Solid State

Solids are characterised by the state of matter in which particles are closely packed and held together by strong inter molecular attractive force.

Properties of Solids :

- (a) In solid state the particles are not able to move randomly.
- (b) They have definite shape and volume.
- (c) Solids have high density.
- (d) Solids have high and sharp melting point which is depend on the strength or value of binding energy.
- (e) They are very low compressible.
- (f) They show very slow diffusion.

Types of Solids :



Crystalline solids :

- (a) In this type of solids the atoms or molecule are arranged in a regular pattern in the three dimensional network.
- (b) They have well defined geometrical pattern, sharp melting point, definite heat of fusion and anisotropic nature.
- (c) Anisotropic means they exhibit different physical properties in all directions.
- e.g. The electrical and thermal conductivities are different directions.
- (d) They are generally incompressible.
- (e) The general examples of crystalline solids are as Quartz, diamond etc.

Amorphous Solids :

- (a) In this type of solids, the arrangement of building constituents is not regular.
- (b) They are regarded as super cooled liquids with high viscosity in which the force of attraction holding the molecules together are so great, that the material becomes rigid but there is no regularity in structure.
- (c) They do not have sharp melting points.
- (d) They are isotropic as they exhibit same physical properties in all the directions.
- (e) The general examples of this solids are as glass, Rubber, plastics etc.

Difference between crystalline and amorphous solids :

Property	Crystalline solids	Amorphous solids
1. Shape	They have definite and regular	They do not have definite and regular
	geometrical form.	geometrical form.
2. Melting point	They have definite melting point	They do not have definite melting point.
Heat of fusion	They have a definite heat of fusion	They do not have definite heat of fusion.
4. Compressibility	They are rigid and incompressible.	These may be compressed to any appreciable extent.
5. Cutting with a Sharp edged tool	They are given cleavage i.e. they break into two pieces with plane surfaces.	They are given irregular cleavage i.e.they break into two pieces with irregular surface.
	Temperature Time	Temperature
6. Isotropy and Anisotropy	They are anisotropic.	They are isotropic.

	— Solved E	xamples ——				
Ex.1	A solid X melts sligh following categories (1) lonic solid	ntly above 273K and is a does it belong : (2) Covalent solid	a poor conductor of hea (3) Metallic	t and electricity. (4) Molecular	To which Ans.	of the (4)
Ex.2	In a crystal, the atom (1) Zero P.E.	ns are located at the posi (2) Infinite P.E.	tion of : (3) Minimum P.E.	(4) Maximum	P.E. Ans.	(3)
Ex.3	Graphite is an exam (1) Ionic solid (3) Vander waal's cr	ple of : ystal	(2) Covalent solid (4) Metallic crystal		Ans.	(2)
Ex.4	Amorphous solids : (1) Possess sharp m (2) Undergo clean cl (3) Do not undergo c (4) Possess orderly a	elting points eavage when cut with kn clean cleavage when cut arrangement over long di	ife with knife istances		Ans.	(3)

STUDY OF CRYSTALS :

• **Crystal** : A crystal is a homogeneous portion of a solid substance made by regular pattern of structural units bonded by plane surface making definite angles with each other.

• **Space lattice :** The arrangement of constituents like atom, ions and molecules in different sites in three dimensional space is called space lattice.

• **Unit cell :** The smallest repeating unit in space lattice which when repeats over and over again, results in a crystal of the given substance called unit cell.



- Face : The plane surface of the crystal are called faces.
- Edge : An edge is formed by the intersection of two adjacent faces.
- Interfacial angles : The angle between the perpendiculars two intersecting faces called interfacial angles.

UNIT CELL

UNIT CELL IN TWO DIMENSIONS :

Now in order to uniquely explain a regular arrangement in two dimensions we need the help of three parameters, two distance parameters and one angular parameter. Based upon their different relationships we can define different cases

> Case 'B'(a \neq b) angle = 90° 0

> > 0

The unit cell formed in this case is a rectangle.

0

0

0 0

The unit cell in such a case is a **square**. Placing such square side by side we will obtain the entire two dimensional arrangement.

UNIT CELL IN THREE DIMENSIONS :

It has six parameters, 3-distance parameters and 3-angular parameter.



a, b, c are lengths of unit cell (also known as the crystallographic axes).

 α , β , γ are known as the crystallographic angles.

DIFFERENT CLASSES OF CRYSTALS :

Based on different permutations of a, b, c and α , β , γ we define different crystal classes.

Seven Crystal System Table · 4

Crystal System	Edge length	Angles	Unit cell found	Examples		
Cubic	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$	SC, BCC, FCC	NaCl, ZnS, Fe, Al, Cu, C		
			(3)	(diamond), CsCl, CaF ₂ , Na ₂ O,		
				KCl, Pb, Alum.		
Tetragonal	$a = b^{1} c$	$\alpha = \beta = \gamma = 90^{\circ}$	SC, BC	Sn (white tin), SnO_2 , TiO_2 , ZnO_2 ,		
			(2)	NiSO ₄ , urea.		
Orthorhombic	a¹b¹c	$\alpha = \beta = \gamma = 90^{\circ}$	SC, BC, FC, EC	Rhombic sulphur, BaSO4, KNO3,		
			(4)	PbCO ₃ , CaCO ₃ (aragonite)		
Rhombohedra	a = b = c	$\boldsymbol{\alpha} = \boldsymbol{\beta} = \boldsymbol{\gamma} 90^{\circ}$	SC	CaCO ₃ (Calcite), HgS(Cinnabar),		
or			(1)	NaNO3, ICl.		
Trigonal						
Hexagonal	$a = b^{-1} c$	$\alpha = \beta = 90^{\circ},$	SC	Graphite, ZnO, CdS, Mg, PbI ₂ ,		
		γ = 120°	(1)	SiC.		
Monoclinic	a b¹c	$\alpha = \gamma = 90^{\circ};$	SC, EC	Monoclinic sulphur, PbCrO ₄		
		β ¹ 120°,	(2)	Na ₂ SO ₄ .10H ₂ O, Na ₂ B ₄ O ₇ .10H ₂ O.		
		¹ 90°, ¹ 60°				
Triclinic	a¹b¹c	α ¹ β ¹ γ ¹ 90°	SC	K ₂ Cr ₂ O ₇ , CuSO ₄ .5H ₂ O, H ₃ BO ₃ .		
			(1)			

Hint for memorise : CaTORacHMT

CHEMISTRY FOR NEET

Note : In 3-D 14 different types of unit cell are found and these are also known as 14 Bravais lattice.

TYPES OF UNIT CELL :

In every crystal class, the positioning of the lattice points may be different. Based upon these different positions occupied by the lattice points, we have different types of unit cells.

- **1. Simple / primitive type of unit cell :** If lattice points or the particles of the solid are present only at the corners of the unit cell.
- 2. Body centred unit cell : lattice point are at the corners as well as at the body centre.
- **3. Face centred unit cell :** lattice points are at corners as well as at each of the face centres.
- **4. End centred unit cell :** lattice points are at the corners as well as at centre of any of two opposite faces.

Each of these arrangements corresponds to a unique and different type of arrangement. These 14 different arrangements are called the 14 Bravais lattices.

In any lattice, the surrounding of each and every lattice point is exactly identical.

MATHEMATICAL ANALYSIS OF CUBIC SYSTEM (TYPES AND ANALYSIS) :

Simplest crystal is to be studied in cubic system. Three types of cubic systems are following.

- (a) Simple Cubic (SC) : Atoms are arranged at the corners of the cube.
- (b) Body Centered Cubic (BCC) : Atoms are arranged at the corners and at the centre of the cube.
- (c) Face Centered Cubic (FCC) : Atoms are arranged at the corners and at centered of the each faces.

Contribution of different Lattice point in one Cubical unit cell :

(i) Contribution from **one corner lattice point** = $\frac{1}{8}$ th.

(shared in 8 identical cubes)

(ii) Contribution from **one face centered lattice point** = $\frac{1}{2}$.









Contribution from *edge centered lattice point* = $\frac{1}{4}$ th.

(iii)

(shared in 2 identical cubes)

(shared in 4 identical cubes)

(iv) Contribution from *body centered lattice point* = 1.

(it is present inside or at the centre of cube)

...

Number of atoms per unit cell / unit cell contents :

The total number of atoms contained with in the unit cell for a simple cubic called the unit cell content.

(a) Simple cubic structure (sc) :

: Each corner atom is shared by eight surrounding cubes. Therefore, it contributes for
$$\frac{1}{8}$$
 of an atom.



(b) Body centered cubic structure (bcc) :

(i) Eight Corner atoms contribute one atom per unit cell.

 $z = 8 \times \frac{1}{8}$

- (ii) Centre atom contribute one atom per unit cell.
- (iii) So, total 1 + 1 = 2 atoms per unit cell.

$$Z = 8 \times \frac{1}{8} + 1 = 2$$



(c) Face centered cubic structure (fcc) :

- The eight corners atoms contribute for $\frac{1}{8}$ of an atom and thus one atom per unit cell. (i)
- (ii) Each of six face centered atoms is shared by two adjacent unit cells and therefore one face centred atom contribute half of its share. Means

$$6 \times \frac{1}{2} = 3$$
 atom per unit cell.

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Τ	•	Ι.
1	•	Ľ
Ζ	•	\boldsymbol{V}

a__

1.

(iii) So, total Z = 3 + 1 = 4 atoms per unit cell.

ATOMIC RADIUS :

(c)

It is defined as the half of the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge (a) of the unit cell of the crystal.

Simple cubic structure [S.C.] (a)

Radius of atom 'r' =
$$\frac{a}{2}$$

(b) Face centered cubic structure (FCC) 'r' = $\frac{a}{2\sqrt{2}}$
(c) Body centered cubic structure (BCC) 'r' = $\frac{\sqrt{3}a}{4}$ a
 $a = b = c$
 $\alpha = \beta = \gamma = 90^{\circ}$

Solved Examples -

- **Ex.5** A compound formed by elements A and B has a cubic structure in which A atoms are at the corners of the cube and B atoms are at the face centres. Drive the formula of the compound.
- Sol. As A atoms are present at the 8 corners of the cube, therefore numbers of atoms of A in the unit cell

$$=\frac{1}{8} \times 8 = 1$$

As B atoms are present at the face centres of the 6 faces of the cube, therefore, numbers of atoms of

atoms of B in the unit cell =
$$\frac{1}{2} \times 6 = 3$$

:. Ratio of atoms A : B = 1 : 3 Hence, the formula of the compound is AB_{a}

- **Ex.6** A cubic solid is made up of two elements X and Y. Atoms Y are present at the corners of the cube and atoms X at body centre. What is the formula of the compound ?
- **Sol.** As atoms Y are present at the 8 corners of the cube, therefore, numbers of atoms of Y in the unit cell = $1/8 \times 8 = 1$

As atoms X are present at the body centre. therefore, numbers of atoms of X in the unit cell = 1

 \therefore ratio of atoms X : Y = 1 : 1

Hence, the formula of the compound is XY

Arrangement of the atom / particles of the solids in three dimensions :

Now having gained a knowledge of some of the terms, let us study how the different arrangements in space are brought about.

Firstly we will focus our attention on the solids containing only one type of lattice points.

The solids which contain only one type of lattice points are:

- metallic solids (eg. Iron)
- molecular solids (eg. dry ice)
- covalent network solids (eg. diamond)

(lonic solids do not fall into this category as they contain more than one type of particles, they will be studied in the later parts of the chapter)

All the atoms or particles of the solids will be represented by solid spheres, each of radius 'r'.

We will be taking these spheres of radius 'r' and explore how we can arrange these in three dimensions. Firstly we will begin with arrangement in one dimension.

ARRANGEMENT IN 1-D: In one dimension it is possible to arrange the spheres in two possible ways.

Not Stable [because the potential energy of the system is not minimum]

2.
$$a = 2r$$

1.

Coordination number = 2

1-D close packing stable arrangement

This is the predominant way of packing in one dimension and as such most of the space lattices will show such an arrangement in one dimension along the planes of close packing.

ARRANGEMENT IN TWO DIMENSION :

In two dimensions also there are two ways of packing the spheres(in moving from one dimension to two dimensions it can be imagined that the two dimensional array will be made up of 1-D closed pack arrays / lines which are stacked one on top of other.

1. Square packing : If the one dimensional arrays are placed on top of one another, we get the square packing in two dimensions.

One sphere will be in contact with 4 other spheres. area of square = $a^2 = 4r^2$

area of atoms in the square = $\frac{1}{4} \times \pi r^2 \times 4 = \pi r^2$



fraction of area occupied by spheres = $\frac{\pi}{4} \frac{r^2}{r^2} = \frac{\pi}{4} = 78\%$

2. Hexagonal close packing : (in 2-D) If in a two dimensional arrangement, every one dimensional array is placed in the cavity of the just preceding array, we get the hexagonal packing in two dimensions.

area of hexagon = 6 ×
$$\frac{\sqrt{3}}{4}$$
 a² = 6 × $\frac{\sqrt{3}}{4}$ × 4r² = 6 $\sqrt{3}$ r²

area of atoms =
$$\pi r^2 + \frac{1}{3} \times 6\pi r^2 = 3\pi r^2$$

fraction of area occupied =
$$\frac{3\pi}{6\sqrt{3}} r^2 = \frac{\sqrt{3}\pi}{6}$$
 91%

As is evident from the above calculations, the spheres are in closer contact in the hexagonal arrangement, hence the hexagonal arrangement is considered to be a better way of packing as compared to the square packing.

• ARRANGEMENT IN THREE DIMENSIONS :

1. Simple cubical arrangement in three dimensions :

(will be made up of 2-D sheets arranged one over other)

The simple cubical packing is obtained by arranging the square pack sheets of two dimension one over the other such that spheres of the second sheet are exactly (vertically) above the spheres of first sheet.



(Note that $\begin{array}{l} \mathbf{a} = \mathbf{b} = \mathbf{c} \\ \alpha = \beta = \gamma = 90^{\circ} \end{array}$, hence crystal thus formed will belong to the cubic crystal class, and as the lattice points are only at the corners, hence the unit cell will be simple, therefore what we get is the **simple cubic**)

(i) Relation between 'a' and 'r'

a = 2r (because atoms along the edge are touching each other)

(ii) Effective no. of atoms per unit cell :

$(Z) = \times 8 = 1$

(iii) Packing fraction :

Volume of atoms in a unit cell ×100% Packing efficiency = Total volume of a unit cell

$$= \frac{\frac{4}{3}\pi}{a^3}r^3 = \frac{4}{3}(2r)^3\pi r^3 = \frac{4\pi}{3\times8}r^3 = 0.52 \text{ (or 52\%)}$$

(Note : This is not a very efficient way of packing as the packing fraction is very low)

(iv) Coordination Number :

It is defined as the number of atoms touching any one particular atom. For simple cubic, coordination number = 6.



this sphere touches the numbered

(v) Density of unit cell : It is the ratio of mass of the spheres present in unit cell and total volume of unit cell.

$$d = \frac{Z(M/N_A)}{a^3 \times 10^{-30}} \text{gcm}^{-3} \quad \Rightarrow \quad d = \frac{ZM}{N_A (a^3 \times 10^{-30})} \text{gcm}^{-3}$$

Where Z = no, of atoms in a unit cell

 M/N_{A} = mass of a single atom

M = molar mass

 N_{A} = Avogadro number (6.023 × 10²³)

2. Body centred cubic :

The body centred cubic is a unique way of packing, as the 2D-arrays that can be imagined to constitute the space lattice are themselves formed in a unique way. The lattice points in the 2D array do not touch each other. The spheres start touching each other only upon moving from 2D to 3D, i.e. when the 2D arrays are placed on top of each other in such a fashion that the spheres of the next plane are into the cavities of the first plane of spheres. The third plane of spheres is then exactly identical to the first plane of spheres.



(i) $a \neq 2r$ (as atoms along the edge are not touching each other) they touch along the body diagonal, hence $\sqrt{3} a = 4r$.

(ii) Effective number of atoms (Z) = 1 +
$$\frac{1}{8}$$
 × 8 = 2.

(iii) Packing fraction =
$$\frac{2 \times \frac{4}{3}\pi r^3}{4 \times 4 \times 4 r^3} \sqrt{3} \times \sqrt{3} \times \sqrt{3} = \frac{\pi \sqrt{3}}{8} 0.68 = 68\%$$

(iv) Coordination No.= 8

(the sphere at the body centre will be touching the spheres at the eight corners)

(v) **Density =**
$$\frac{ZM}{N_A a^3} = \frac{2M}{N_A a^3}$$
 (:: Z = 2)

3. Close packing in three dimensions :

(These are made up of two dimensional hexagonally packed sheets) In second layer we have two kinds of voids.

(i) Voids of second layer below which there are spheres of first layer (all voids of type 'a').

(ii) Voids of second layer below which there are voids of first layer (all voids of type 'b').

For third layer, we have two possibilities.

(A) If spheres of IIIrd layer are placed in voids of IInd layer below which there are spheres of Ist layer (voids of type 'a') then Ist layer and IIIrd layer are identical so this is called AB–AB pattern repeat or hexagonal close packing)



Hcp unit cell : a = 2r = b

(i) Calculation of 'c' :

For the estimation of 'c', consider the spheres marked 1,2,3,4 in the unit cell as shown. These four spheres form a regular tetrahedron. The length of the perpendicular from '4' to the equilateral triangle 1-2-3 will be equal to c/2.





Volume of the hexagon = Area of base x Height.

$$= \frac{6\sqrt{3}}{4} a^2 \times c = \frac{6\sqrt{3}}{4} (4r^2) \times \sqrt{\frac{2}{3}} (4r) = 24 \sqrt{2} \cdot r^3$$

(ii) Effective no. of atoms per unit cell :

 $Z = \frac{1}{6} \times (no. of atoms at corner) + \frac{1}{2} \times (no. of atoms at face centres) + 1 \times (no. of atoms inside$

the body)

$$=\frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 1 \times 3 = 2 + 1 + 3 = 6$$

(iii) Packing fraction : =
$$\frac{\text{volume of the atoms}}{\text{volume of unit cell}} = \frac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}r^3} = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$$

- (iv) Coordination No. : C.N. = 12
- (v) **Density** = $\frac{\text{Mass}}{\text{Volume}} = \frac{\text{ZM}}{\text{N}_{\text{A}}(\text{volume})} = \frac{6\text{M}}{\text{N}_{\text{A}}(\text{volume})}$ (: Z = 6)

(B) ABC-ABC ARRANGEMENT :

If the third layer spheres are placed in those voids of second layer under which there are voids of the first layer of spheres (voids of type 'b'), then the first and the third layer of spheres will not be identical.Such an arrangement will lead to an ABC-ABC type of arrangement.It is also known as the cubical close packing (ccp) or also as the Face Centred Cubic structure (FCC).



(b = octahedral voids)

In the ABC – ABC pattern, the spheres of 4th layer are vertically above the spheres of 1st layer then these consecutive layers are different from each other, fourth layer will be idential to first layer so it will be called ABC – ABC repeat pattern. It is also called the ccp (cubical close packing) because a cubical type of unit cell is used for the study of this arrangement.





(i) Relation between 'a' and 'r' : $a \neq 2r$

 $\sqrt{2}a = 4r$ (as the spheres touch along the face diagonal)

(ii) Effective no. of atoms :

(iii) Packing fraction :
$$\frac{4 \times \frac{4}{3} \pi r^{3}}{4 \times 4 \times 4 r^{3}} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$$

(iv) Coordination number : 12

(v) Density =
$$\frac{Z \times M}{N_A \cdot a^3} = \frac{4 \times M}{N_A \times a^3}$$

Note : In close packings, whenever two consecutive layers are of different kinds(FCC, HCP) then packing efficiency will always be 74%

• TYPES OF VOIDS FOUND IN CLOSE PACKINGS :

Tetrahedral void (3-Dimensional 4 co-ordinate) :

The tetrahedral void is formed whenever a sphere is placed on top of the triangular arrangement as in case of the triangular void.

r = 0.225 R

1.



Location of tetrahedral voids in FCC unit cell :



The FCC unit cell has eight tetrahedral voids per unit cell. Just below every corner of the unit cell, there is one. As there are eight corners, there are eight tetrahedral voids. The spheres 1, 2, 3, 4 form a tetrahedral void.

2. Octahedral void (3-Dimensional 6 coordinate void) The octahedral void is formed whenever two spheres are placed, one on top and the other below a square arrangement of spheres



Location of octahedral voids in a FCC unit cell :

In a FCC unit cell, there are four octahedral voids. They are present at all the edge centres and at

the body centre. The contribution of the edge centre void per unit cell is $\frac{1}{4}$.

Hence, total number of octahedral voids =
$$\left(12 \times \frac{1}{4}\right)$$
 + (1) = 4

edge centres body centre

Note : Let the no. of close packed spheres be N then the no. of octahedral void gemetrated = N and the number of tetrahedral void generated = 2N

3. Cubical void (3-Dimensional 8-coordinate void)

The cubical void is generally not found in closed packed structures, but is generated as a result of distortions arising from the occupancy of voids by larger particles. Along body diagonal

r = 0.732 R



Solved Examples

Ex.7 Sodium has a bcc structure with nearest neighbour distance 365.9 pm. Calculate its density (Atomic mass of sodium = 23)

Sol. For the bcc structure, nearest neighbour distance (d) is related to the edge (a) as $d = \frac{\sqrt{3}}{2}a$

or
$$a = \frac{2}{\sqrt{3}} d = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm}$$

For bcc structure, Z = 2
For sodium, M = 23
 $\therefore D = \frac{Z \times M}{a^3 \times N_0} = \frac{2 \times 23 \text{gmol}^{-1}}{(422.5 \times 10^{-10} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})} = 1.51 \text{ g/cm}^3$

CHEMISTRY FOR NEET

- Solid State
- **Ex.8** X-ray diffraction studies shows that copper crystallizes 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.

Sol.
$$D = \frac{Z \times M}{a^3 \times N_0} \qquad : \qquad M = \frac{D \times a^3 \times N_0}{Z}$$

For fcc lattice, Z = 4 hence,
$$\frac{(8.92 \text{ g cm}^{-3})(3.608 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23} \text{ atoms mol}^{-1})}{4 \text{ atoms}} = 63.1 \text{ g mol}^{-1}$$
$$\therefore \text{ Atomic mass of copper} = 6.3.1$$

- **Ex.9** Density of Li atom is 0.53 g/cm³. The edge length of Li is 3.5 Å Find out the number of Li atoms in a unit cell (N = 6.023×10^{23} , M = 6.94)
- Sol. The aim is to find Z in the formula

$$D = \frac{Z \times M}{a^3 \times N_0}$$

$$Z = \frac{D \times a^3 \times N_0}{M} = \frac{0.53 \text{ gcm}^{-3} \times (3.5 \times 10^{-8} \text{ cm})^3 \times (6.023 \times 10^3 \text{ mol}^{-1})}{6.94 \text{ g mol}^{-1}} = 1.97 \text{ 2}$$

Ex.10 Transition metals, when they form interstitial compounds, the non-metals (H, B, C, N) are accomodated in:

	(1) Occupy tetrahedral(3) Are arranged in ccp	voids	(2) Occupy octahedral(4) Are arrange in hcp	voids	Ans.(3)
Ex.12	In antiflourite structure,	the negative ions -			
Ex.11	In a close pack array of (1) 4N	N spheres, the number (2) N/2	of tetrahedral holes are (3) 2N	- (4) N	Ans. (3)
	(1) Voids or holes in cul(3) Octahedral voids	bic-packed structure	(2) Tetrahedral voids(4) All of these		Ans. (4)

IONIC SOLIDS :

lonic solids are characterised by the presence of atleast two types of particles,viz: the cation and the anion,even the simplest of ionic solids contains one cation and one anion.

The Cations are generally found to be of smaller size, and the anions of larger sizes. The anions thus form the lattice by occupying the lattice positions and the cations are found inside the voids in such structures.

The types of void occupied by the cation would depend upon the the ratio of its radius to that of the anion, popularly termed as the radius ratio. Hence, radius ratio = r_{+} / r_{-}

C.No.	Limiting radius ratio	Type of Void Occupied
3	0.155 – 0.225	Triangular
4	0.225 – 0.414	Tetrahedral
6	0.414 - 0.732	Octahedral
8	0.732 - 0.999	Cubical

Examples of ionic crystals :

(a) Rock Salt (NaCl) Coordination number (6 : 6) NaCl crystallizes in the face centred cubic structure. The chloride ions are present at all the lattice position and the sodium ions occupy all the octahedral voids.



Every sodium is in contact with four chloride ions, and every chloride is in contact with four sodium ions





Caesium chloride (CsCl) structure.

The cesium ion is at the body centre and the chloride ions are at the corners.

(c) Zinc Blend (ZnS) C.No. (4:4)

F.C.C. in S²⁻+ Zn²⁺ in alternate tetrahedral voids



(d) Fluorite structure (CaF_2) C.No. (8 : 4)



CRYSTAL DEFECT (POINT DEFECTS) :

Imperfection can be because of :

- Conditions under which crystals have been developed.

– Impurities

- Temp (because of thermal conductivity some atoms/ions can get displaced

These imperfections can be

(a) Point defects – defects will be only at certain lattice positions.

(b) Line defects - If atoms/ions are misplaced/missing/replaced by some other ions along a line

(c) **Plane (screw) defects** – If atoms/ions are misplaced/missing/replaced by some other ions along a line in a plane.

Types of point defects

Point defect can be classified into three types : (a) stoichiometric defects, (b) impurity defects and (c) non-stoichiometric defect

(a) Stoichiometric defect

These are the point defects that do not distrub the stoichiometry of the solid. They are also called intrinsic ot thermodynamic defects. basically these are two types. Vacancy defecs and interstitial defects.

(i) Vacancy defect : When some of the lattice site are vacant, the crystal is said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.



(ii) Interstitial defect : When some constituent particles (atoms or molecules)

occupy an interstitial site. the crystal is said to have interstitial defect. This defect increases the density of the substance.

Vacancy and interstitial defects as explained above can be shown by non ionic solids. Ionic solids must always maintain electrical neutrality.

Rather than simple vacancy or interstitial defects, they show these defects as Frenkel and schottky defects.



(iii) Frenkel defect : This defect is shown by ionic solids. The smaller ion
 (usually cation) is dislocated from its normal site to an interstitial site. It creates a vacancy defect at its
 original site and an interstitial defect at its new location.
 Frenkel defect is also called dislocation defect. It does not change the density of the solid. Frenkel
 defect is shown by ionic substance in which there is a large difference in the size of ions, for example,
 ZnS, AgCl,AgBr and Agl due to small size of Zn²⁺ and Ag⁺ ions.
 Eg. ZnS, AgCl, AgBr, Agl etc.



(iv) Schottky defect : It is basically a vacancy defect in ionic solids. In order

to maintain electrical netrality. The number of missing cations and anions are equal.

Like simple vacancy defect, schottky defect also decreases the density of the substance, Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately 10⁶ schottky pairs per cm³ at room temperature. In 1 cm³ there are about 10²² ions. Thus, there is one schottky defect per 10¹⁶ ions. Schottky defect is shown by ionic substance in which the cation and anion are of almost similar sizes. For example,NaCl, KCl, CsCl and AgBr.

Note : It may be noted that AgBr shows both, Frenkel as well as schottky defects.



(b) Impurity defects

If molten NaCl containing a little amount of SrCl₂ 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 the other site remains vacant. The cationic vacancies thus produced are equal in number is the solid solution of CdCl₂ and AgCl.



(c) Non-stoichiometric defect

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types : (i) metal excess defect and (ii) metal deficiency defect.

(i) metal excess defect

(a) metal excess defect due to anionic vacancies : Alkali halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapours, 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 atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na⁺ ions. The released electrons diffuse into the crystal and occupy anionic site. As a result the crystal and now has an excess of sodium. The anionc sites occupied by unpaired electrons are called F-centres (from german word farbenzenter for colour centre). They impart yellow colour to the

crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals.



Metal excess defects due to anion vacancies

- **Eg.**: * The excess sodium in NaCl makes the crystal appears yellow.
 - * Excess potassium in KCI makes it violet.
 - * Excess lithium in LiCl makes it pink.

Greater the number of F-centres greater is the intensity of colour. This type of defects are found in crystal which are likely to possess schottky Defects.

(b) metal deficiency defect due to the presence of extra cations at interstitial sites : Zinc oxideis white in colour at room temperature. On heating it loses oxygen and turns yellow.



Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neghbouring interstitial sites.

(ii) metal deficiency defect : There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of $Fe_{0.95}O$. it may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

	— Solved Examples ———				
Ex.13	CsCl has cubic structure. Its density is 3.99 g cm ⁻³ . What is the distance between Cs ⁺ and Cl ⁻ ions ? (At mass of Cs = 133)				
Sol.	CsCl has BCC structure. It has one formula unit in the unit cell So $Z = 1$				
	$D = \frac{Z \times M}{a^3 \times N_0} \text{ or } \mathbf{a}^3 = \frac{Z \times M}{D \times N_0} = \frac{1 \times (133 + 35.5)g \text{ mol}^{-1}}{3.99 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{mlo}^{-1}} = 70.15 \times 10^{-24} \text{ cm}^3$				
	a = $(70.15)^{1/3} \times 10^{-8}$ cm = $(70.15)^{1/3} \times 10^{2}$ pm (1 pm = 10^{-10} cm) = 4.124×10^{2} pm = 412.4 pm Interionic distance = $\frac{\sqrt{3}a}{2} = \frac{1.732}{2} \times 412.4 = 357$ pm				
Ex.14	In a crystal both ions are missing from normal sites in equal number. This is an example of - (1) F-centres (2) Interstitial defect (3) Frankel defect (4) Schetty defect				
Sol.	Schottky defects are arised when one positive ion and one negative ion are missing from their respective positions leaving behind a pair of holes. These are more common in ionic compounds with high coordination number and having almost similar size of cations and anions.				
Ex.15	Frenkel defect is noticed in -				
	(1) AgBr (2) ZnS (3) AgI (4) All Ans (4)				
Sol.	Frenkel defect is arised when the cations are missing from their lattice sites and occupy interstitial sites. As a result of Frenkel defect, density remains unchanged but dielectric constant increases.				
Sol.	 Frenkel defect is arised when the cations are missing from their lattice sites and occupy interstitial sites. As a result of Frenkel defect, density remains unchanged but dielectric constant increases. PROPERTIES OF SOLIDS : Electric Properties : On the basis of electrical conductivity the solids can be broadly classified into the three types: (a) Metals (conductors) (b) Insulators (c) Semi-conductors. Following are salient features of electrical conductance in solids. (i) The electrical conductivity of metallic conductors is due to the motion of electrons or positive holes (electronic conductivity) or through the motion of ions (ionic conductivity) (ii) The conductance through electrons is called n-type conduction and through positive holes is called p-type conduction. (iii) The conductance in insulators and semiconductors is mainly due to the presence of interstitial electrons and positive holes in the solids due to imperfections. (iv) The conductivity of semiconductors and insulators increases with increase in temperature while that of metals decreases. (v) Electrical conductivity of metal is in the order of 10⁶-10⁸ ohm⁻¹ cm⁻¹ while that of inculator is of the order of 10⁻¹² ohm⁻¹ cm⁻¹. Semiconductors have intermediate value in the range 10⁻⁹ ohm⁻¹ cm⁻¹. 				

Based on the behaviour of substances when placed in the magnetic field, they are classified into five classes.

Properties	Description	Alighment	Examples	Application
Diamagnetic	Replled by the magnetic field. They contains paired electron and unpaired	All paired e-	TiO ₂ , V ₂ O ₅ .	Insulator

	electrons are absent. Non metallic elements (excepts O_2 ,S).			
Paramagnetic	Attracted by the magnetic field due to the presence of permanent magnetic dipoles	At least unpaired electron.	O ₂ , Cu ²⁺ , Fe ³⁺ , VO ₂ , CuO	Electronic appliances
Ferromagnetic	Permanent magnetism even in the absence of magnetic field.	Dipoles are aligned in the same direction	Fe, Ni, CO, CrO ₂	CrO ₂ is used in audio and video tapes
Antiferromagn etic	This arises when the dipole alignment is zero due to equal and opposite alignment.		$\begin{array}{llllllllllllllllllllllllllllllllllll$	_
Ferrimagnetic	This arises when there is net dipole moment.	$\uparrow \downarrow \downarrow \downarrow \downarrow \uparrow \downarrow \downarrow$	$FeO_{3}O_{4}$ (Magnetite), ferrites like MgFe ₂ O ₄ , ZnFe ₂ O ₄	_

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

- 1. Calculate the number of formula units in each of the following types of unit cells :
 - (a) MgO in a rock salt type unit cell
 - (b) ZnS in zinc blende structure
 - (c) platinum in a face-centred cubic unit cell.
 - (a) 4 (the same as in NaCl)
 - (b) 4

Sol.

- (c) 4 (1 at the corner, 3 at the face-centres)
- **2.** A mineral having the formula AB₂ crystallises in the cubic close-packed lattice, with the A atoms occupying the lattice points. What is the coordination number of the A atoms and B atoms ? What percentage fraction of the tetrahedral sites is occupied by B atoms ?
- **Sol.** C.N. of A atom = 8 C.N. of B atom = 4
 - tetrahedral sites occupied by atoms B = 100% (all tetrahedral voids are occupied).
- 3. (a) What is the C.N. of Cr atom in bcc structure ?
 - (b) Cobalt metal crystallises in a hexagonal closest packed structure. What is the C.N. of cobalt atom ?
 - (c) Describe the crystal structure of Pt, which crystallises with four equivalent atoms in a cubic unit cell.
- Sol. (a) 8, (b) 12, (c) fcc or cubic close packed.
- **4.** Titanium metal has a density of 4.54 g/cm³ and an edge length of 412.6 pm. In what cubic unit cell does titanium crystallise? (Ti = 48)
- **Sol.** Density $d = \frac{zM}{a^3N_0}$
 - d = 4.54 g/cm³ , M = 48g mol⁻¹ , Z = ? $N_0 = 6.023 \times 10^{23} \text{ mol}^{-1}$

If value of z is known, structure can be decided

$$z = \frac{dN_0a^3}{M} = \frac{4.54 \times 6.023 \times 10^{23} \times (412.6 \times 10^{-10})^3}{48} = 4$$

Thus, titanium has **face-centred cubic** structure.

5. MgO has a structure of NaCl and TiCl has the structure of CsCl. What are the coordination numbers of ions in each (MgO and TiCl).

Sol. C.N. of Na⁺ in NaCl = 6 C.N. of Cl⁻ in NaCl = 6 hence C.N. of Mg²⁺ is also = 6 and that of O⁻⁻ or O²⁻ = 6 in MgO We know in CsCl C.N. of Cs⁺ = 8 C.N. of Cl⁻ = 8 Hence, Ti⁺ and Cl⁻, in TiCl, have also C.N. 8 each.

- 6. A solid AB has the NaCl structure, If radius of cation A⁺ is 120 pm, calculate the maximum possible value of the radius of the anion B[−].
- **Sol.** We know for the NaCl structure, for maximum of radius of B⁻, the ratio r⁺ / r⁻ should be minimum for octahedral void i.e. 0.414.

radius of cation/radius of anion = 0.414

$$\frac{\mathbf{r}_{A^+}}{\mathbf{r}_{B^-}} = 0.414$$
$$\mathbf{r}_{B^-} = \frac{\mathbf{r}_{A^+}}{0.414} = \frac{120}{0.414} = 290 \text{ pm.}$$

- **7.** The C.N. of the barium ion Ba^{2+} , in BaF_2 is 8. What must be the C.N. of F⁻ ion ?
- **Sol.** C.N.of barium ion tells us that it is surrounded by eight fluoride ions (charge $8 \times (-1) = -8$). In order to balance out the eight negative charges, we need four barium ion (charge $4 \times (+2) = +8$). Hence, the C.N. of F⁻ ions must be **4**.
- 8. The radius of calcium ion is 94 pm and of oxide ion is 146 pm. Predict the crystal structure of calcium oxide.
- **Sol.** The ratio $\frac{r_+}{r_-} = \frac{94}{146} = 0.644$

The prediction is an octahedral arrangement of the oxide ions around the calcium. Because the ions have equal but opposite charges, there must also be an octahedral arrangement of calcium ions around oxide ions. Thus CaO structure is similar to Rock Salt(NaCl) structure.

- **9.** Sodium metal crystallises in body centred cubic lattice with cell edge = 4.29 Å. What is radius of sodium atom?
- **Sol.** In 'BCC' structure.

body diagonal = $4 \times r_{Na} = \sqrt{3} \times a$

$$r_{Na} = \sqrt{3} \times 4.29$$
$$r_{Na} = \frac{\sqrt{3}}{4} \times 4.29 = 1.86 \text{ Å}$$

- **10.** CsCI crystallises in a cubic that has a CI⁻ at each corner and Cs⁺ at the centre of the unit cell. If $(r_{Cs+}) = 1.69 \text{ Å}$ and $r_{CI-} = 1.81 \text{ Å}$, what is value of edge length a of the cube?
- Sol. We assume that the closest Cs⁺ to Cl⁻ distance is the sum of the ionic radii of Cs[⊕] and Cl[⊕].

= 1.69 + 1.81 = 3.50 Å

This distance is one-half of the cubic diagonal = $\frac{a\sqrt{3}}{2}$

∴
$$\frac{a\sqrt{3}}{2} = 3.50 \text{ Å}$$
 ∴ $a = 4.04 \text{ Å}$

11. Platinum (atomic radius = 1.38 Å) crystallises in a cubic closest packed structure. Calculate the edge length of the face-centred cubic unit cell and the density of the platinum (Pt = 195).

Sol.
$$r = \frac{a}{2\sqrt{2}}$$
 (for fcc), $a = 2\sqrt{2}$ $r = 3.9$ Å

density = $\frac{ZM}{a^3 N_0} = \frac{4 \times 195}{(3.9 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = 21.83 \text{ g/cm}^3$.

- **12.** Calculate the edge length of the unit cell of sodium chloride given density of NaCl is 2.17×10^3 kg m⁻³ and molecular weight 58.5×10^{-3} kg mol⁻¹.
- **Sol.** NaCl is face-centred cubic lattice so that number of NaCl molecules in a unit cell (z) = 4.

We know density
$$d = \frac{zM}{a^3N_0}$$

where a = length of the unit cell

Volume =
$$a^3 = \frac{Mz}{dN_0} = \frac{4 \times 58.8 \times 10^{-3}}{2.17 \times 10^3 \times 6.02 \times 10^{23}} = 1.79 \times 10^{-28} \text{ m}^3$$

a = 5.64 × 10⁻¹⁰ m
a = 5.64 Å = **564 pm**

13. The effective radius of an iron atom is 1.42 Å. It has a rock-salt structure. Calculate its density (Fe = 56).

Sol. Due to rock-salt (fcc) structure, number of atoms in a unit cell (z) = 4.

Thus, d (density) =
$$\frac{zM}{a^3N_0}$$
 a = 2 √2 r = 2 √2 × 1.42 × 10⁻⁸ cm
∴ d = $\frac{4 \times 56}{6.02 \times 10^{23} \times (2\sqrt{2} \times 1.42 \times 10^{-8})^3}$ = 5.743 g/cm³

- 14. In a CPS (close packed structure) of mixed oxides, it is found that lattice has O²⁻ (oxide ions), and one-half of octahedral voids are occupied by trivalent cations (A³⁺) and one-eighth of tetrahedral voids are occupied by divalent cations (B²⁺). Derive formula of the mixed oxide.
- **Sol.** Number of octahedral voids per ion in lattice = 1

Hence,number of trivalent cations $(A^{3+}) = 1 \times \frac{1}{2} = \frac{1}{2}$ number of tetrahedral voids per ion in lattice = 2Hence,number of divalent cations $(B^{2+}) = 2 \times \frac{1}{8} = \frac{1}{4}$

Thus, formula is $A_{1/2} B_{1/4} O$ or $A_2 BO_4$.

15. If the length of body diagonal for CsCl, which crystallise into a cubic structure with Cl⁻ ions at the corner and Cs⁺ ions at the centre of unit cell, is 7 Å and the radius of Cs⁺ ion is 1.69 Å, what is the radius of Cl⁻ ion ?

Sol. For CsCl structure, body diagonal = $2r_+ + 2r_-$ 7 Å = 2 × 1.69 Å + $2r_-$ 3.5 Å = 1.69 Å + $r_$ r = 3.5 Å - 1.69 Å = 1.81 Å

- **16.** A compound AB crystallises in bcc lattice with unit cell edge length of 380 pm. Calculate (i) the distance between oppositely charged ions in the lattice, (ii) radius of A⁺ if radius of B⁻ is 175 pm. (assuming that cation fits exactly in the cubic void)
- **Sol.** In bcc structure, body diagonal = 2 ($r_+ + r_-$) If 'a' is the edge length of unit cell, then Body diagonal = a $\sqrt{3} = 2(r_+ + r_-)$
 - (i) The distance between oppositely charged ions,

$$(r_{+} + r_{-}) = \frac{a.\sqrt{3}}{2} = \frac{380 \times 1732}{2} = 329.1 \text{ pm}$$

(ii) For exact fitting the radius ratio for cubic void,

$$\frac{r_{+}}{r_{-}} = 0.732$$

$$\therefore$$
 r₊ = 0.732 × 175 pm = 128.1 pm

17. The density of NaCl is 2.163 g cm⁻³. The edge length of its cell is 564 pm. Calculate value of Avogadro's number. Molar mass of NaCl is 58.45 g.

Sol. Density,
$$d = \frac{zM}{a^3N_A}$$

$$N_{A} = \frac{zM}{da^{3}} = \frac{4 \times 58.45 \text{ g mol}^{-1}}{(564)^{3} \times 10^{-30} \text{ cm}^{3} \times 2.163 \text{ g cm}^{-3}} = 6.02 \times 10^{23}$$