SOLID STATES THEORY WITH ASSIGNMENT

TOPIC 1: UNIT CELLS

1. Solids are substances which have fixed shape and volume. They are characterised by rigidity, incompressibility, slow diffusion and mechanical strength. They are classified as:

a. Crystalline solids: A solid is said to be crystalline if the various constituent particles like atoms, ions, or molecules are arranged in a definite geometric pattern within the solid, e.g., NaCl, KNO_3, LiF and $CuSO_4.5H_2O$.

b. Amorphous solids: A solids is said to be amorphous if the various constituent particles are not arranged in any regular fashion, e.g., glass and rubber.

2. Differences between crystalline and amorphous solids:

Crystalline solids	Amorphous solids
a. They have a definite geometrical shape due to the definite and orderly arrangement of particles in the three dimensional space.	a. They do not have an orderly arrangement of particles and therefore, do not possess a definite geometrical shape.
b. They have sharp melting point.	b. They do not have sharp melting point.
c. When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth.	c. When they care cut, they split into two pieces and the newly generated surfaces are irregular in shape.
d. They have crystal symmetry.	d. They do not have crystal symmetry.
e. They possess anisotropic properties, i.e., the magnitude of some of the physical properties of crystalline solids like refractive index, coefficient of thermal expansion and electrical and thermal conductivities is different in different directions within the crystal.	e. They have isotropic properties, i.e., the magnitude of physical properties is same in all directions.

3. The crystalline solids are further classified as:

a. Metallic solids:

(i) Their constituent particles are atoms which are packed together as closely as possible.

(ii) In a metallic lattice, the positive ions are embedded in a sea of electrons.

(iii) They are generally good conductors of heat and electricity.

(iv) They have moderate to high melting point. (v) Examples are Cu, Ag, Mg, Al, etc.

b. Ionic solids:

(i) Their constituent particles are positive and negative ions, which are held together by strong electrostatic (coulombic) attractions.

(ii) The crystal structure depends largely upon the relative sizes of the concerned cations and anions.

(iii) They have high melting points and are insulators in the solid state, and conducting in molten state.

(iv) Examples are NaCl, MgO, KCl, $BaCl_2$, etc.

c. Covalent solids:

(i) Their constituent particles are atoms.

(ii) The bonding is covalent and directional in nature.

(iii) They have high melting points and are insulators and do not conduct electricity.

(iv) Examples are diamond, silica (SiO_2), silicon carbide (SiC), etc.

d. Molecular solids:

(i) Their constituent particles are molecules.

(ii) The molecules are held together by weak van der Waals forces and hydrogen bonding.

(iii) They have low melting points.

(iv) They are electrical insulators and poor thermal conductors.

(v) Examples are iodine, ice, solid CO_2, etc.

(vi) Type of molecular solids :

Non-polar molecular solids: In these solids, atoms are held together by weak dispersion forces or London forces.

Polar molecular solids: In these solids, molecules are held together by relatively stronger dipole-dipole interactions.

Hydrogen bonded molecular solids: The molecules are held together by hydrogen bonds.

4. 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.

5. A unit cell is the smallest unit of the crystal which when repeated again and again gives the crystal of the gives the crystal of the given substance.

ILLUSTRATIONS

1. Why do solid have a definite volume?

Sol. Due to close packing and strong inter-particle forces of attraction. The constituent particles do not move away easily and thus solids have a definite volume.

Q 2. 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?

Sol. Since value of refractive index is same in all direction means ‘isotropy’ which is property of an amorphous substance. Because of random arrangement of particles, It will not show a clean cleavage property. When cut with a knife instead, It would break into pieces with Irrangular surfaces.

Q 3. Classify the following solids in different categories based on the nature of intermolucular forces operating in them potasium sulphate, tin, benzene, urea, ammonia, water, zincsulphide, graphite, rubidium, argon, silicon carbide.

Sol.i. **Ionic solids-**Potasium sulphate, zinc sulphide,

ii. **Molecular solids** (a) Nonpolar -Benzene, Argon, (b) Polar-Urea, (c) Hydrogen bonded- Ammonia, water

iii. **Metallic solid**-Tin, Rubidium, **iv. Covalent solid-**Graphitc, silicon carbide.

Q 4. Solid A is very hard electrical insulator in solid as well as in molten state and melts at extermely high temperature. What type of solid is it?

Sol. It must be a covalent newtwork crystal.

Q 5. Ionic solids conduct electrical in molten state but not in solid state explain it.

Ans. In solid state the charge carriers (ions) are rigidly held and they donot have any translational motion. on melting these ions can move and thus conduct electricity,

PRACTICE PROBLEMS

1. Classify each of solid as ionic, metallic, molecular, covalent

a. Dry ice **b.** Diamond **c.** Bronze **d.** Rock Salt **e.** Silica **f.** Aluminium

g. Ice **h**. Ammonium Chloride **i.** Glass **j.** Potassium sulphate

k. Tin **l.** Benzene **m.** water **n.** Ammonia **o.** ZnS **p**. Rb **q.** SiC

2. What is difference between ionic and metallic solid?

3. Give two points of difference between a crystalline solid and an amorphous solid. Why is glass regarded as an amorphous solid?
4. How to convert quartz into glass?
5. Why glass of ancient building become milky over period of time?
6. Explain the term Antisotropic and Isotropic.
7. Name the three types of crystalline solids having the formula AB.
8. Write the three types of solids on the basis of their ability to conduct electric current.
9. Give three points of difference between a crystalline solid and amorphous solid with reference to melting point, arrangement and cleavage?
10. Why the window glass of the old buildings thick at the bottom ?
11. What is observed when :

    (a) Quartz has a much higher melting point than CO_2

    (b) NaCl is harder than Na metal,

    (c) BeO has a higher melting point than LiF.

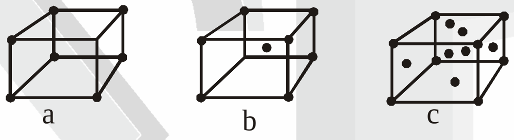
TOPIC 2: CLOSE PACKED STRUCTURES

1. There are three types of unit cells based on the cube. These are:

   a. Primitive or simple cube which has one constituent at reach corner.

   b. Body-centred cube in which one constituent at the centre of the cube as well as one at each corner.

   c. Face-centred cube in which there is one constituent at the centre of each face as well as one at each corner.



2. **Calculation of number of particles per unit cell:**

   a. Contribution by a constituent on the corner of a unit cell = 1/8

   b. Contribution by a constituent on the face of a unit cell = 1/2

   c. Contribution by a constituent on the edge of a unit cell = 1/4

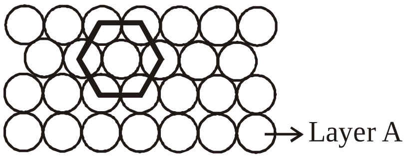
   d. Contribution by a constituent within the body of unit cell = 1

Type of cell	**No. of constituent at corners**	**No. of constituent of faces**	**No. of constituent in the centre of cube**	**Total no. of constituents in the unit cell**
Primitive or simple cube	$8\times\frac{1}{8}=1$	0	0	1
Body-centred cube	$8\times\frac{1}{8}=1$	0	1	2
Face-centred cube	$8\times\frac{1}{8}=1$	$6\times\frac{1}{2}=3$	0	4

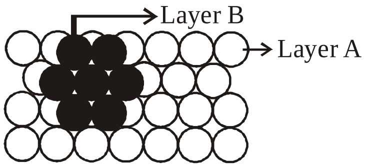
3. A pure metal in the solid crystalline state is composed of atoms that are identical in shape and size. The identical spheres can be packed in a number of ways:

   a. The most economical way in which the identical spheres can be packed in a single layer is the hexagonal arrangement as shown in fig a. It can be seen that each sphere is in contact with six other spheres arranged in a hexagonal arrangement around it.

b. The second layer of spheres is kept over the first layer, the spheres in the second layer will fit into the depressions of the first layer as shown in fig. b.



a

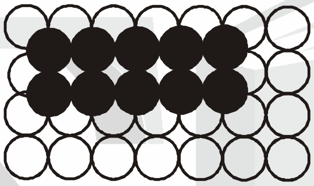


b

c. For the third layer, there are two possibilities: (i) The spheres can be placed in the depressions of the second layer in such a way so that they are directly above the first layer. Here the third layer is directly above the first, the fourth directly above the second and so on. This leads to the arrangement ABABAB...... This type of arrangement is known as **hexagonal close-packing (hcp)** structure, e.g., Zn and Mg. There are 6 spheres per unit cell in such arrangement.

(ii) Alternatively, the spheres can be placed in those depressions of the second layer, that do not lie directly above the atoms of the first layer. It follows that all the spheres in the third layer are not exactly above the spheres in the first layer. In this type of arrangement, the pattern repeats every fourth layer, i.e., the spheres in the fourth layer lie exactly above the first, the fifth above the second, the sixth above the third and so on. If the three layers are represented by A, B and C then the resulting structure has on ABCABCABC ...... arrangement. This is known as **cubic- closed packing (ccp) structure or face-centred cubic (fcc)** arrangement, e.g., Cu, Ag and Au.

4. In a body-centred cubic (bcc) arrangement, the first layer of atoms is arranged in rows and columns. The second layer of atoms fits into the hollows of the first layer and the third layer is identical to the first layer as shown in fig (c). Each layer is having square close packing in which the spheres are horizontally and vertically aligned.



c

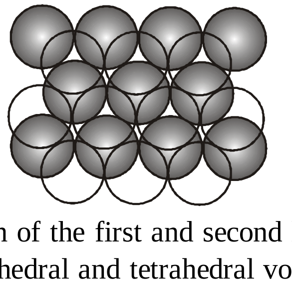
5. The number of nearest neighbours of an atom, ion or a molecule is called its **coordination number.**
Ion ionic crystals, the coordination number may be defined as the number of oppositely charged ions surrounding a particular ion.

Metallic elements	Lattice types	Coordination numbers
Be, Mg, Cd, Zn, Ti	HCP	12
Cu, Ca, Si, Ag, Au	CCP or FCC	12
Li, Na, K, Rb, Cs	BCC	8

6. 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.

7. When the spheres are stacked together in different layers there is always a **void** or **hole** (or **interstices**) between the touching spheres.

8. Two types of voids or holes are created among the spheres in close-packed arrangement of spheres:
a. Tetrahedral void: It is created by four spheres in contact with each other. Its coordination number is four.
b. Octahedral void: It is created when six spheres are in contact with each other. Its coordination number is 6.



Schematic representation of the first and second layers of hard spheres.
O and T are octahedral and tetrahedral voids respectively.

c. In a closed packed arrangement, the octahedral voids are present at edge centres and at body centres. As each edge is shared between four unit cells, so 1/4th of the void belongs to each unit cell. The void at a body centre is not shared. So in f.c.c. the no. of octahedral voids will be 1/4 × 12 (there are 12 edges in an unit cell) + 1 i.e. 4.

9. The density of the unit cell, $d = \frac{ZM}{a^3 N_A}$

10. In close packing structures (hcp or ccp), the radii of the voids are related to the sizes of the spheres. If R = Radius of the sphere then, Radius of the tetrahedral void (r) = 0.225 R

Radius of the octahedral void (r) = 0.414 R ; Radius of the cubic void (r) = 0.732 R

11. In ionic compounds, anions usually form closed packed structure and cations occupy the voids, thus

a. for cations occupying the tetrahedral voids, $r_+ = 0.225 r_-$ b. for cations occupying the octahedral voids, $r_+ = 0.414 r_-$

12. Radius ratio = $\frac{\text{Radius of cation } (r_+)}{\text{Radius of cation } (r_-)}$

RADIUS RATIO RULES FOR AB TYPES STRUCTURES

Radius ratio	Coordination number	Structural arrangement	Structure type	Examples
0.155–0.225	3	Planar triangular	–	B_2O_3
0.225–0.414	4	Tetrahedral	Sphalerite, ZnS	CuCl, CuBr, Cul, BaS, HgS
0.414–0.732	6	Octahedral	Sodium chloride (Rock Salt)	NaBr, KBr, MgO, MnO, CaO, CaS
0.732–1	8	Body-centred cubic	Cesium chloride	CsI, CsBr, TlBr, NH_4Br

13. Relationships between atomic radius r (= $\frac{d}{2}$ for crystal of pure elements) and edge (a) of the unit cell of a cubic crystal:

Simple	r = a/2
Face-centred	r = $a/2\sqrt{2} = 0.3535a$
Body-centred	r = $\sqrt{3}/4a = 0.433a$

14. Relation between the nearest neighbour distance (d) and the edge (a) of a unit call of a cubic crystal: d is always twice of r

Simple	d = a
Face-centred	d = $a/\sqrt{2} = 0.707\, a$
Body centred	d = $\sqrt{3}/2a = 0.866a$

ILLUSTRATIONS

1. A solid AB has the NaCl structure. If the radius of cation is 100 pm, what is the radius of anion B^- ?

Sol. In NaCl, there is coordination number of 6. Thus, radius ratio of AB should also be in the range of 0.414 and 0.732.

$$\frac{r^+}{r^-} = 0.414 \;;\; \frac{100}{r^-} = 0.414 \;;\; r- = 241.54 \text{ pm} \qquad \text{(Maximum radius)}$$

When, $$\frac{r^+}{r^-} = 0.732 \;;\; \frac{100}{r^-} = 0.732 \;;\; r- = 136.61 \text{ pm} \qquad \text{(Minimum radius)}$$

2. The two ions A^+ and B^- have radii 88 and 200 pm, respectively. In the close packed structure of compound AB, predict the coordination number of A^+.

Sol.
$$\frac{r^+}{r^-}=\frac{88}{200}=0.44$$

Radius ratio lies in the range of 0.414 – 0.732. Thus, coordination number of A+ ion will be 6.

3. A solid AB has NaCl structure. If the radius of the cation A+ is 170 pm, calculate the maximum possible value of the radius of the anion B^-.

Sol. For NaCl, coordination number is 6.

$\therefore \quad \frac{r^+}{r^-}=0.414$ (For maximum radius of anion) ; $\frac{170}{r^-}=0.414$; r^- = 410.162 pm

4. A solid AB has NaCl type structure. If the anion has radius of 241.5 pm, what should be the minimum radius of the cation? Can cation C^+ having radius of 50 pm be fitted into the tetrahedral hole of the crystal $A^+ B^-$?

Sol. Solid AB has NaCl type structure. Thus, coordination number will be six. The radius ratio for coordination number six will be in the range: $\frac{r^+}{r^-}=0.414 — 0.732$

For minimum radius of cation : $\frac{r^+}{r^-}=0.414$; $\frac{r^+}{241.5}=0.414$ $\therefore$ $r^+ = 99.98 \approx 100$ pm

Radius of tetrahedral hole = $r^- \times 0.225$ = $241.5 \times 0.225 = 54.33$ pm

Thus, cation C^+ having radius of 50 pm may be fitted into the tetrahedral hole.

5. In a compound AX, the radius of A^+ ion is 95 pm and that of X^- ion is 181 pm. Predict the crystal structure of AX and the coordination number of each ion.

Sol. Coordination number of ionic crystalline solids is determined with the help of radius also.

$$\frac{r^+}{r^-}=\frac{95}{181}=0.524$$

Radius ratio lies in the range of 0.414 — 0.732. Thus, coordination number of both cation and anion will be **six** (6) and the solid will have NaCl type structure.

6. If the radius of the bromide ion is 0.182 nm, how large can a cation fit in each of the tetrahedral holes?

Sol. For tetrahedral void,

$\frac{r^+}{r^-}=0.225 — 0.414$; $r^+ = 0.414 \times r^-$ = 0.414×0.182 nm = 0.0753 nm

$\therefore$ The cation of radius 0.0753 nm (maximum) can fit into each tetrahedral void.

7. Br^- ions form a close packed structure. If the radius of Br^- ion is 195 pm, calculate the radius of the cation that just fits in the tetrahedral hole.

Can a cation A^+ having a radius of 82 pm be slipped into the octahedral hole of the crystal $A^+ Br^-$?

Sol. For tetrahedral void, $\frac{r^+}{r^-}=0.225 — 0.414$; r+ = $0.414r^-$ = 0.414×195 = 80.73 pm

Thus, the cation having maximum radius 80.73 pm can just fit into the tetrahedral hole.

For octahedral void, $\left(\frac{r^+}{r^-}\right)$ ratio should lie between 0.414 to 0.732.

$\frac{r_{A^+}}{r_{Br^-}}=\frac{82}{195}=0.4205$. Thus, A+ ion can be slipped into the octahedral hole.

8. Edge length of unit cell of NaCl crystal lattice is 5.6 Å. The density is 2.2 g cm^{-3}. Find the number of formula units of NaCl per unit cell.

Sol. We know, $Z = \dfrac{a^3 \times f \times N_A}{M}$

$$a = 5.6 \times 10^{-8}\ cm \quad ; \quad f = 2.2\ g\ cm^{-3} \quad ; \quad M = 58.5 \quad ; \quad N_A = 6.023 \times 10^{23}$$

Putting these values in eqn. (i) we get $Z = \dfrac{(5.6\times10^{-8})^3 \times 2.2 \times 6.023\times10^{23}}{58.5} \approx 4$

9. Lead(II) sulphide crystal has NaCl structure. What is its density? The edge length of the unit cell of PbS crystal is 500 pm. ($N_A = 6.023 \times 10^{23}$, atomic masses: Pb = 207.2, S = 32)

Sol. We know, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

Given, Z = 4 (for NaCl structure, fcc); M = Formula mass PbS = 207.2 + 32 = 239.2

$a = 500\ pm = 500 \times 10^{-10}\ cm$ and $N_A = 6.023 \times 10^{23}$

$$\therefore \quad \rho = \frac{4 \times 239.2}{(500\times10^{-10})^3 \times 6.023\times10^{23}} = \frac{956.8}{75.2875} = 12.7\ g\ cm^{-3}$$

10. An element crystallises in a structure having a fcc unit cell of an edge 200 pm. Calculate its density if 200 g of this element contains 24×10^{23} atoms.

Sol. Density of a unit cell = $\dfrac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$; Mass of one atom = $\dfrac{200}{24\times10^{23}}$ g ; Z for fcc unit cell = 4

$\therefore$ Mass of unit cell = $\dfrac{4\times200}{24\times10^{23}} = 33.3 \times 10^{-23}$ g

Volume of unit cell = $a^3 = (200 \times 10^{-10})^3\ cm^3 = 8 \times 10^{-24}\ cm^3$ $\therefore$ Density of unit cell = $\dfrac{33.3\times10^{-23}}{8\times10^{-24}} = 41.6\ g\ cm^{-3}$

11. Calculate the value of Avogadro's number from the following data:
Density of NaCl = 2.165 g cm^{-3},
Distance between Na^+ and Cl^- ions in NaCl crystal = 281 pm

Sol. NaCl has fcc structure. Therefore, number of formula units or molecules per unit cell, Z = 4.
Formula mass, M = 23 + 35.5 = 58.5
Edge length of the unit cell

$$= 2(r_{Na^+} + r_{Cl^-}) = 2 \times \text{distance between } Na^+ \text{ and } Cl^- \text{ ions} = 2 \times 281 = 562\ pm = 562 \times 10^{-10}\ cm$$

Applying the formula, $N_A = \dfrac{Z \times M}{a^3 \times \rho} = \dfrac{4 \times 58.5}{(562\times10^{-10})^3 \times 2.165} = 6.09 \times 10^{23}$

12. A metal crystallises as face-centred cubic lattice with edge length of 450 pm. Molar mass of metal is 50 g mol^{-1}. Find the density of metal.

Sol. Z for fcc unit cell = 4 ; $a = 450 \times 10^{-10}$ cm ; M = 50 g mol^{-1} ; $N_A = 6.023 \times 10^{23}$

On applying the formula, $f = \dfrac{ZM}{a^3 N_A} = \dfrac{4 \times 50}{(450\times10^{-10})^3 \times 6.023\times10^{23}} = 3.64\ g\ cm^{-3}$

13. Which of the following lattices has the highest packing efficiency?

a. Simple cubic b. Body-centred cubic c. Hexagonal close packed lattice

Sol. Simple cubic : 52.33% occupied space

Body-centred cubic : 67.98% occupied space

Hexagonal closed packed lattice : 74.01% occupied space.

Thus, hexagonal packed lattice has the highest packing efficiency.

14. 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 unit cell?

Sol. We know, $Z = \dfrac{a^3 \times \rho \times N_A}{M}$

Where $a = 405$ pm $= 405 \times 10^{-10}$ cm ; $\rho = 2.7 \times 10^3$ kg m–3 $= 2.7$ g cm^{-3}

$M = 2.7 \times 10^{-2}$ kg mol^{-1} $= 27$ g / mol ; $N_A = 6.023 \times 10^{23}$

Putting these values in eqn. (i),

we get $Z = \dfrac{(405 \times 10^{-10})^3 \times 2.7 \times 6.023 \times 10^{23}}{27} = 4$

$\therefore$ The element has fcc (ccp) unit cell.

PRACTICE PROBLEMS

1. How many lattice point are there in one unit cell in each of following lattices.

2. Distinguish between hexagonal and monoclinic unit cell.

3. What are crystal parameter of following type of unit cell

a. Tetragond **b.** Triclinic **c.** Orthorthombic **d.** Trigonal

4. How many atoms are present per unit cell in a body centred cube?

5. How many atoms are present in the unit cell of : **a.** Simple cubic **b.** bcc **c.** fcc

6. What is a body centred cubic?

7. Define face centred structure?

8. Explain the packing hcp and fcc. What is coordination number in each?

9. In the solids atoms at A forms fcc and atoms at B occupy 2/3rd oct void. What is simplest formula of the solid.

10. In the solid atom at B forms hcp and atom of C occupy 1/3rd Td void. What is simplest formula at solid?

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

12. A solid between A and B has the following arrangement at atom :

a. Atoms A arranged in ccp array

b. Atoms B occupy all oct void and half Td void

What is formula at the compound

13. In a solid oxide ions are arranged in ccp and cations A occupy 1/6th of Td void and cation occupy 1/3rd oct void. What is the formula of the compound.

TOPIC 3: DEFECTS

1. Any departure from perfectly ordered arrangement of atoms or ions in crystals is called **imperfection** or **defects.** These are of two types:

a. Point defects: When there exists irregularities (from the ideal arrangement) around a point or an atom in a crystalline substance, it is called point defect.

b. Line defects: When there exists irregularities (from the ideal arrangement) along the entire row of lattice points, it is called line defect.

2. **Schottky defects** occurs hen 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.

3. 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.

4. **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. For example, AgX, the Ag^+ ions are considerably smaller than the X^-ions and thus, can get into the interstitial sites. It does not change the density of the crystal.

5. **In impurity defects** some other atoms (foreign atoms) are present at the lattice sites in place of original atoms (host atoms) or at the vacant interstitial sites. For example, if molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}.

Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and other site remains vacant.

6. **Non-stoichiometric defects:** There 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.** These compound do not obey the Laws of Chemical Combination, e.g., oxides and sulphides of transition elements.

The ratio of Fe : O in FeO is not exactly 1 : 1 It is $Fe_{0.98}$ O. There can be either an excess of metal ions or a deficiency of metal ions in the crystal.

7. 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.** F centres are associated with the colour of compounds.

For example, excess of K in KCl makes the crystal of KCl violet and excess of Li in LiCl makes it pink. In the metal deficiency defect, a metal ion of lower oxidation state is replaced by metal ion of higher oxidation state.

For example in the example sited above of $Fe_{0.98}$ O, some of Fe^{+2} are replaced by Fe^{+3}, that is why amount of iron is less than its stoichiometric requirement.

ILLUSTRATIONS

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

Sol. Vacancy defect is created when a solid is heated. This defect reduces the density of solid.

e.g. Metal excess defect of NaCl is obtained when NaCl is heated in the atmosphere of sodium vapour. The solid (NaCl) contains anionic vacancy with an electron, which develops yellow colour in it.

2. What type of stoichiometric defect is shown by:

(i) ZnS (ii) AgBr?

Sol. (i) ZnS shows Frenkel defect. (ii) AgBr shows both Frenkel and Schottky defect.

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

Sol. When a cation of higher valency is added then two or more cations of lower valency are replaced to maintain electricity neutrality, thus some cation vacancies are produced, *e.g.*, when $CdCl_2$ is added to AgCl, cation vacancies are created because two Ag^+ ions are replaced by a Cd^{2+} ion.

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

Sol. When NaCl is heated in the atmosphere of sodium vapour, sodium atoms are deposited on the surface of solid. The Cl^- ions diffuse to the surface of solid and combine with sodium atoms to form NaCl.

$$Na \longrightarrow Na^+ + e^-$$

$$Na^+ + Cl^- \longrightarrow NaCl$$

The electrons released, diffuse into the solid and occupy the anionic vacancy. The anionic vacancies occupied by electrons are called F-centres (Farbenzenter); F-centre is responsible for colour. NaCl with metal excess defect show light yellow colour.

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PRACTICE PROBLEMS

1. Explain interstitial and vacancy defect.

2. State the meaning of a non-stoichiometric defect'.

3. State the consequences of Schottky and Frenkel defects in crystals.

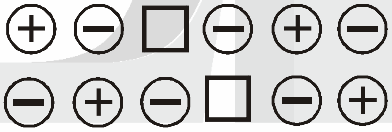
4. Why Nacl cannot show frenkel defect.

5. What happens when AgCl doped units $SrCl_2$.

6. What happens when NaCl doped with $CdCl_2$.

7. Why are the solids containing f-centres paramagnetic?

8. Examine the illustration of a portion of the portion at the defective crystal given below, answer following questions :



a. What are these of vacancy defect called

b. How is density affected by these defect

c. Name ionic compound which can show this defect

d. How is stoichiometry of compound affected

9. Addition of $CdCl_2$ to the crystals of AgCl with produce Schottky defects but the same is not produced when NaCl crystals are added. Discuss.

10. What are voids or interstitial sites?

11. Which point defect is observed in a crystal when a vacancy is created by an atom or ion missing from its normal position?

TOPIC 4 : SOLID AND CLASSIFICATION OF SOLIDS ON THE BASIS OF ELECTRICAL CONDUCTIVITY AND MAGNETIC PROPERTIES

1. Based on their electrical conductivity, solids are classified as:

a. **Conductors:** Metals are good conductors of electricity having conductivities of the order of $10^7 \Omega^{-1}$ m^{-1}.

b. **Insulators:** They have very low conductivities, ranging between 10^{-20} to $10^{-10} \Omega^{-1}$ m^{-1}.

c. **Semi conductors:** Semiconductors having conductivities intermediate between those of conductors and insulators, varying between 10^{-6} to $10^4 \Omega^{-1}$ m^{-1}.

2. The conductivity difference between conductors, semiconductors and insulators is due to the energy gap between the valence band and the conduction band.

a. In conductors, the conduction band is partially filled or it overlaps with the valence band.

b. In insulators, the energy gap is so large that the electrons form the valence band cannot cross it.

c. In semiconductors, the energy gap is small. At room temperature some electrons have enough energy to jump the gap and enter the conduction band. The conductivity of a semiconductor increases with increase of temperature.

3. Pure substances that show conducting behaviour like that of silicon and germanium are called **intrinsic semiconductors.**

4. **Extrinsic semiconductors** are obtained by adding an impurity to a pure substance, i.e., to an intrinsic semiconductors.

5. An **n-type semiconductor** is obtained by doping silicon with a group 15 element (P, As, Sb). The impurity provides an excess of electrons.

6. An **p-type semiconductor** is obtained by doping silicon with a group 13 element (B, Al, Ca, In). The impurity provides an excess of positive charge which are termed as holes.

7. 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. (iii) Examples are TiO_2, NaCl, C_6H_6, N_2, Zn and Cd.

b. Paramagnetic substances:

(i) These substances are weakly attracted by the magnetic field. They are magnetised in magnetic field but lose their magnetism in the absence of a magnetic field.

(ii) These substances have permanent magnetic dipoles due to the presence of atoms, molecules or ions containing unpaired electrons.

(iii) Examples are Cu^{2+}, Fe^{3+}, O_2, NO and CuO.

8. Substances having unpaired electrons are classified as:

a. Ferromagnetic substances:

(i) These substances are strongly attracted by a magnetic field and can be made into permanent magnates.

(ii) These substances show magnetism even in the absence of a magnetic field. The large magnetism is due to the spontaneous alignment of magnetic moment.

↑↑↑↑↑↑↑↑

(iii) Examples are Fe, Co, Ni and CrO_2 (used to make magnetic tapes for audio recording).

b. Antiferromagnetic substances:

(i) In these substances, equal number of magnetic moments are aligned in opposite directions so as to give zero net moment.

↑↓↑↓↑↓↑↓

(ii) Examples are MnO, MnO_2 and Mn_2O_3.

c. Ferrimagnetic substances:

(i) In these substances, the number of magnetic moments oriented in one direction out number those in the other direction.

↑↑↓↑↑↓↑↓

(ii) Examples are Fe_3O_4 and ferrites of formula $M^{2+} Fe_3O_4$ where M = Mg, Cu, Zn, etc.

ILLUSTRATIONS

1. 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?

Sol. n-type semiconductors are obtained by doping of a higher group impurity.

Hence, to convert group 14 element to n-type semiconductor, it should be doped with a group 15 element.

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

Sol. Ferromagnetic materials would make better permanent magnets than ferrimagnetic materials because in ferromagnetic solids, the magnetic moments of unpaired electrons spontaneously align themselves in same direction. However, in ferrimagnetic solids the magnetic moments of the domains are aligned in parallel and antiparallel direction in unequal numbers.

PRACTICE PROBLEMS

1. What is the difference between anti ferromagnetic & ferromagnetic substances? What is the cause of this difference?

2. Define : a. Diamagnetism b. Paramagnetism c. Ferromagnetism d. Pyroelectricity.

3. What are ferromagnetic substances?

4. What do you understand by paramagnetism and diamagnetism?

5. Give one example of anti-ferroelectric solid and one example of ferroelectric solid?

6. What is the difference between anti ferromagnetic and ferromagnetic substances? What is the cause of this difference?

7. With the help of electron spin, distinguish between ferromagnetism, anitiferromagnets, ferrimagnets.

IMPORTANT TIPS

1. Main characteristics and examples of some simple ionic solids:

Crystal structure	**Brief description**	**Examples**	**Coordination number**	**Number of formula unit per cell**
Type: AB				
(a) NaCl (Rock salt)	FCC arrangement, Cl^- ions occupy the corners and face centres of a cube while Na^+ ions are present at the body and edge corners.	Halides of Li, K Rb, AgF, AgBr, NH_4Cl, NH_4Br, and NH_4I.	$Na^+ = 6$ $Cl^- = 6$	4
(b) Cesium chloride	BCC arrangement, Cs^+ ions are present at the body centre and Cl^- ions at the corners of a cube or vice versa.	CsCl, CsBr, CsI, CsCN, TlCl, TlI and TlCN.	$Cs^+ = 8$ $Cl^- = 8$	1
(c) Zinc Blende (ZnS)	CCP arrangement in which S^{2-} ions form fcc and each Zn^{2+} ions is surrounded tetrahedrally by four S^{2-} ions and vice versa.	CuCl, CuBr, Cul, AgI, BeS.	$Zn^{2+} = 4$ $S^{2-} = 4$	4
Type: AB				
(a) Fluorite (CaF_2)	CCP arrangement in which Ca^{2+} ions form fcc each Ca^{2+} ion surrounded by eight F^- ions and each F^- ions by 4 Ca^{2+} ions. F^- ions occupy all the tetrahedral voids.	BaF_2, $BaCl_2$, SrF_2, $SrCl_2$, CdF_2, PbF_2	$Ca^{2+} = 8$ $F^- = 4$	4
(b) Anti fluorite (A_2B)	Anions form the ccp arrangement so that each cation is surrounded by four anions and each anion by eight cations. The cations occupy half of the tetrahedral voids.	Na_2O	$Na^+ = 4$ $O^{2-} = 8$	4

2. **The spinel structure:** The compound $MgAl_2O_4$ occurs in nature as the mineral spinel. It has a ccp structure of oxide ions in which one-eight of the tetrahedral voids are occupied by Mg^{2+} ions and one half of the octahedral voids are occupied by Al^{3+} ions. The spiral structure is adopted by mixed oxides like $FeCr_2O_4$, $ZnFe_2O_4$ and $ZnAl_2O_4$.

3. **Extrinsic imperfection:** This type of defect is due to departure from regular chemical composition and is also known as chemical defect.

4. **Piezo electricity:** The electricity or electric polarity produced by the mechanical stress on a crystal.

5. **Pyro electricity:** The electricity or electric polarity produced in a non-conducting crystal by temperature change.

6. **Photo-voltaic:** The substance which coverts sunlight into electricity is called photo-voltaic, e.g., amorphous silica.

7. In NaCl crystal, at room temperature, there are about 10^{22} ions and 10^6 schotty pairs per cm^3. This means that there is one schottky pair defect per 10^{16} ions. Thus, there are large number of holes present in the crystal. This results in the decrease in the density.

8. On applying high pressure, NaCl type structure having 6 : 6 coordination number changes to CsCl type structure having 8 : 8 coordination, number.

9. On apply high temperature, i.e., 760 K, CsCl type structure changes to NaCl type structure.

$$\underset{(6.6)}{\text{NaCl type structure}} \underset{\text{High temperature}}{\overset{\text{High pressure}}{\rightleftharpoons}} \underset{(8.8)}{\text{CsCl type structure}}$$

10. **13 – 15 compounds:** Solid state materials obtained by combination of elements of group 13 and 15, e.g., AlP, GaAs and InSb.

11. **12 – 16 compounds:** Solid state materials obtained by combination of elements of group 12 and 16, e.g., ZnS, CdS, CdSe and HgTe.

    a. TiO, CrO_2 and ReO_3 behave like metals.

    b. Rhenium oxide, ReO_3 is like metallic copper in its conductivity and appearance.

    c. Oxides like VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending on temperature.

PART I VERY SHORT ANSWER QUESTIONS

1. An ionic compound AB_2 possess CaF_2 type crystal structure. Write the coordination number of A^{2+} and B^- ions in crystal of AB_2.
2. What is meant by 'point defects' in crystals?
3. How many atoms are there in a unit cell of a metal crystallising in fcc structure?
4. In a rock-salt structure, how many Na^+ ions occupy second nearest neighbour locations of Na^+?
5. What do you understand by ferrimagnetism?
6. Define coordination number.
7. What is the cause of electrical conductivity in a. metal b. ionic solids c. semiconductors?
8. Why common salt is sometimes yellow instead of being pure white?
9. Which of these two $CdCl_2$ and NaCl will produce schottky defect, if added to a AgCl crystal?
10. Why is Fe_3O_4 ferrimagnetic at room temperature but becomes paramagnetic at 850 K?
11. Name a solid substance in which the cation occupies all of the tetrahedral voids.
12. Name the three types of crystalline structures generally found in ionic solids of the type AB.
13. What is meant by doping?
14. How can you convert NaCl structure into CsCl structure and vice versa?
15. Which type of crystals exhibits piezoelectricity?
16. Which positions are occupied by Na^+ and O^{2-} in Na_2O structure?
17. What is schottky defect relating to crystals?
18. What is frenkel defect?
19. How is ferromagnetism different from paramagnetism?
20. What is the coordination number of an octahedral void?
21. What is the effect of mechanical stress on a piezoelectric crystal?
22. What are coordination number of each ion present in the cubic close packed structure of Na_2O at ordinary temperature and pressure?
23. Why is frenkel defect found in AgCl?
24. Why does pure silicon, which is an insulator, behave as a semiconductor on heating?
25. Give three examples of amorphous solids.
26. What is a body centred cubic?
27. What are stoichiometric defects or intrinsic defects in ionic crystals?
28. Which transition metal oxide has appearance and conductivity like that of copper?
29. What are interstitials in a crystal?

30. Explain the term ‘Dislocations’ in relation to crystals.

31. AgI crystallises in cubic close packed ZnS structure. What fraction of tetrahedral sites are occupied by Ag^+ ions?

32. What causes the conduction of electricity by semiconductors?

33. The unit cell of substances has cation A^+ at the corners of the unit cell and the anion B^- in the centre. What is the simplest formula of the substance?

34. What is the coordination number of HCP and CCP?

35. Why does the conductivity of metals decreases with rise of temperature?

36. A compound AB_2 possess the CaF_2 type crystal structure. Write the coordination numbers of A^{2+} and B^- ions in its crystals.

37. Why does frenkel defect not change the density of AgCl crystals?

38. How does the electrical conductivity of metallic conductors vary with temperature?

39. How does the electrical conductivity of semiconductors vary with temperature?

40. Define void.

41. Mention one property which is caused due to the presence of F-centre in a solid.

42. Name a salt that can be added to AgCl so as to produce cation vacancies.

43. What type of crystal defect is produced when sodium chloride is doped with $MgCl_2$?

44. Define superconductivity of a substance.

45. How does the electrical conductivity of superconductors vary with temperature?

46. What is energy gap in band theory? Compare its size in conductors, semiconductors and insulators?

47. Name the non-stoichiometric point defect responsible for colour in alkali metal halides.

48. What makes the crystal of KCl appear sometimes violet?

49. What are the packing efficiencies of different closed packed structures.

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

PART II SHORT ANSWER QUESTIONS

1. MgO has the structure of NaCl and TlCl has the structure of CsCl. What are the coordination numbers of the ions is MgO and TlCl?

2. A solid AB ad NaCl structure. If the radius of the cation is 100 pm, what is the radius of the anion, B?

3. How do the electrical resistivity of the following classes of material very with temperature: Semiconductor, metallic conductor, superconductor.

4. What is the difference between schottky defects and frenkel defects?

5. Pure silicon is an insulator. Silicon doped with phosphorus is a semiconductor. Silicon doped with gallium is also a semiconductor. What is the difference between the two doped silicon semiconductors?

6. How does amorphous silica differ from quartz?

7. Account for following:

a. Silicon is an insulator but silicon doped with phosphorous acts as a semiconductor.

b. Some of glass objects recovered from ancient monuments look milky instead of being transparent.

8. What is the relation between edge length of a fcc unit cell and radii of cation and anion of ionic solid of type AB? Give two examples of ionic solid of this type.

9. What is the coordination number of each sphere in the following types of closed packed structure of uniform hard spheres:

a. Simple cubic lattice   b. bcc lattice   c. fcc lattice   b. hcp lattice

10. A cubic unit cell has one atom on its each corner and two atoms on its each diagonal. Find the number of atoms in the unit cell.

11. Find the edge length of a unit cell of an element having fcc structure and radius of atom is 100 pm.

12. A metallic element has bcc structure and atoms has radius of 250 pm. Calculate the edge of unit cell.

13. The radius of anion in an ionic solid is 100 pm. Find the radius of cation, which just fits in its

a. cubic hole b. octahedral hole and c. tetrahedral hole.

14. In a face centred cubic arrangement of A and B atoms, A atoms are present at corners and B atoms at face-centres; one of A atoms is missing from one corner in each unit cell. What is the simplest formula of compound?

15. In a compound AX, the radius of A^+ ion is 95 pm and that of X^- ion is 181 pm. Predict the crystal structure of AX and write the coordination numbers of each of the ions.

16. A solid $A^+ B^-$ has NaCl type closed packed structure. If the anion has a radius of 241.5 pm, what should be the minimum radius of cation? Can a cation C^+, having a radius of 50 pm be fitted into tetrahedral hole of crystal $A^+ B^-$?

17. Copper crystallises in fcc lattice and has density of 8.930 g cm^{-3} at 293. K. Calculate the radius of copper atom. Atomic mass of Cu = 63.55 amu, Avogadro's constant, $N_A = 6.02 \times 10^{23}$.

18. A compound AB crystallises in bcc lattice with unit cell edge length of 380 pm. Calculate a. the distance between oppositely charged ions in the lattice, b. radius of A^+ if radius of B^- is 175 pm.

19. A solid AB and NaCl structure. If the radius of cation A+ is 110 pm, calculate the maximum value of the radius of the anion B^-.

20. a. What type of compounds exhibit schottky defect? Give examples.

b. What is the effect on density of crystal due to schottky defect?

c. Mention one example of a compound in which schottky and frenkel defects are present together.

21. a. Crystal gas lighters are based on.....

b. What is the basic principle on which quartz watches work?

c. Give one example of a ferroelectric solid and one example of anti-ferroelectric solid.

22. a. What are molecular crystals? b. Give one example of hydrogen bonded crystals.

c. Give one example of metallic crystal with low melting point of about 100 °C.

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

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

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

26. 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?

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

28. Distinguish between:

a. Hexagonal and monoclinic unit cells. b. Face-centred and end-centred unit cells.

29. Name the parameters that characterise a unit cell.

30. Classify the following as amorphous or crystalline solids:

Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper.

31. 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.

32. Enlist the applications of n-type and p-type semiconductors.

PART III LONG ANSWER QUESTIONS

1. What are the properties of ferromagnets, ferroelectric and piezoelectrics? Give an example of each of these.

2. Describe the general characteristics of metallic crystals.

3. Calculate the number of atoms in different cubic unit cells of monoatomic substances.

4. a. Zinc oxide is white solid at room temperature and is almost non-conducting. On heating, it turns yellow and becomes quite conducting. Explain.

b. Describe the structure of ZnS.

c. The radius of Li^+ is 60 pm and that of F^- is 136 pm. Predict the structure of LiF. What is the coordination number of each ion?

5. What type of substances would make better permanent magnets — ferromagnetic or ferrimagnetic? Justify your answer.

PART IV SKILL ANALYSER

TIME: 30 MIN. **MAX. MARKS: 15**

Directions: (i) Attempt all questions

(ii) Question 1 to 3 carry 1 mark each.

(iii) Question 4 and 5 carry 2 marks each.

(iv) Question 6 carry 3 marks

(v) Question 7 carry 5 marks

1. How many spheres are there in an HCP structure

2. AgI crystallises in cubic close packed ZnS structure. What fraction of tetrahedral sites and octahedral sites are vacant.

3. Define coordination number of a sphere in its own layer in HCP.

4. Copper crystallizes into a fcc lattice with edge length 3.61×10^{-8} cm. Find the density.

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

a. What is the length of the side of the unit cell? b. How many unit cells are there in 1.00 cm^3 of aluminium?

6. 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?

7. Explain the following with suitable examples:

a. Ferromagnetic substances b. Paramagnetic substances

c. Ferrimagnetic substances d. Anti-ferromagnetic substances

e. Diamagnetic substances