SOLID STATE

1.1 General Characteristics of Solid State :

Q. Define solids and why do some substance exist as solids ?

Solution : A solid is defined as that form of matter which possesses rigidity and hence possesses a definite shape and a definite volume. Some substance exists as solids because of the following two reasons :

(i) Intermolecular forces. These are the forces existing among the constituent particles which try to keep the constituent particles close together.

(ii) Thermal energy. This is the energy possessed by the constituent particles due to temperature. This energy tries to keep the constituent particles apart as it tends to make them move faster.

Q. What are the general characteristics of solid state ?

Solution : (i) They have definite mass, volume and shape.

(ii) Intermolecular distances are short.

(iii) Intermolecular forces are strong.

(iv) Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.

(v) They are incompressible and rigid.

Q. At sufficiently low temperature which forces dominate between particles.

Solution : At sufficiently low temperature, the thermal energy is low and intermolecular forces bring them so close that they cling to one another and occupy fixed positions.

1.2 Amorphous and Crystalline Solids :

Q. What are the types of solids depending on nature of order present in the arrangement of their constituent particles ?

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

Q. Write down the different between crystalline solids and amorphous solids.

Solution : Amorphous solids or Pseudo Solids / **Crystalline solids**

	Amorphous solids or Pseudo Solids	Crystalline solids
(i)	There is random arrangement of atoms molecules or ions	There is a fixed arrangement of atoms, molecules or ions.
(ii)	They are of short range order	They are of long range order
(iii)	They are isotropic i.e., same physical properties in all the directions. When cut with a knife or otherwise break with irregular surface and do not show clean cleavage	They are anisotropic i.e., different physical properties in different directions.
(iv)	Do not possess sharp melting point	Possess sharp melting point.
(v)	Also known as super cooled liquids	These are true solids.
(vi)	Are not very rigid, these can be distorted by bending or by applying external forces	Are rigid and there shape is not distorted by mild distorting forces.
(vii)	Examples of Amorphous solid are Starch, Protein, Glass, Plastics, Rubber etc.	Almost all metals have fine granular shapes.

Q. Why are solids rigid ?

Solution : In a solid, the constituent particles are very closely packed. Hence, the forces of attraction among these particles are very strong. Moreover, the constituent particles in solids have fixed positions and can only oscillate about their mean positions. Hence, they are rigid.

Q. Why do solids have a definite volume ?

Solution : 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 a definite volume.

Q. Classify the following as amorphous or crystalline solids :

Polyurethane, napthalene, benzoic acid, teflon, potassium nitrate, cellophone, polyvinly chloride, fibre glass, copper.

Solution : Amorphous solids : Polyurethane, teflon, cellophone, polyvinyl chloride, fibre glass.

Crystalline solids : Benzoic acid, potassium nitrate, copper.

Q. Why is glass considered a super-cooled liquid ?

Solution : Glass is an amorphous solid. Like liquids, it has a tendency to flow, through very slowly. The proof of this fact is that the glass panes in the windows or doors of old buildings are invariably found to be slightly thicker at the bottom that at the top. This is evidently due to the reason that glass flows down very slowly and makes the bottom portion slightly thicker.

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

Solution : As the solid has same value of refractive index along all directions, this means that it is isotropic and hence amorphous. Being an amorphous solid, it would not show a clean cleavage when cut with a knife. Instead, it would break into pieces with irregular surfaces.

1.3   Classification of Crystalline Solids :

Q. How the crystalline solids are classified on the basis of nature of intermolecular forces operating in them.

Solution :

Type of crystal	Structural units at the lattice sites	Bonding force	Example
Ionic	Ions	Electrostatic, it do not conduct in solid state	CsCl, NaCl, LiBr $(NH_4)_3PO_4$
Covalent	Atoms	Sharing of electron pairs (covalent)	Diamond, Graphite, Asbestos, SiC, Si
Metallic	Metal ions	Electrostatic attraction between metals ions and electrons surrounding the metal ions. Forces of attraction are weaker then the ionic solids. They can conduct in the solid state.	Fe, Cu, Ag, Brass, Rb etc.
Molecular	Molecules	Van der Waals, dipole-dipole, hydrogen bonds.	Ice, solid carbon dioxide (dry ice). P_4O_{10}, I_2, P_4

Q. What are the different catagories to which molecular solids are subdivided.

Solution : (i) Non polar Molecular Solids : They comprise of either atoms, for example, argon and helium or the molecules formed by non polar covalent bonds for example H_2, Cl_2 and I_2. In these solids, the atoms or molecules are held by weak dispersion forces or London forces about which you have learnt in Class XI. These solids are soft and non-conductors of electricity. They have low melting points and are usually in liquid or gaseous state at room temperature and pressure.

(ii) Polar Molecular Solids : The molecules of substances like HCl, SO_2, etc. are formed by polar covalent bonds. The molecules in such solids are held together by relatively stronger dipole-dipole interactions. These solids are soft and non-conductors of electricity. Their melting points are higher than those of non polar molecular solids yet most of these are gases or liquids under room temperature and pressure. Solid SO_2 and solid NH_3 are some example of such solids.

(iii) Hydrogen Bonded Molecular Solids : The molecules of such solids contain polar covalent bonds between H and F, O or N atoms. Strong hydrogen bonding binds molecules of such solids like H_2O (ice). They are non-conductors of electricity. Generally they are volatile liquids or soft solids under room temperature and pressure.

Q. Explain briefly ionic solids.

Solution : Ions are the constituent particles of ionic solids. Such solids are formed by the three dimensional arrangements of cations and anions bound by strong coulombic (electrostatic) forces. These solids are hard and brittle in nature. They have high melting and boiling points. Since the ions are not free to move about, they are electrical insulators in the solid state. However, in the molten state or when dissolved in water, the ions become free to move about and they conduct electricity.

Q. Explain briefly about metallic solids.

Solution : Metals are orderly collection of positive ions surrounded by and held together by a sea of free electrons. These electrons are mobile and are evenly spread out throughout the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons. These free and mobile electrons are responsible for high electrical and thermal conductivity of metals. When an electric field is applied, these electrons flow through the network of positive ions. Similarly, when heat is supplied to one portion of a metal, the thermal energy is uniformly spread throughout by free electrons. Another important characteristic of metals is their lustre and colour in certain cases. This is also due to the presence of free electrons in them. Metals are highly malleable and ductile.

Q. Write a short note about covalent or network solids with examples.

Solution : Crystalline solids of non-metals result from the formation of covalent bonds between adjacent atoms throughout the crystal. They are also called giant molecules. Covalent bonds are strong and directional in nature, therefore atoms are held very strongly at their positions. Such solids are very hard and brittle. They have extremely high melting points and may even decompose before melting. They are insulators and do not conduct electricity. e.g., diamond and silocon carbide are typical examples of such solids. Graphite is soft and a conductor of electricity. Its exceptional properties are due to its typical structure. Carbon atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between different layers and is free to move about. These free electrons make graphite a good conductor of electricity. Different layers can slide one over the other. This makes graphite a soft solid and a good solid lubricant.

Q. 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.

Solution : Potassium sulphate = Ionic, Tin = Metallic, Benzene = Molecular (non-polar), Urea = Molecular (Polar), Ammonia = Molecular (Hydrogen bonded), Water = Molecular (Hydrogen bonded), Zinc sulphide = Ionic, Graphite = Covalent or Network, Rubidium = Metallic, Argon = Molecular (Non-polar), Silicon carbide = Covalent or Network.

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

Solution : Covalent Network Solid like SiO_2 (quartz) or SiC or C (diamond)

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

Solution : In the molten state, ionic solids dissociates to give free ions and hence can conduct electricity. However, in the solid state, as the ions are not free but remain held together by strong electrostatic forces of attraction, they cannot conduct electricity in the solid state.

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

Solution : Metallic solids.

1.4   Crystal Lattices and Unit Cells :

Q. Define crystal lattice and also given the characteristics of a crystal lattice.

Solution : Such a regular arrangement of the constituent particles (i.e., atoms, ions or molecules) of a crystal in a three dimensional space is called crystal lattice or space lattice.

There are only 14 possible three dimensional lattices. These are called **Bravais Lattices**. The following are the 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.

Q. Define unit cell and also write its characteristics.

Solution : Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice. A unit cell is characterised by :

(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, α (between b and c) β (between a and c) and γ (between a and b). Thus, a unit cell is characterised by six parameters a, b, c, α, β and γ.

Q. What are the different types of unit cells or crystal lattices ?

Solution : There are seven types of unit cells :

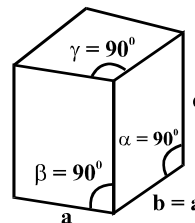**(i) Cubic :** $a = b = c$, $\alpha = \beta = \gamma = 90^0$
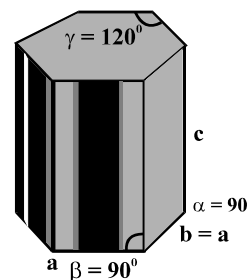
Example : NaCl, Zinc blende, Cu
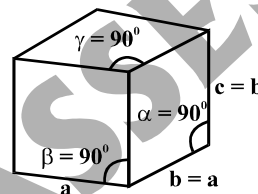
(ii) Tegragonal : $a = b \neq c$, $\alpha = \beta = \gamma = 90^0$,
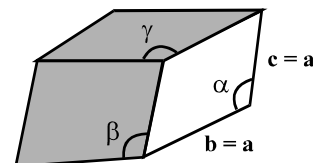
Examples : TiO_2, SnO_2, white Sn, $CaSO_4$

(iii) Hexagonal : $a = b \neq c$, $\alpha = \beta = 90^0$, $\gamma = 120^0$

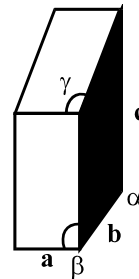**Examples :** Graphite, CdS, ZnO etc.

(iv) Rhombohedral : $a = b = c$, $\alpha = \beta = \gamma \neq 90^0$
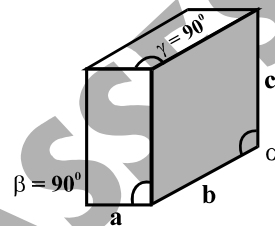
Examples : Calcite ($CaCO_3$), HgS (cinnabar)

(v) Triclinic : $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^0$.

Examples : $CuSO_4.5H_2O$, $K_2Cr_2O_7$, H_3BO_3 etc.

(vi) Monoclinic : $a \neq b \neq c$, $\alpha = \gamma = 90^0$, $\beta \neq 120^0$.

Examples : $Na_2SO_4.10H_2O$, monoclinic sulphur etc.

(vii) Orthorhombic : $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^0$.

Examples : Rhombic Sulphur, KNO_3, $BaSO_4$
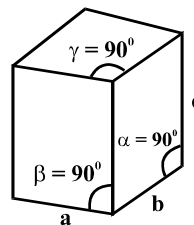
Q. Explain the primitive and centered unit cells.

Solution : Primitive unit cells : When constituent particles are present only on the corner positions of a unit cell, it is called as primitive unit cell.

Centred unit cells : When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. Centred unit cells are of three types;

(i) Body-Centred Unit Cells : Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.

(ii) Face-Centred Unit Cells : Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.

(iii) End-Centred Unit Cells : In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

1.5   Number of Atoms in a Unit Cell :

Q. In simple cubic unit cell, how the atoms of equal sized are packed ?

Solution : In simple cubic, atoms of equal sized are in square closed packing.

Q. In simple cubic unit cell findout the effective atom present in a unit cell.

Solution : Therefore effective number of atoms in one unit cell $(Z_{eff}) = 8 \times \dfrac{1}{8} = 1$.

Q. What is the relation between edge length of simple cube (a) and size of an atom (r).

Solution : Relation between edge length 'a' and size of atom 'r' : a = 2r.

Q. What is the coordination number in simple cube ?

Solution : six

Q. Find the Effective atoms in bcc.

Solution : $(Z_{eff}) = 8 \times \dfrac{1}{8} + 1 = 2$.

Q. What is the relation between edge length 'a' and size of atom 'r' in bcc ?

Solution : $\sqrt{3}a = 4r$.

Q. What is the coordination number in bcc ?

Solution : eight

Q. What type of packing is present in fcc unit cell ?

Solution : ABCABC.... type of packing.

Q. Find effective atoms in fcc unit cell.

Solution : $(Z_{eff}) = 8 \times \dfrac{1}{8} + 6 \times \dfrac{1}{2} = 4$.

Q. What is the relation between edge length 'a' and size of atom 'r' in fcc unit cell.

Solution : $\sqrt{2}a = 4r$

1.6 Closed Packed Structure :

Q. What are the different types of interstitial voids are present in ccp packing ?

Solution : In the closed packing of spheres there is some empty space left in between the spheres, this is known as Interstitial sites or voids. We come across two common interstitial sites **tetrahedral and octrahedral** sites in the closed packed lattices.

1. Tetrahedral void

2. Octahedral void

Tetrahedral void : If one sphere is placed upon three other spheres which are touching one other tetrahedral structure results.
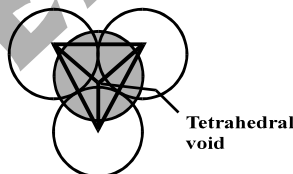
Since the four sphere touch each other at one point only they leave small space in between known as tetrahedral void. The size of the void is much smaller than that of the spheres.

In ccp near every corner inside the unit cell there is one tetrahedral void.

Total and effective tetrahedral voids = 8.

Co-ordiantion number of tetrahedral void atom = 4.

There would be two tetrahedral voids associated with each sphere in fcc.

Octahedral void : This interstitial site or void is formed at the centre of six spheres, the centres of which lie at the apices of a regular octahedral.
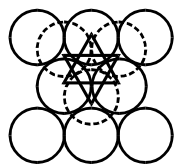
 The figure shows two layers of closed-packed sphered. The full circles represent the spheres in one plane while the dotted circles represent those in second plane. Two triangles have been drawn. One of these joins the cetres of these spheres in one plane while the second (dotted lines) joins the centres of three spheres in the second plane. The octahedral sites, marked by x, are formed where two

triangles of different layers are superimposed one above the other. In this position the apices of these triangles point in opposite direction, as shown. Thus, each octahedral site is created by two equilateral triangles with apices in opposite direction.

Effective octahedral void in fcc = 4.

Coordination number of octahedral void = 6.

General relation for ccp and hcp packings

Effective atom = effective octahedral voids

Effective tetrahedral void = 2 × octahedral void.

Q. What is the type of packing is present in hcp ?

Solution : In hcp it is known as ABAB..... type of packing.

Q. Find the effective atoms in hcp.

Solution : $(Z_{eff}) = \dfrac{1}{6} \times 12 + 3 + \dfrac{1}{2} \times 2 = 6$.

Q. Find the coordination number in hcp

Solution : Twelve

Q. What is the relation between 'a' and size of atom 'r' in hcp ?

Solution : a = 2r

Q. A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make ccp and those of the elements X (as cations) occupy all the octahedral voids. What is the formula of the compound ? [NCERT solved example]

Solution : XY

Q. Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the element A and B ? [NCERT solved example]

Solution : A_4B_3

1.7   Packing Efficiency :

Q. Find the packing fraction in simple cubic unit cell.

Solution : Packing Fraction $\mathbf{(P.F)} = \dfrac{\textbf{Volume occupied by effective atoms in a unit cell}}{\textbf{Total volume of unit cell}}$

$$\mathbf{P.F} = \dfrac{\mathbf{Z_{eff}}\ \mathbf{4\pi r^3}}{\mathbf{3a^3}}\ \textbf{......}$$ [a is the edge length of unit cell, Z_{eff} is

the effective atom in a unit cell]

In case of simple cube (P.F) = $\dfrac{\pi}{6}$ = 0.52.

Q. What is the packing fraction in bcc ?

Solution : $\dfrac{\sqrt{3}\,\pi}{8}$ = 0.68 ∴ 68% of the total volume is occupied and 32% of total volume is vacant.

Q. What is the packing fraction of a fcc unit cell also write the coordination number of each atom in fcc unit cell ?

Solution : $\dfrac{\pi}{3\sqrt{2}}$ = 0.74 ∴ 74% of the total volume is occupied and 26% of total volume is vacant.

Co-ordination Number or Nearest Neighbours in fcc is 12.

Q. What is the Packing fraction in hcp ?

Solution : Packing fraction = $6 \times \dfrac{4\pi r^3}{3 \times 24\sqrt{2}\, r^3}$

(volume of hexagon = base area × height, base area = $6 \times \dfrac{\sqrt{3}}{4} \times a^2$, height 'h' = $4r\sqrt{\dfrac{2}{3}}$)

1.8   Calculations Involving Unit Cell Dimensions :

Q. Find the density of unit cell having Z effective atoms and 'a' as a edge length of unit cell.

Solution : $d = \dfrac{\text{mass of a unit cell}}{\text{volume of a unit cell}}$, $d = \dfrac{Z_{eff}\, M}{N_A a^3}$.

Q. 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/cm³. How many atoms are present in 208 g of the element ? [NCERT solved example]

Solution : 24.16×10^{23} atoms

Q. X-ray diffraction studies show that copper crystallises in an fcc unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm³, calculate the atomic mass of copper. [NCERT solved example]

Solution : 63.1 u

Q. Silver forms ccp lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic mass = 107.9 u) [NCERT solved example]

Solution : 10.5 g cm⁻³

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

Solution : In the two-dimensional square close packed layer, the atom touches 4 nearest neighbouring atoms. Hence, its coordination number = 4.

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

Solution : 9.033×10^{23}, 6.022×10^{23}

Q. 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 ?

Solution : M_2N_3

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

Solution : hexagonal close-packed lattice.

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

Solution : Thus, there are 4 atoms of the element present per unit cell. Hence, the cubic unit cell must be face-centred of cubic close packed (ccp).

1.9   Imperfections in Solids :

Q. What are the types of points defects ?

Solution : (i) stoichiometric defects (ii) impurity defects and (iii) non-stoichiometric defects.

Q. What are stoichiometric defects ? Explain them.

Solution : The constituents in a solid are present in the same ratio as predicted by their formula. These defects are also called intrinsic or thermodynamic defects.

Types of stoichiometric defects :

(a) Vacancy defect : when some of the lattice sites are vacant, the crystal is said to be vacancy defect. As a result the density of the solid decreases. This defect can also be develop upon heating.

(b) Intestitial defect : When some constituent particles (atom or molecules) occupy an intenstial site, this defect is created. This defect increases the density of the solid. Both defects are shown by non-ionic compound. The ionic solids always exhibit electrical neutrality and show schottky and frenkel defect.

(c) Schottky defect : It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality the number of missing cations and anions are equal. In this the density decreases. Scottky defect is shown by those ionic compound in which the cation and anion are of almost similar sizes. e.g. NaCl, KCl, CsCl, AgBr.

(d) Frenkel defect : If smaller ions dislocate from lattice site to interstitial site then the vacancy defect arise at lattice site and interstitial defect arises at new location. It does not change the density of the solid. This defect shown by ionic solids in which there is large difference in the size of ions. e.g., AgCl, AgBr, AgI, ZnS, ZnO etc. (AgBr shows both Frenkel and Schottky defect).

Q. What are non-stoichiometric defect ? Explain briefly.

Solution : Non-stoichiometric defects are of two types (a) Metal excess defects (b) Metal deficiency defects.

(a) Metal excess defects : arise in two ways

(i) Due to anion vacancies : Alkali halides like NaCl, LiCl and KCl show this type of defect when crystal of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na^+ ion to give NaCl. The loss of electron by sodium atom occupy anonic vacant site to maintain the electrical neutrality called **F-centre**. F-centre impart the colour to the crystal. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. NaCl impart yellow colour. Excess of lithium makes LiCl $\rightarrow$ pink colour. Excess of potassium makes KCl $\rightarrow$ Violet.

(ii) Due to the presence of extra cations at interstitial sites : ZnO white in colour at room temperature on heating it loses oxygen and turns yellow. The excess of Zn^{2+} ions move to interstitial sites and to maintain the electrical neutrality electrons trap to neighbouring interstitial sites.

$$\underset{\text{(white colour)}}{ZnO} \xrightarrow{\Delta} Zn^{2+} + \frac{1}{2}O_2 \uparrow + 2e^-.$$
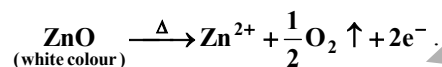
(b) Metal deficiency defect :

(i) By cation vacancies : This defect is generally shown by transition metals capable of showing variable oxidation states. In this defect some cations are missing from lattice sites and to maintain the electrical neutrality their positive charges are balanced by the presence of extra charges (i.e., higher oxidation state) on the neighbouring site. e.g., In FeO, Fe^{2+} ions missing from lattice site & neighbour lattice site occupied by Fe^{3+}. Similarly in Cu_2O some Cu^+ ions have been replaced by Cu^{2+} ions for every two Cu^+ ions displaced from the lattice site one Cu^{2+} ion will be replaced to maintain the electrical neutrality. Thus there will be holes in the lattice. These positive holes will be responsible for conduction of electricity in Cu_2O. Hence it is a p-type conductor.

(ii) By the presence of extra anions at the interstitial sites

1.10 Electrical Properties :

Q. What are the types of solids on the basis of their conductivities ?

Solution : Solids can be classified into three types on the basis of their conductivities.

(i) Conductors : The solid with conductivities ranging between 10^4 to 10^7 ohm^{-1}m^{-1} are called conductors. Metals have conductivities in the order of 10^7 ohm^{-1}m^{-1} are good conductors.

(ii) Insulators : These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1}m^{-1}.

(iii) Semiconductors : These are the solids with conductivities in the intermediate range from 10^{-6} to 10^4 ohm^{-1}m^{-1}.

Q. What are impurity defects ? Explain briefly.

Solution : (a) Impurity defect in ionic solids : e.g., NaCl doped with $SrCl_2$ to produce one cation vacancy as to maintain the electrical neutrality. Sr^{2+} occupy one lattice site of Na^+ vacancy and other Na^+ lattice site is vacant. AgCl doped with $CdCl_2$ produce one cation vacancy.

(b) Impurity defects in covalent solids :

(i) n-type (electron rich impurities) : Group-14 element (like Si and Ge) which have four valence electrons and doped with gp-15 element like P or As which contain 5 valence electrons, they occupy some of the lattice sites in silicon crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth extra electron increase silicon atoms. The fifth extra electron increase the conductivity due to negatively charged electron. Silicon doped with electron rich impurity is called n-type (n = negative) semiconductor

(ii) p-type (electron deficient impurities) : Si or Ge doped with a gp-13 element like B, Al or Ga which contain only 3-valence electrons and hence the fourth valence electron is missing called electron hole or electron vacancy which appear as it positively charged and are moving towards negatively charged plate. This type of semiconductor is called p-type.

1.11 Magnetic Properties :

Q. On the basis of magnetic properties what are the different categories in which solids can be classified.

Solution : Substances can be classified into five categories : (i) diamgnetic (ii) paramagnetic (iii) ferromagnetic (iv) antiferromgnetic and (v) ferrimagnetic.

(i) Diamagnetic substances : Those substances which are weakly repelled by the magnetic field, are known as dimagnetic substances. They do not contain any unpaired electron.

(ii) Paramagnetic : These substances are attached by magnetic field. They contain unpaired electrons.

(iii) Ferromagnetic : These substances show permanent magnetism even in the absence of magnetic field. For example : Ni, Co.

(iv) Antiferromagnetic : These substances show much reduced paramagnetism than expected from their electronic structure. For example : MnO, FeO.

(v) Ferrimagnetic : These materials show small paramagnetic character. For example : Fe_3O_4. At a particular temperature ferromagnetic, antiferromagnetic and ferrimagnetic solids change into paramagnetic. Orientation of Unpaired Electrons is :

Paramagnetic substance	Antiferromagnetic substance	Ferrimagnetic substance	Ferromagnetic substance
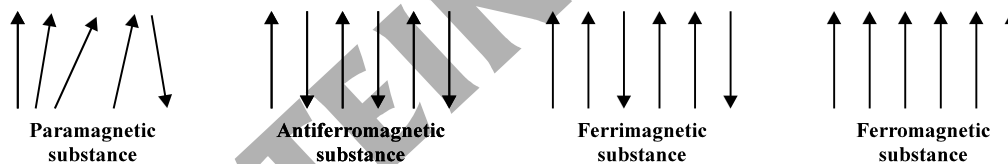
Q. What type of defect can arise when a solid is heated ? Which physical property is affected by it and in what way ?

Solution : When a solid is heated, vacancy defect is produced in the crystal. This is because on heating, some atoms orions leave the lattice site completely, i.e., some lattice site become vacant. As a result of this defect, the density of the substance decreases because some atoms/ions leave the crystal completely.

Q. What type of stoichiometric defect is shown by : (i) ZnS (ii) AgBr ?

Solution : (i) ZnS shows Frenkel defect because its ions have a large difference in size.

(ii) AgBr shows both Frenkel and Schottky defects.

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

Solution : Two or more cations of lower valency are replaced by a cation of higher valency to maintain electrical neutrality. Hence, some cation vacancies are created. For example, if in the ionic solid, Na^+Cl^-, impurity of Sr^{2+} is added (as $SrCl_2$), two Na^+ lattice sites will become vacant and one of these will be occupy by Sr^{2+} ion and the other will remain vacant.

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

Solution : Taking the example of NaCl, when its crystals are heated in presence of sodium vapour, some chloride ions leave their lattice sites to combine with sodium to form NaCl. For this reaction to occur, Na atoms lose electrons to form Na^+ ions. The electrons thus released diffuse into the crystal to occupy the

anion vacancies created by Cl^- ions. The crystal now has excess of sodium. The sites occupied by unpaired electrons are called F-centres. They impart yellow colour to the crystal because they absorb energy from the visible light and get excited.

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

Solution : n-type semiconductor means conduction due to presence of excess of negatively charged electrons. Hence, to convert group 14 element into n-type semiconductor, it should be doped with group 15 element.

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

Solution : Ferromagnetic substances make better permanent magnets. This is because the metal ions of a ferromagnetic substance are grouped into small regions called 'domains'. Each domain acts as a tiny magnet. These domains are randomly oriented. When the substance is placed in a magnetic field, all the domains get oriented in the direction of magnetic field and a strong magnetic field is produced. This ordering of domains persists even when the external magnetic field is removed. Hence, the ferromagnetic substance becomes a permanent magnet.

NCERT EXERCISE

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

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

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 ($NH_4)_3PO_4$

(iii) SiC   (iv) I_2

(v) P_4 (v) Plastics

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

(ii) What is the coordination number of atoms :

(a) in a cubic close-packed structure ?

(b) in a body-centred cubic structure ?

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

1.6 'Stability of a crystal is reflected in the magnitude of its melting points'. Comment. Collect data of 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 ?

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

(i) Hexagonal close-packing and cubic close-packing ?

(ii) Crystal lattice and unit cell ?

(iii) Tetrahedral void and octahedral void ?

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

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

1.9 Explain :

(i) The basis of similarities and differences between metallic and ionic crystals.

(ii) Ionic solids are hard and brittle.

1.10 Calculate the efficiency of packing in case of a metal crystal for

(i) simple cubic

(ii) body-centred cubic

(iii) face-centred cubic (with the assumptions that atoms are touching each other).

1.11 Silver crystallises in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3}, calculate the atomic mass of silver.

1.12 A cubic solid is made of two elements P and Q. Atoms of Q are the corners of the cube and P at the body-centre. What is the formula of the compound ? What are the coordination numbers of P and Q ?

1.13 Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass of 93 u.

1.14 If the radius of the octahedral void is r and radius of the atoms in closepacking is R, derive relation between r and R.

1.15 Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}.

1.16 Analysis shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions ?

1.17 What is a semiconductor ? Describe the two main types of semiconductors and contrast their conduction mechanism.

1.18 Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide. copper to oxygen ratio is slightly less than 2 : 1. Can you account for the fact that this substance is a p-type semiconductor ?

1.19 Ferric oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

1.20 Classify each of the following as being either a p-type or a n-type semiconductor :

(i)　　　Ge doped with In

(ii)　　　B doped with Si.

1.21 Gold [atomic radius = 0.144 nm] crystallises in a face-centred unit cell. What is the length of a side of the cell ?

1.22 In terms of band theory, what is the difference

(i) between a conductor and an insulator

(ii) between a conductor and a semiconductor ?

1.23 Explain the following terms with suitable examples :

(i)　　　Schottky defect　　　　(ii)　　　Frenkel defect

(iii)　　　Interstitials　　　　(iv)　　　F-centres.

1.24 Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.

(i) What is the length of the side of the unit cell ?

(ii) How many unit cells are there in 1.00 cm^3 of aluminium ?

1.25 If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancies ?

1.26 Explain the following with suitable examples :

(i)　　　Ferromagnetism　　　　(ii)　　　Paramagnetism

(iii)　　　Ferrimagnetism　　　　(iv)　　　Antiferromagnetism

(v)　　　12-16 and 13-15 group compounds.

ANSWERS

1.1 Amorphous solids are those solids in which the constituent particles may have a short range order but do not have a long range order. They have irregular shapes and are isotropic in nature. They do not undergo a clean cleavage. They do not have sharp melting point for definite heats of fusion.

Examples. Glass, rubber and plastics.

1.2 Glass is an amorphous solid in which the constituent particles (SiO_4 tetrahedra) have only a short range order and there is no long range order. In quartz, the constituent particles (SiO_4 tetrahedra) have short range as well as long range order. On melting quartz and then cooling it rapidly, it is converted into glass.

1.3 Ionic = $(NH_4)_3PO_4$ and LiBr ; Metallic = Brass, Rb ; Molecular = P_4O_{10}, I_2, P_4 ; Network (covalent) = Graphite, SiC, Si ; Amorphous = Plastics.

1.4 (i) The coordination number of a constituent particle (atom, ion or molecule) in a crystal is the number of constituent particles which are the immediate neighbour of that particle in the crystal. In ionic crystals, coordination number of an ion in the crystal is the number of oppositely charged ions surrounding that particular ion. (ii) (a) 12 (b) 8.

1.6 (a) Higher the melting point, greater are the force holding the constituent particles together and hence greater is the stability.

(b) The intermolecular forces in water and ethyl alcohol are mainly the hydrogen bonding. Higher melting point of water then alcohol shows that hydrogen bonding in ethyl alcohol molecules is not as strong as in water molecules. Diethyl ether is a non-polar molecule. The only forces present in them are the weak van der Waal's forces (London dispersion forces).

1.9 (a) Similarities. (i) Both ionic and metallic crystals have electrostatic forces of attraction. In ionic crystals, these are between the oppositely charged ions. In metals, these are among the valence electrons and the kernels. That is why both have high melting point. (ii) In both cases, the bond is non-directional.

Differences. (i) In ionic crystals, the ions are not free to move. Hence, they cannot conduct electricity in the solid state. They can do so only in the molten state or in aqueous solution. In metals, the valence electrons are free to flow. Hence, they can conduct electricity in the solid state. (ii) Ionic bond is strong due to electrostatic forces of attraction. Metallic bond may be weak or strong depending upon the number of valence electrons and the size of the kernels. (b) Ionic crystals are hard because there are strong electrostatic forces of attraction among the oppositely charged ions. They are brittle because ionic bond is non-directional.

1.11 107.8 u

1.13 14.29 nm

1.15 8.97 g cm^{-3}

1.16 Ni^{2+} = 96% and Ni^{3+} = 4%

1.17 Substances whose conductance lies inbetween that of metals (conductors) and insulators are called semiconductors. Two main types of semiconductors are n-type and p-type.

1.18 The ratio less than 2 : 1 in Cu_2O shows that some cuprous (Cu^+) ions have been replaced by cupric (Cu^{2+}) ions. To maintain electrical neutrality, every two Cu^+ ions will be replaced by one Cu^{2+} ion thereby creating a hole. As conduction will be due to presence of these positive holes, hence it is a p-type semiconductor.

1.20 (i) Ge is Group 14 element and In in Group 13 element. Hence, an electron deficit hole is created and therefore, it is p-type.

(ii) B is Group 13 element and Si is Group 14 element, there will be a free electron. Hence, it is n-type.

1.22 (i) The energy gap between the valence band and conduction band is an insulator is very large whereas in a conductor, the energy gap is very small or there is overlapping between valence band and conduction band.

(ii) In a conductor, there is very small energy gap or there is overlapping between valence band and conduction band but in a semiconductor, there is always a small energy gap between them.

1.24 (i) 354 pm (ii) 2.26×10^{22} unit cells

1.25 6.02×10^{18} cation vacancies mol^{-1}

ADDITIONAL QUESTIONS AND PROBLEMS

Q. **Explain the structures of ionic compounds like NaCl, CsCl, ZnS.**

A. **(i) NaCl type or Rock salt type :** It has fcc arrangement of ions. Na^+ and Cl^- ions have 6 : 6 coordination. Each unit cell has four NaCl units. For example : Halides of Ag, halides of alkali metals, oxides and sulphides of alkaline earths.

(ii) CsCl type structure : It has bcc arrangement. Cs^+ and Cl^- ions have 8 : 8 coordination. Each unit cell has only one CsCl unit. For example : CsI, CsBr, CsCN, TlI, TlCl, and TlCN.

(iii) Zinc blende (ZnS) type structure : It has fcc arrangement of S^{2-} ions. Zn^{2+} occupies the alternate position of tetrahedral void. Zn^{2+} and S^{2-} ions have 4 : 4 coordination. For example : CuCl, CuI, CuBr, AgI and BeS.

Q. **Explain the structures of ionic compounds like CaF$_2$ and Na$_2$O.**

A. **(i) Calcium fluorite (CaF$_2$) type structure :** It has ccp/fcc arrangement of Ca^{2+} ions. F^- occupies all the position of tetrahedral voids. Ca^{2+} and F^- ions have 8 : 4 coordination number.

(ii) Antifluorite structure : Na$_2$O has this type of structure. Oxide ions has fcc arrangement whereas Na^+ occupies all the tetrahedral position. Na^+ and O^{2-} ions have 4 : 8 coordination number.

Q. **What is the limiting radius ratio in ionic solids ?**

A. The radius ratio of cation to that of anion is known as radius ratio of ionic solid. i.e., $\dfrac{r^{+n}}{r^{-m}} = \text{radius ratio}$.

It was found that greater is the radius ratio, greater will be the coordination number.

	r^{+n}/r^{-m}	C.N.	Structural Unit	Example
(a)	0.155 – 0.225	3	plane triangular	B$_2$O$_3$
(b)	0.224 – 0.414	4	Tetrahedral (bcc)	ZnS, CuX, AgI
(c)	0.414 – 0.732	6	Octahedral (fcc)	NaCl, NaI, KCl, RbI, FeO
(d)	0.732 – 1.00	8	Cubic	CsCl

Large number of ionic compounds obey this rule although there are many exceptions.

Q. **Diamond and solid rhombic sulphur both are covalent solids but the latter has very low melting point than the former. Explain why.**

A. Diamond is three dimensional net work covalent solid with strong interatomic forces whereas sulphur is a molecular solid consisting of puckered eight membered rings (S$_8$) held together by weak van der Waals forces.

Q. **Sodium metal is quite soft whereas sodium chloride crystals are quite hard. Explain why.**

A. In sodium metal, the atoms are held together by metallic bonds which are quite weak because it has only one valence electron and large sized Na^+ ions as kernels. Sodium chloride is an ionic compound. The oppositely charged Na^+ and Cl^- ions are held together by strong electrostatic forces of attraction. Hence, it oppositely charged Na^+ and Cl^- ions are held together by strong electrostatic forces of attraction. Hence, it is quite hard.

Q. **Why is coordination number of 12 not found in ionic crystals ?**

A. Maximum radius ratio in ionic crystals lies in the range 0.732 – 1 which corresponds to a coordination number of 8. Hence, coordination number greater than 8 is not possible in ionic crystals.

Q. **Out of NaCl and CsCl, which one is more stable and why ?**

A. CsCl is more stable than NaCl. This is because higher the coordination number, greater are the forces of attraction between the cations and the anions in the close-packed arrangement. As CsCl has co-ordination number of 8 : 8 while NaCl has a coordination number of 6 : 6, therefore, CsCl is more stable.

Q. **In a crystal, Frenkel defect is not shown by alkali metal halides but silver halides show. Why ?**

A. Frenkel defect is found in silver halides due to small size of Ag^+ ion. It is not found in alkali metal halides, as the alkali metal ions are too big to fit into the interstitial sites.

Q. A metallic element exists as a cubic lattice. Each edge of the unit cell is 2.88 Å. The density of the metal is 7.20 g/cm³. How many unit cells will be present in 100 gm of the metal ?

A. 5.82×10^{23}

Q. NH_4Cl crystallizes as a body centred cubic lattice with a unit distance of 387 pm. Calculate (a) The distance between the oppositely charged ions in the lattice and (b) The radius of the NH_4^+ ion if the radius of the Cl^- ions is 181 pm.

A. (a) 335.15 Pm (b) 154.15 Pm

Q. In a cubic closed packed structure of mixed oxides the lattice is made up of oxide ions, one eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids occupied trivalent ions (B^{3+}). What is the formula of the oxide ?

A. AB_2O_4

Q. CsCl has bcc arrangement and its unit edge length is 400 pm. Calculate the interionic distance in CsCl.

A. 346.4 pm

Q. A metal crystallises into two cubic phases, face centered cubic (fCC) and body centred cubic (bCC), whose unit cell length are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of fCC and bCC.

A. 1.88×10^{-6}

Q. The composition of sample of solid is $Fe_{0.93}O_{1.00}$. What percentage of the iron is present in the form of Fe (III) ?

A. 11.5 %

Q. Iron changes its crystal structure from body-centred to cubic close-packed structure when heated to 916⁰C. Calculate the ratio of the density of the bcc crystal to that of ccp crystal, assuming that the metallic radius of the atom does not change.

A. 0.919