particles at the corners and one particle each at the centre of any two opposite faces.

1.13. Explain how much portion of an atom located at (i) corner and (ii) bodycentre of a cubic unit cell is part of its neighbouring unit cell.

Ans. (i) An atom at the corner is shared by eight adjacent unit cells. Hence, portion of the atom at the corner that belongs to one unit cell = $\frac{1}{8}$

(ii) An atom at the body centre is not shared by any other unit cell. Hence, it belongs fully to unit cell.

1.14. What is the two dimensional coordination number of a molecule in square close-packed layer?

Ans. In 2D, square close packed layer, an atom touches 4 nearest neighbouring atoms. Hence, its CN = 4

1.15. A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

Ans. No. of atoms in close packing = 0.5 mol
 $= 0.5 \times 6.022 \times 10^{23}$
 $= 3.011 \times 10^{23}$

No. of octahedral voids
 $= \text{No. of atoms in packing}$
 $= 3.011 \times 10^{23}$

No. of tetrahedral voids
 $= 2 \times \text{No. of atoms in packing}$
 $= 2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$

Total no. of voids
 $= 3.011 \times 10^{23} + 6.022 \times 10^{23}$
 $= 9.033 \times 10^{23}$

1.16. A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

Ans. Atoms of N form ccp, therefore, if the lattice points are n, then

$$\begin{aligned} \text{No. of atoms of N} &= n \\ \text{No. of oct voids} &= n \end{aligned}$$

$$\text{No. of td voids} = 2n = 2 \times \frac{1n}{3} = \frac{2n}{3}$$

\therefore Formula of compound is :

$$M : N$$

$$\frac{2}{3}n : n$$

$$2n : 3n$$

$$2 : 3$$

i.e., M_2N_3

1.17. Which of the following lattices has the highest packing efficiency (i) simple cubic (ii) body-centred cubic and (iii) hexagonal close-packed lattice?

Ans. Packing efficiency of :

$$\text{Simple cubic} = 52.4\%$$

$$bcc = 68\%$$

$$hcp = 74\%$$

\therefore *hcp* lattice has the highest packing efficiency.

1.18. An element with molar mass $2.7 \times 10^{-2} \text{ kg mol}^{-1}$ forms a cubic unit cell with edge length 405 pm. If its density is $2.7 \times 10^3 \text{ kg m}^{-3}$, what is the nature of the cubic unit cell?

Ans.

$$d = \frac{Z \times M}{a^3 N_A}$$

Given: Density, $d = 2.7 \times 10^3 \text{ kg m}^{-3}$

$$a = 405 \text{ pm}$$

$$= 405 \times 10^{-12} \text{ m}$$

$$M = 2.7 \times 10^{-2} \text{ kg mol}^{-1}$$

$$\Rightarrow Z = \frac{d a^3 N_A}{M}$$

$$= \frac{(2.7 \times 10^3)(405 \times 10^{-12})^3 (6.022 \times 10^{23})}{2.7 \times 10^{-2}}$$

$$= 3.99 \simeq 4$$

Therefore, it is a *fcc* unit cell.

1.19. What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?

Ans. When a solid is heated, vacancy defect is produced in the crystal. On heating, some atoms or ions leave the lattice site completely, i.e., lattice sites become vacant. As a result of this defect, density of the substances decreases.

1.20. What type of stoichiometric defect is shown by:

(i) ZnS

(ii) AgBr

Ans. (i) ZnS shows Frenkel defect

(ii) AgBr shows Frenkel as well as Schottky defect.

1.21. Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.

Ans. Let us take an example NaCl doped with SrCl_2 impurity when SrCl_2 is added to NaCl solid as an impurity, two Na^+ ions will be replaced and one of their sites will be occupied by Sr^{2+} while the other will remain vacant. Thus, we can say that when a cation of higher valence is added as an impurity to an ionic solid, two or more cations of lower valency are replaced by a cation of higher valency to maintain electrical neutrality. Hence, some cationic vacancies are created.

1.22. Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.

Ans. Let us take an example of NaCl. When NaCl crystal is heated in presence of Na vapour, some Cl^- ions leave their lattice sites to combine with Na to form NaCl. The e^- s lost by Na to form Na^+ ($\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl}$) then diffuse into the crystal to occupy the anion vacancies. These sites are called F-centres. These e^- s absorb energy from visible light, get excited to higher energy level and when they fall back to ground state, they impart yellow colour to NaCl crystal.

1.23. A group 14 element is to be converted into *n*-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

Ans. Impurity from group 15 should be added to get *n*-type semiconductor.

1.24. What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer.

Ans. Ferromagnetic substances make better permanent magnets. This is because when placed in magnetic field, their domains get oriented in the directions of magnetic field and a strong magnetic field is produced. This ordering of domains persists even when external magnetic field is removed. Hence, the ferromagnetic substance becomes a permanent magnet.

NCERT EXERCISES

1.1 Define the term ‘amorphous’. Give a few examples of amorphous solids.

Sol. Amorphous solids are those substances, in which there is no regular arrangement of its constituent particles, (*i.e.*, ions, atoms or molecules). The arrangement of the constituting particles has only short range order, *i.e.*, a regular and periodically repeating pattern is observed over short distances only, *e.g.*, glass, rubber and plastics.

1.2 What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?

Sol. Glass is made up of SiO_4 tetrahedral units. These constituent particles have short range order only. Quartz is also made up of SiO_4 tetrahedral units. On heating it softens and melts over a wide range of temperature. It is a crystalline solid having long range ordered structure. It has a sharp melting point.

Quartz can be converted into glass by first melting and then rapidly cooling it.

1.3 Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous:

(i) Tetra phosphorus decoxide (P_4O_{10})

(ii) Ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$

(iii) SiC

(iv) I_2

(v) P_4

(vi) Plastics

(vii) Graphite

(viii) Brass

(ix) Rb

(x) LiBr

(xi) Si

Sol.

Ionic	Metallic	Molecular	Network (covalent)	Amorphous
$(\text{NH}_4)_3\text{PO}_4$	Brass	P_4O_{10}	Graphite	Plastics
LiBr	Rb	I_2	SiC	
		P_4	Si	

1.4 (i) What is meant by the term ‘coordination number’?

(ii) What is the coordination number of atom

(a) in a cubic close packed structure?

(b) in a body centred cubic structure?

Sol. (i) The number of nearest neighbours of a particle are called its coordination number.

(ii) (a) 12 (b) 8

1.5 How can you determine the atomic mass of an unknown metal if you know its density and the dimensions of its unit cell? Explain.

Sol. Let the edge length of a unit cell = a

Density = d

Molar mass = M

Volume of the unit cell = a^3

Mass of the unit cell

= No. of atoms in unit cell \times Mass of each atom

= $Z \times m$

Mass of an atom present in the unit cell

$$= m = \frac{M}{N_a}$$

$$\therefore d = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{Z \cdot m}{a^3} = \frac{Z \cdot M}{a^3 N_a}$$

$$\therefore \text{Atomic mass, } M = \frac{d \cdot a^3 \cdot N_a}{Z}$$

1.6 ‘Stability of a crystal is reflected in the magnitude of its melting points’. Comment.

Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

Sol. Higher the melting point, greater are the forces holding the constituent particles together and thus greater is the stability of a crystal. Melting points of given substances are following.

Water = 273 K, Ethyl alcohol = 155.7 K, Diethylether = 156.8 K, Methane = 90.5 K.

The intermolecular forces present in case of water and ethyl alcohol are mainly due to the hydrogen bonding which is responsible for their high melting points. Hydrogen bonding is stronger in case of water than ethyl alcohol and hence water has higher melting point than ethyl alcohol.

Dipole-dipole interactions are present in case of diethylether. The only forces present in case of methane is the weak van der Waal's forces (or London dispersion forces).

1.7 How will you distinguish between the following pairs of terms:

- (i) Cubic close packing and hexagonal close packing?
- (ii) Crystal lattice and unit cell?
- (iii) Tetrahedral void and octahedral void?

Sol. (i) Cubic close packing: When the third layer is placed over the second layer in such a way that the spheres cover the octahedral voids, a layer different from first (*A*) and second (*B*) is produced. If we continue packing in this manner, then a packing is obtained where the spheres in every fourth layer will vertically aligned. This pattern of packing spheres is called *ABCABC.....* pattern or cubic close packing.

Hexagonal close packing: When a third layer is placed over the second layer in such a manner that the spheres cover the tetrahedral void, a three dimensional close packing is obtained where the spheres in every third or alternate layers are vertically aligned. If we continue packing in this manner, then the packing obtained would be called *ABAB.....* pattern or hexagonal close packing.

(ii) **Crystal lattice:** It is a regular arrangement of the constituent particles (*i.e.*, ions, atoms or molecules) of a crystal in three dimensional space.

Unit cell: The smallest three dimensional portion of a complete space lattice which when repeated over and over again in different directions produces the complete crystal lattice is called the unit cell.

(iii) **Tetrahedral void:** A simple triangular void in a crystal is surrounded by four spheres and is called a tetrahedral void.

Octahedral void: A double triangular void is surrounded by six spheres and is called a octahedral void.

1.8 How many lattice points are there is one unit cell of each of the following lattices?

- (i) Face centred cubic
- (ii) Face centred tetragonal
- (iii) Body centred cubic

Sol. Lattice points in face centred cubic

- (i) and face centred tetragonal
- (ii) = 8 (at corners) + 6 (at face centres) = 14

$$\text{Particle per unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Lattice points in body centred cubic

- (iii) = 8 (at corners) + 1 (at body centre) = 9

$$\text{Particles per unit cell} = 8 \times \frac{1}{8} + \frac{1}{1} = 2.$$

1.9 Explain:

- (i) The basis of similarities and differences between metallic and ionic crystals.
- (ii) Ionic solids are hard and brittle.

Sol. (i) Metallic and ionic crystals

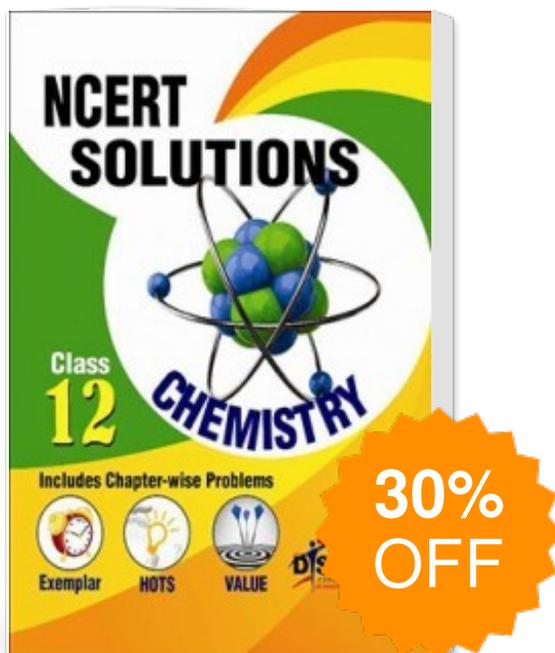
Similarities:

- (a) There is electrostatic force of attraction in both metallic and ionic crystals.
- (b) Both have high melting points.
- (c) Bonds are non-directional in both the cases.

Differences:

- (a) Ionic crystals are bad conductors of electricity in solids state as ions are not free to move. They can conduct electricity only in the molten state or in aqueous solution. Metallic crystals are good conductors of electricity in solid state as electrons are free to move.
- (b) Ionic bond is strong due to strong electrostatic forces of attraction. Metallic bond may be strong or weak depending upon the number of valence electrons and the size of the kernels.
- (ii) Ionic solids are hard and brittle. Ionic solids are hard due to the presence of strong electrostatic forces of attraction. The brittleness in ionic crystals is due to the non-directional bonds in them.

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