

ST. LAWRENCE HIGH SCHOOL A JESUIT CHRISTIAN MINORITY INSTITUTION STUDY MATERIAL FOR CHEMISTRY (CLASS-11) <u>TOPIC-</u> SOLID STATE <u>PREPARED BY</u>: MR. ARNAB PAUL CHOWDHURY



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"Solid state of matter possesses fixed mass, volume, shape and rigidity ".

Solids are classified on the basis of arrangement of constituent particles. Due to their specific arrangements, it shows wide range of properties and hence varied applications like as superconductors, magnetic materials, polymers etc.

GENERAL CHARACTERISTICS OF SOLID STATE:

In nature the particular state of matter is governed by two opposing forces at given set of temperature and pressure. These forces are intermolecular force of attraction and thermal energy. If intermolecular force of attraction is high as compared to thermal energy, particles remains in closest position and hence very less movement in particles is observed. In this case solid state is the preferred state of matter.

Let us revise the general characteristics of solid:

- i) Fixed mass, volume and shape
- ii) Strong intermolecular force of attraction
- iii) Least intermolecular space
- iv) Fixed position of constituent particles
- v) Incompressible and rigid

CLASSIFICATION OF SOLIDS:

Solids are classified on the basis of arrangement of their constituent particles. If the arrangement of constituent particles is same throughout the solid (long range order) it is called *crystalline*. If the arrangement of particles does not follow any regular pattern throughout the solid (short range order) it is called *amorphous* solid.



Characteristics of crystalline solid:

- It consists of large number of small crystals having a definite geometrical shape.
- The arrangement of constituent particles is regular throughout the solid (long range order). That is a fixed pattern of constituent particles repeat itself periodically over the entire range of solid.
- They have sharp melting points.
- They are anisotropic in nature.

Anisotropy is defined as" Difference in properties when measured along different axes or different directions".

Crystalline solid show different values of some of the physical properties like electrical resistance, refractive index etc.when measured along the different directions. The anisotropy arises due to the different arrangement of particles in different directions. Look the different arrangement of particles along the axis AB and CD in diagram given below.



Characteristics of amorphous solid:

- The arrangement of constituent particles is irregular throughout the solid. Regular pattern of constituent particle is visible in small areas only. That is it shows short-range order.
- Melting point is not sharp. Amorphous solid melts over a range of temperature.
- They have tendency to flow at slower rate.
- They are isotropic in nature.

"Isotropic means no difference in properties taken from any direction."

Property	Crystalline solid	Amorphous solid
Order of arrangement	Long-range order	Short-range order
Shape	Definite shape	Irregular shape
Melting point	Sharp melting point	Melting point is not
		sharp.
Heat of Fusion	Definite and	Heat of fusion is neither
	characteristic heat of	definite and nor
	fusion	characteristic
Anisotropy	Anisotropic	Isotropic

Difference between crystalline solid and amorphous solid as follows:

Intext Questions:

- **Q.1** Classify the following solids as crystalline and amorphous. Sodium chloride, quartz glass, quartz, rubber, polyvinyl chloride, Teflon
- **A.1 Crystalline solid:** Sodium chloride, Quartz

Amorphous solid: Quartz glass, rubber, polyvinyl chloride, Teflon.

Q.2 why glass is considered as super cooled liquid?

A.2 Glass shows the tendency to flow at slower rate like liquid. Hence they considered as super cooled liquid.

Q.3 why the window glass of old buildings show milky appearance with time?

A.3 Glass is an amorphous solid. Amorphous solid has the tendency to develop some crystalline character on heating. Due to heating in day over the number of years, glass acquires some crystalline character and show milky appearance.

Q.4 why the glass panes fixed to window or doors of old building become slightly thicker at bottom?

A.4 Glass is super cooled liquid. It has the tendency to flow down very slowly. Due to this glass pane becomes thicker at the bottom over the time. **Q.5** Sodium chloride is a crystalline solid. It shows the same value of refractive index along all the direction. True (False, Cive reason)

refractive index along all the direction. True/False. Give reason.

A.5 False

Crystalline solid shows anisotropy in properties. That is, it shows different values for the given physical property in different direction. All the crystalline

solids show anisotropy in refractive index. Therefore sodium chloride will show different values of refractive index on different directions.

Q.6 Crystalline solid are anisotropic in nature. What does this statement means?[CBSE 2011]

A.6 Anisotropy is defined as" Difference in properties when measured along different axis or from different directions". Crystalline solid show different values of some of the physical properties like electrical resistance, refractive index etc.when measured along the different directions. The anisotropy in crystalline solid arises due to the different arrangement of particles in different directions.

CLASSIFICATION OF CRYSTALLINE SOLIDS:

Crystalline solid can be classified on the basis constituent particles and intermolecular force of attraction in between them. Constituent particles are molecules, ions, metal kernel in sea of electrons and atoms. Force of attraction operate in between the particles are dispersion force, dipole-dipole interaction, hydrogen bonding, electrostatic attraction, metallic bonding and covalent bonding.

Classification with properties of solid in tabular form:

Classification with properties	of solid in tabular form:
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Types of solid	Constituen t particles	Attractive force	Exampl es	Phys ical natu re	Electrical conductiv ity	Melti ng point
1.Molecular solid i) Non-polar	Molecules	Dispersion or London forces	H ₂ , I ₂ , CCl ₄	soft	Insulator	Very Low
ii) Polar	molecules	Dipole- dipole interaction s	HCl, SO ₂	soft	Insulator	Low
iii) Hydrogen Bonded	molecules	Hydrogen bonding	H ₂ O(Ice)	hard	Insulator	Low
2. Ionic Solid	Ions	Electrostat ic force	NaCl	hard	Insulator in solid state but conductor in molten or aqueous state	High
3. Metallic solid	Kernels in sea of electrons	Metallic bonding	Fe, Cu	Hard	Conductor	high
4.Covalent or network solid	Atoms	Covalent bonding	SiO ₂ , C(diamo nd), C(graphi te)	Hard or soft	Insulator	Very high

Intext Questions:

- Q.1 Classify the following solids as Molecular, ionic, metallic or covalent solid. P₄O₁₀, graphite, (NH₄)₃PO₄, brass, SiC, Rb, I₂, LiBr, P₄, Na₂SO₄, Cu, H₂
- A.1 Ionic solid: LiBr, (NH4)3PO4 , Na2SO4

Metallic solid: Brass, Rb, Cu Molecular solid: P₄O₁₀, I₂, P₄, H₂ Covalent solid: Graphite, SiC

Q.2 what type of interactions hold the molecules together in a polar molecular solid.[CBSE 2010]

A.2 The molecules in a solid are held together by van der Waals forces. The term van der Waals forces include hydrogen bonding, dipole-dipole attraction and London dispersion forces. All molecules experience London dispersion forces. In addition, polar molecules can also experience dipole-dipole interactions. So, the interactions that holds the molecule together in polar molecular solid are London dispersion force and dipole-dipole interactions.

Q.3 Write a feature that will distinguish a metallic solid from an ionic solid. [CBSE 2010]

A.3 Metals are malleable and ductile whereas ionic solid are hard and brittle. Metallic solid has typical metallic lustre. But ionic solid looks dull.

Q.4 Write a point of distinction between a metallic solid and an ionic solid other than metallic lustre? [CBSE 2012]

A.4 Metals are malleable and ductile whereas ionic solid are hard and brittle. **Q.5** Write a distinguish feature of metallic solid. [CBSE 2010]

A.5 The force of attraction in between the constituent particles is special kind of electrostatic attraction. That is the attraction of positively charged kernel with sea of delocalized electrons.

Q.6 which group of solid is electrical conductor as well as malleable and ductile? [CBSE 2013]

A.6 Metallic solid

Q.7 why graphite is good conductor of electricity although it is a network (covalent solid)?

A.7 The exceptional property of graphite is due to its typical structure. In graphite, each carbon is covalently bonded with 3 atoms in same layer. The fourth valence electron of each atom is free to move in between different layers.

This free electron makes the graphite a good conductor of electricity.

DO YOU KNOW?

Pseudo solids: Pseudo solids can easily distort by applying forces. It has the tendency to flow. Glass is an example of pseudo solid.

Isomorphism: The existence of two or more crystalline solids having similar chemical composition in the same crystalline form is called **isomorphism**. For example: Na₃PO₄ and Na₃AsO₄. Or in simple words we can say that "similar chemical composition and same crystalline form ".

Polymorphism: The existence of one compound in more than one crystalline form is called polymorphism and different crystalline form is known as polymorph. For example: CaCO₃ exist in two crystalline form named as calcite and aragonite.

This is similar to allotropy in elements.

CRYSTAL LATTICE AND UNIT CELL

The characteristic feature of crystalline solid is regular and repeating arrangement of constituent particles in space. *The regular three dimensional arrangement of constituent particle in a crystal is known as crystal lattice.* The smallest part of the crystal lattice is known as *unit cell*. Look at the role of unit cell in crystal lattice.



A unit cell is characterised by 6 parameters:

- 3- edges a, b and c (refer the diagram given above). The edges may or may not be perpendicular to each other.
- 3 angles a (between b and c) , β (between a and c) and γ (between a and b). Classification of unit cell:

i) Primitive unit cells: The constituent particles are only present at corners of unit cell.

ii) Centred unit cells: The constituent particles occupy other positions also beside the corners.

Centred unit cell can be further classified into 3-types:

a) Body- centred unit cells: Other than corner it contains one constituent particle at the centre of the body of unit cell.

b) Face-centred unit cells: Other than corner it contains one constituent particle at the centre of each face of unit cell.

c) End- centred unit cells: Other than corner it contains one constituent particle at the centre of any two opposite faces of unit cell.

On the basis of 6 parameters (3 edges and 3 angles) of unit cell mentioned above, total seven types of primitive unit cells are possible. The primitive

unit cells show variations in form of centred unit cells. The total number of possible unit cells (primitive and centred) in 3-dimensional lattice is 14. This is called *Bravais Lattice*. The detail of the lattice structure in tabular form is given below.

Point to be noted is primitive unit cell structure is 7 but total (primitive + centred) is 14.

Crystal System	Possible variations	Edge length	Axial angles
CUBIC	Primitive	a=b=c	α=β=γ=90°
	Body-centred		
	Face-centred		
TETRAGONAL	Primitive	a=b≠c	α=β=γ=90°
	Body-centred		
ORTHORHOMBIC	Primitive	a≠b≠c	α=β=γ=90°
	Body-centred		
	Face-centred		
	End-centred		
HXAGONAL	Primitive	a=b≠c	α=β=90°, γ=120°
RHOMBOHEDRAL or	Primitive	a=b=c	α=β=γ≠90°
TRIGONAL			
MONOCLINIC	Primitive	a≠b≠c	α=γ=90°, β≠90°
	End-centred		
TRICLINIC	Primitive	a≠b≠c	α ≠β ≠γ≠ 90°

The structure of above mentioned 14 Bravias lattice is as follows:



NUMBER OF ATOMS IN UNIT CELL

Primitive unit cell: In Primitive unit cell, atoms are present at corner only. An atom is shared by 8 unit cell. Hence only 1/8 th of the atom belong to particular unit cell. There are total 8 corners in each unit cell therefore, 1/8 part of 8 atoms would give the value of number of atoms per unit cell. In brief

8 corners , 1 atom at each corner

1/8 of each atom in unit cell



Centred unit cell (body-centred):

a) Body-centred unit cell -



Number of atoms present at different position is as follows:

- 8 corners, 1 atom at each corner (1/8 of each atom in unit cell)
- 1 atom at centre of body (1 atom completely present in the unit cell) Total number of atom present in each unit cell:

= Contribution of atoms at corner + contribution of atom at the centre of the body

a) Face-centred unit cell -



Number of atoms present at different position is as follows:

- 8 corners, 1 atom at each corner (1/8 of each atom in unit cell)
- 6 faces, 1 atom at each face of unit cell (¹/₂ of each atom in the unit cell)

Total number of atom present in each unit cell:

= Contribution of atoms at corner + contribution of atom at the face of unit cell

Intext Questions:

Q.1 How many atoms can be assigned to its unit cell if an element forms (i) body centred cubic cell, and (ii) a face centred cubic cell? [CBSE 2005, 2008, 2009]

A.1 (i) For body centred unit cell:

(ii) For face centred unit cell:

Q.2 How many lattice points are there in one unit cell of following lattices? (i) body centred cubic cell, and (ii) a face centred cubic cell?

A.2 (i) For body centred unit cell:

8 lattice points at corner + 1 lattice point at centre of the body = 9 lattice points

(ii) For face centred unit cell:

8 lattice points at corner + 6 lattice point at face-centre of each face = 14 lattice points

Q.3 A cubic solid is made of two elements X and Y. Atoms Y are at the corners of the cube and X at the body centre. What is the formula of the compound? [CBSE 2006]

A.3 Number of X atom per unit cell = 1

Number of Y atom per unit cell = $1/8 \times 8 = 1$

Formula of compound = XY

Q.4 What is the number of atom in a unit cell of simple cubic crystal?[CBSE (F) 2010]

A.4 8 Corners x 1/8 atom at each corner =1 atom per unit cell

Q.5 A cubic solid is made of two elements X and Y. Atoms Y(anions) are at the corners of the cube and X(cations) at present at face-centre of the cubic lattice. What is the formula of the compound?

A.5 Number of X atom per unit cell = $1/2 \times 6 = 3$

Number of Y atom per unit cell = $1/8 \times 8 = 1$

Formula of compound = XY_3

CLOSED PACKED STRUCTURE

As we the constituent particles in solid are in form of sphere. The spheres in solid are arranged in different way to leave minimum vacant space. These arrangements of spheres in different layers form the closed packed structure

of solid. The crystals are formed in closed packed structures. Similarly spheres in solid are also arranged in 3-dimension to form close-packed structure.

- a) Close-packing in one-dimension :
- Spheres are arranged in a row with touching each other as shown below :



b) Close-packing in two- dimension :

There are two possible ways to arrange spheres in two dimensions.

- (i) Square-closed packing in two dimension :
- · Sphere in the first row are exactly aligned with sphere of second row.



In this type of arrangement, each sphere is in contact with 4 other sphere that forms a square. The 4 other sphere that are in direct contact of the central sphere is known as *nearest neighbour*. Since each layer is exactly same, this type of arrangement is known as AAA type of closed packing.

- (ii) Hexagonal-closed packing in two dimension:
- Spheres in the second row are fit in the depression of first row.



In this type of arrangement, each sphere is in contact with 6 other sphere that forms a hexagon. Here the number of nearest *neighbour* is 6. The second layer is not exactly aligned with the first layer hence it is termed as B. The third layer is aligned exactly with first layer. This type of arrangement is known as ABAB type of closed packing.

c) Close-packing in three - dimension:

A 3-dimensional network is made by placing two 2-dimensional layers one above another. Therefore there are also two different ways to arrange the sphere in 3-dimension.

- (i) Square closed packing in three dimension :
- Spheres in the second layer are exactly placed above the first layer.



In this type of arrangement spheres of both the layers are perfectly aligned horizontally and vertically. This type of arrangement is known as AAA type closed packing of sphere in 3-dimension. The possible smallest geometrical 3-dimensional shape would be cube. Thus this type of arrangement generate simple cubic lattice with primitive type of unit cell.

(i) Hexagonal closed packing in three dimension:

- Placing second layer over the first layer-
 - Spheres in the second layer are fit in the depression of first layer.



Let the number of close packed spheres be N, then: The number of octahedral voids generated = N The number of tetrahedral voids generated = 2N

Placing the third layer above second layer –

- Covering tetrahedral voids : If all the tetrahedral voids of second layer is covered by third layer, then third layer would be exactly aligned with the first layer as shown below :

The alignment of second layer is different from first layer hence it is mentioned as layer B. Two types of triangular voids are generated in this type of arrangement.

Tetrahedral voids:

Triangular voids in first layer are covered by sphere of second layer. A regular tetrahedron is formed when centres of all 4 sphere is joined.



Octahedral voids:

Triangular voids in first layer are not covered by sphere of second layer. The triangular void in second layer is above the triangular void of first layer. A regular octahedron is formed when centres of all 6 sphere is joined.





Hexagonal close packing (ABABAB...)

This forms the ABA... type of arrangement of sphere and is known as *Hexagonal closed packing* (hcp).

Covering octahedral voids: If all the octahedral voids of second layer is covered by third layer, then <u>third layer would not be exactly aligned</u> with the first layer as shown below :



This forms the ABCABC... type of arrangement of sphere and is known as *Cubic closed packing* (ccp) or *face centred cubic* (fcc) structure. Coordination number: The number of nearest neighbour touching a particle in closed packed structure is known as the coordination number of constituent particles.

In both type of crystal lattice (hcp, ccp or fcc) the coordination number for the constituent particle is 12.

Formula of compound:

Formula of the compound is deduced by calculating number of atoms present at lattice point and number of atoms present in voids. Generally anions are bigger and they occupy the lattice point while cations are occupied in voids.

In a given compound, it is not necessary that all the voids are occupied by constituent particles. Some time only fraction of voids are occupied depend on the formula of compound. Therefore it is necessary to know the position of voids in crystal lattice.

Position of tetrahedral voids in ccp or fcc :



To understand this structure divide the unit cell of <u>ccp</u> in 8 small cubes as shown above. Each small cube contains 4 constituent particles at alternate lattice point. If we join all the lattice point, it will form a regular tetrahedron. So, Total 8 cubes per unit cell means 8 tetrahedral voids per unit cell. As we know number of atom per unit cell for <u>ccp</u> is 4. Therefore:

The number of tetrahedral voids generated = 2N(twice the number of atom per unit cell)

Position of octahedral voids in ccp or fcc :



If all the face-centres of fcc unit cell is joined it will form the regular octahedron and is located at the centre of the body.

Beside the body-centre, edge-centre is also surrounded by 6 constituent particles form an octahedron. But in this octahedron 4 atoms belong from same unit cell (2 from the corners and 2 from the face-centres) and 2 from adjacent unit cell. -Each edge is shared by 4 unit cell therefore contribution of each atom in unit cell present on edge is ¹/₄

- There are total 12 edges in each unit cell. Contribution of atoms from edges in unit cell = $12 \times \frac{1}{4} = 3$.

Total number of octahedral voids = 1(body-centre) + 3(edge-centre) = 4

As we know number of atom per unit cell for ccp is 4. Therefore: The number of octahedral voids generated = N(number of atoms per unit cell)

Intext Questions:

Q.1 A compound is formed by two element A and B. Element B occupy all the *ccp* position and element A occupy all the octahedral voids. Find the formula of compound.

A.1 In ccp number of atoms per unit cell = 4

Number of octahedral voids = same as number of atoms present at ccp = 4

Number of atoms of element B (at ccp) = 4

Number of atoms of element A (octahedral voids) = 4

Ratio of element A : B = 4 : 4 = 1 : 1

Formula of compound = AB

Q.2 A compound is formed by two elements A and B. The element B form *ccp* and element A occupy 2/3 of tetrahedral voids. What is the formula of compound?

A.2 Let the number of atoms of element B form ccp: N The number of tetrahedral voids would be: 2N

Since 2/3 of tetrahedral voids are occupied therefore number of atom of element A would be: $2N \times 2/3 = 4/3 N$

Ratio of element A: B = 4/3: 1 or

Simple whole number ratio A: B = 4: 3

Formula of compound: A₄B₃.

Q.3 An oxide of aluminium is formed where oxide ions occupy all the *hcp* positions and aluminium ion occupy 2/3 of octahedral voids. What is the formula of compound?

A.3 Let the number of atoms of oxide form hcp: N

The number of aluminium ions in octahedral voids would be: N

Since 2/3 of octahedral voids are occupied therefore number of aluminium ion would be: N x 2/3 = 2/3 N

Ratio of element Aluminium ion: oxide ion = 2/3N: 1N or

Simple whole number ratio Aluminium ion: oxide ion = 2: 3

Formula of compound: AI_2O_3 .

Q.4 What is the coordination number of each type of ion in rock-salt type crystal structure. [CBSE 2008]

A.4 Rock salt (NaCl) has fcc type of crystal structure.

In fcc the cations in voids touches 6 nearest neighbour as well as anion at lattice point also touches 6 nearest neighbour.

Coordination number of Na⁺ = 6 Coordination number of Cl⁻ = 6 **Q.5** what is the two-dimensional coordination number of a molecule in square-closed packed layer. [CBSE(F)2013] **A.**54 **PACKING EFFICIENCY:**

Packing efficiency is defined as percentage of total space filled by the constituent particles in crystal.

Packing efficiency in *hcp* and *ccp* structures:

Let us consider the unit cell of ccp in which sphere ABCDEFGH are occupied at corner. And sphere a,b,c,d,e,f are placed at centre of face.



Let the unit cell edge length be 'a' and face diagonal AC = b.

For calculation of packing efficiency consider the right angle triangle ABC.

In triangle ABC

 $AC^{2} = BC^{2} + AB^{2}...(1)$ AC = b(face diagonal), BC and AB = a (edge length)Putting the value of AB, BC and AB in above eq..(1) we get $b^{2} = a^{2} + a^{2}$ $b^{2} = 2a^{2}$ $b = \sqrt{2}a...(2)$ If r is the radius of the sphere, we find b = 4r ...(3)By equating eq..(2) and (3) we get $4r = \sqrt{2}a$ $a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}r \text{ or}$ $r = \frac{a}{2\sqrt{2}}$

Number of atom per unit cell in ccp = 4Volume of the sphere is $= \frac{4}{3}\pi r^3$ So, the volume of each unit cell: $4 \ge \frac{4}{3}\pi r^3$ Volume of cube $= a^3$ Therefore, $Packing efficiency = \frac{Volume occupied by four spheres in the unit cell}{Total volume of the unit cell (volume of cube)} \times 100$

$$=\frac{4 \times \frac{4}{3}\pi r^{3}}{(2\sqrt{2}r)^{3}} \times 100$$
$$=\frac{\frac{16}{3}\pi r^{3}}{16\sqrt{2}r^{3}} \times 100$$
$$= 74\%$$

Packing efficiency = 74 %

Packing efficiency in Body-centred cubic structures:

Now consider the unit cell of body-centred cubic in which sphere ABCDEFGH are occupied at corner. And sphere c is placed at body-centre of unit cell as shown below:



In Δ ABG,

 $b^{2} = a^{2} + a^{2}$ $b^{2} = 2a^{2}$ $b = \sqrt{2}a = 2a$ Now in Δ ADG $c^{2} = a^{2} + b^{2}$ $= a^{2} + (\sqrt{2}a)^{2}$

 $= 3a^2$

The length of the body diagonal c is equal to 4r, where r is the radius

of the sphere (atom). Therefore, c = 4r....(5)Equating eq..(4) and (5) we get $\sqrt{3}a = 4r$ $a = \frac{4r}{\sqrt{3}}$ or $r = \frac{\sqrt{3}}{4}a$

Number of atom per unit cell in body-centre structure = 2 Volume of the sphere is = $\frac{4}{3}\pi r^3$ So, the volume of each unit cell: 2 x $\frac{4}{3}\pi r^3$ Volume of cube = a³

Therefore,

Packing efficiency =
$$\frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell (volume of cube)}} \times 100$$
$$= \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4}{\sqrt{3}}r\right)^3} \times 100$$
$$= \frac{\frac{8}{3} \pi r^3}{\frac{64}{3\sqrt{3}}r^3} \times 100$$
$$= \frac{68 \%}{9}$$
Packing efficiency = 68 %

Packing efficiency in simple cubic lattice:

In the unit cell of simple cubic lattice, the atoms are occupied only at corner of unit cells.



The edge length 'a' of a cube is equal to twice of the radius of each atom. Or, a = 2rThe volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$ Number of atom per unit cell in simple cubic crystal = 2 Volume of the sphere is $= \frac{4}{3}\pi r^3$ So, the volume of each unit cell: $1 \ge \frac{4}{3}\pi r^3$ Volume of cube = a^3 Therefore, Packing efficiency = $\frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell (volume of cube)}} \times 100$ $= \frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} \times 100$ $= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100$ = 52.4%Packing efficiency = 52.4 %

CALCULATION INVOLVING UNIT CELL DIMENSIONS

Formula used to calculate the dimensions of unit cell is as follows:

 $d = \frac{z M}{a^3 N_A}$ d = density of the unit cell z = Number of atoms present in unit cell M = Molar mass of the element a = Edge length of cube N_A = Avogadro number constant Out of the five parameters (d, z M, a and N_A), if any four are known, we can determine the fifth one.

Intext Questions:

Q.1 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. [CBSE 2010] A.1 Formula used:

$$d = \frac{z M}{a^3 N_A} Or$$
$$M = \frac{d a^3 N_A}{a^3 N_A} Or$$

zd = 10.5 g cm⁻³, a = 4.07 × 10⁻⁸ cm , N_A = 6.022 x 10²³ atoms mol⁻¹ Number of atoms per unit cell (z) = 4 (for fcc) Putting the values in above formula we get:

$$M = \frac{d a^{3} N_{A}}{z}$$

= $\frac{10.5 \text{ g cm}^{-3} \times (4.07 \times 10^{-8} \text{ cm})^{3} \times 6.022 \times 10^{23} \text{ atoms mol}^{-1}}{4 \text{ atoms}}$
= 107.09 g mol⁻¹

Q.2 Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm⁻³, calculate atomic radius of niobium using its atomic mass 93 u.[CBSE 2008]

A.2 Formula used:

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

Given values are: $d = 8.55g \text{ cm}^{-3}$ z = 2 (for bcc)Since atomic mass is 93 u, Molar mass would be $M = 93 \text{ g mol}^{-1}$ $N_A = 6.022 \text{ x } 10^{23}$ Putting the values in given formula we can calculate the edge-length 'a'



The edge length 'a' of a cube is equal to twice of the radius of each atom. Or, a = 2rThe volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$ Number of atom per unit cell in simple cubic crystal = 2 Volume of the sphere is $= \frac{4}{3}\pi r^3$ So, the volume of each unit cell: $1 \ge \frac{4}{3}\pi r^3$ Volume of cube = a^3 Therefore, Packing efficiency = $\frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell (volume of cube)}} \times 100$ $= \frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} \times 100$ $= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100$

= 52.4 % Packing efficiency = 52.4 %

CALCULATION INVOLVING UNIT CELL DIMENSIONS

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d = density of the unit cell z = Number of atoms present in unit cell M = Molar mass of the element a = Edge length of cube N_A = Avogadro number constant Out of the five parameters (d, z M, a and N_A), if any four are known, we can determine the fifth one.

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A.2 Formula used:

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

Given values are: $d = 8.55g \text{ cm}^{-3}$ z = 2 (for bcc)Since atomic mass is 93 u, Molar mass would be $M = 93 \text{ g mol}^{-1}$ $N_A = 6.022 \text{ x } 10^{23}$ Putting the values in given formula we can calculate the edge-length 'a'

$$a^{3} = \frac{z M}{d N_{A}}$$

$$= \frac{2 \times 93 \text{ g mol}^{-1}}{8.55 \text{ g cm}^{-3} \times 6.022 \times 10^{23} \text{ atoms mole}^{-1}}$$

$$a = \left(\frac{930}{8.55 \times 3.01}\right)^{1/3} \times 10^{-8} \text{ cm}$$
To solve this $\left(\frac{930}{8.55 \times 3.01}\right)^{1/3}$ take the log

$$\log x = \log \left(\frac{930}{8.55 \times 3.01}\right)^{1/3}$$

$$= \frac{1}{3} (\log 930 - \log 8.55 - \log 3.01)$$

$$= \frac{1}{3} (2.9685 - 0.9320 - 0.4786)$$

$$= \frac{1}{3} (1.5579)$$

$$= 0.5193$$

$$x = \text{antilog} (0.5139)$$

$$= 3.306$$

Therefore a = 3.306×10^{-8} cm

For calculating the radius of Niobium, the relation between edge lengths a and r (body-centred cubic) is as follows:

$$r = \frac{\sqrt{3}}{4}a$$

$$= \frac{\sqrt{3}}{4} \times 3.306 \times 10^{-8} \text{ cm}$$

$$= \frac{1.732 \times 3.306 \times 10^{-8} \text{ cm}}{4}$$

$$= 1.4315 \times 10^{-8} \text{ cm}$$

$$= 1.4315 \times 10^{-10} \text{ m}$$

$$= 143.15 \times 10^{-12} \text{ m}$$

$$= 143.15 \text{ pm}$$

Q. 3 Aluminium crystallises in a cubic close-packed structure. It's metallic [CBSE 2011] 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 cm³ of aluminium? A.3 (i) For fcc unit cell: $r = \frac{a}{2\sqrt{2}}$ $a = 2\sqrt{2}r$ = 2 x 1.414 x 125 pm = 354 pm (ii) Total volume of unit cell = a3 At first convert the value of a in cm from pm $1 \text{ pm} = 10^{-10} \text{ cm}$ $a = 354 \text{ pm} = 354 \text{ x} 10^{-10} \text{ cm} \text{ or} 3.54 \text{ x} 10^{-8} \text{ cm}$ Then $a^3 = (3.54 \times 10^{-8} \text{ cm})^3$ = 44.36 x 10⁻²⁴ cm³ $= 4.4 \times 10^{-23} \text{ cm}^3$ Number of unit cells in 1.00 cm³ = total volume given / volume of each unit cell $= 1.00 \text{ cm}^{3}/4.4 \times 10^{-23} \text{ cm}^{3}$ $= 2.27 \times 10^{22}$ unit cell

Q.4 The density of the copper metal 8.95 g cm⁻³. If the radius of copper atom is 127.8 pm, is the unit cell simple cubic a body-centred or a face-centred type structure? Molar mass of Cu is 63.54 g mol⁻¹[CBSE 2010]

A.4 Formula used :

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

Given values are:

 $d = 8.95 g cm^{-3}$

r = 127.8 pm

 $M = 63.54 \text{ g mol}^{-1}$

 $N_A = 6.022 \times 10^{23}$

Here two parameters are unknown

z = because we don't know the exact crystal structure

a = because we don't know the exact crystal structure. We need to calculate 'a' from given value of 'r' using the specific crystal type.

For fcc :

 $a = 2\sqrt{2}r$, z = 4

For bcc:

$$a = \frac{4r}{\sqrt{3}}$$
, z =

For simple cubic:

2

a = 2r, z = 1

We will put the various values of 'a' and 'z' in the given formula to check the density value. Start with fcc.

Q.5 A well known mineral fluoride is chemically calcium fluoride. It is known that one unit cell of this mineral there are 4 Ca^{2+} and 8 F^- ions. Ca^{2+} ions are arranged in fcc type crystal lattice and F⁻ occupies all the tetrahedral voids. The edge length of the unit cell is 5.46 x 10⁻⁸ cm. The density of solid is 3.18 g cm⁻³. Use this information to calculate the Avogadro number. Molar mass of CaF₂ is 78.08 g mol⁻¹. [CBSE 2010] A.5 It is directly formula based question.

The given values are: $d = 3.18 \text{ g cm}^{-3}$ $a = 5.46 \text{ x } 10^{-8} \text{ cm}$ $M = 78.08 \text{ g mol}^{-1}$ z = 4 (for fcc) Put the given values in formula:

$$d = \frac{z M}{a^3 N_A}$$
$$N_A = 6.035 \times 10^{23}$$

Q.6 Iron has body-centred cubic unit cell with a cell dimension of 286.65 pm.The density of Fe is 7.87 g cm⁻³. Use this information to calculate the Avogadro number. (Atomic mass of Fe is = 56 u). [CBSE 2012, 2009] A.6 Same as A.5 Molar mass of Fe would be 56 g mol⁻¹

Q.7 Silver crystallises in fcc unit cell. Each side of the unit cell is 400 pm. Calculate the radius of the silver atom. [CBSE 2011]

A.7 For fcc :

$$r = \frac{a}{2\sqrt{2}}$$

a = 400 pm r = 400 pm / 2 x 1.414 = 141.4 pm

ELECRTICAL PROPERTIES:

Solid are classified as conductor, semi-conductor and insulator on the basis of the magnitude of electrical conductivity.

- Conductor: electrical conductivity range 10⁴ to 10⁷ ohm⁻¹m⁻¹.
- Semi-Conductor: electrical conductivity range 10⁻⁶ to 10⁷ ohm⁻¹m⁻¹.
- Insulator: electrical conductivity range 10⁻²⁰ to 10⁻¹⁰ ohm⁻¹m⁻¹.





Ex. Fe₃O₄(magnetite)



Q.16 What is meant by 'forbidden zone' in reference to the band theory of solid? [CBSE (AI) 2008; (F) 2012]

A.16 The energy gap between the valance band and conduction band is known as forbidden zone. As shown below:



Q.17 which group of solid is electrical conductors, as well as malleable and ductile? [CBSE (F) 2013] A.17 Metallic solid

IMPERFECTION IN SOLIDS

Although in crystalline solid there is regular arrangement of constituent particles but yet the crystals are not perfect. There is always some king of irregularity in arrangement of constituent particles in small crystals. These

Irregularities are known as *defects* in crystal. There are 2 types of defects known in crystal lattice.

- Point defect
- Line defect

In our syllabus only point defects are included so we will focus our study on point defects only.

POINT DEFECTS:

- Impurity defect
- Stoichiometric defects
- Non- stoichiometric defects
 Types of stoichiometric defects and Non- stoichiometric defects are mentioned in tabular form.

Stoichiometric defects	Non- stoichiometric defects
Vacancy defect	Metal excess defect
Interstitial defect	Metal deficiency defect
Frenkel defect	
Schottky defect	

Impurity defect:

Impurity defect is arises due to addition of small amount of impurity in ionic solid. It actually creates some kind of cationic vacancy in ionic solid. For example, if some SrCl2 is added in molten salt of NaCl it takes the position of Na+ in the crystal. But charge on Sr is 2+. After removing 2 ions of Na+, Sr2+ occupy one point only. In this way it causes vacancy of 1 point.

Vacancy defect:

It arises when some of the lattice point remains unoccupied during the crystal formation.

- It occurs in non-ionic compounds
- It decreases the density of solid
- It can be created by heating

Interstitial defect:

It arises when some of the constituent particles occupy the interstitial sites other than the lattice points.

It occurs in non-ionic compounds

It increases the density of solid

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- It occurs in non-ionic compounds
- It increases the density of solid

Frenkel defect:

It is actually the combination of vacancy defect and interstitial defect in ionic compound. It arises when smaller ion is dislocated from its normal site and occupies an interstitial site. It is also known as dislocation defect.

- It occurs in ionic compounds
- It does not change the density of solid

• Shown by ionic compound having large difference in their constituent ions. For example: ZnS, AgBr, AgI etc.

Schottky defect:

It is actually a vacancy defect. But it causes vacancy of cation and anion both.

It occurs in ionic compounds

It decrease the density of solid

Shown by ionic compound having similar size of cation and anion.

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For example: ZnS, AgBr, AgI etc.

Schottky defect:

It is actually a vacancy defect. But it causes vacancy of cation and anion both.

- It occurs in ionic compounds
- It decrease the density of solid
- Shown by ionic compound having similar size of cation and anion For example: NaCl, KCl, AgBr.

Important point: AgBr shows both Frenkel and schottky defect.

Metal excess defect:

Due to anionic vacancies:

anionic vacancies are created due to reaction of anion of the crystal with excess of metal present in the atmosphere. For example when crystal of NaCl is heated in presence of sodium vapour, the sodium atoms are deposited on the surface of crystal and later on forms the bond with Cl- ion by losing an electron.

In this way it creates a vacancy for Cl- ion. But the electron removed by sodium metal diffuse in the crystal and occupies the anionic site. This creates a F-centre.The presence of unpaired electron at vacant anionic site in metallic crystal is known as F-centre. This F-centre is responsible for imparting colour to the crystal. Like as:

NaCl - yellow colour

LiCl – pink

KCl-violet.

• It occurs in ionic compounds

• It is responsible for imparting colour to the crystal through F-centres.

For example: NaCl, KCl, LiCl.

Due to presence of extra cations:

Excess cationic sites are generated due to the loss of anion of crystal after any reaction. The excess of cation occupies the interstitial site. ZnO on heating loss oxide ion from the crystal. The excess of Zn2+ ions occupy the interstitial site and electron lost by oxide ion occpy the neighbouring site, in this way maintain the electrical neutrality of crystal.

- It occurs in ionic compounds
- It is responsible for imparting colour to the crystal through free electrons. For example: ZnO (white at room temperature, yellow on heating)

Metal deficiency defect:

Number of metal cations is less as required by metallic crystal. For example in FeO the actual composition ranges from Fe0.930 to Fe0.950.

ELECRTICAL PROPERTIES:

Solid are classified as conductor, semi-conductor and insulator on the basis of the magnitude of electrical conductivity.

- Conductor: electrical conductivity range 10⁴ to 10⁷ ohm⁻¹m⁻¹
- Semi-Conductor: electrical conductivity range 10^{-6} to 10^7 ohm⁻¹m⁻¹.
- Insulator: electrical conductivity range 10⁻²⁰ to 10⁻¹⁰ ohm⁻¹m⁻¹

CONDUCTION OF ELECTRICITY

As we know that free electrons are responsible for the conduction of electricity in metals. Electrons are occupied in atomic orbital. The atomic orbital forms molecular orbital in metallic crystal. Molecular orbital are very closer in energy and known as bands. To be a conductor there must be some electrons in conduction band. But electrons are mainly occupied in valance band. On the basis of conductivity solids are classified in 3 types: Conductor, semi-conductor, insulator.

- In case of conductor there is an overlapping of valance band and conduction band.
- In semi-conductor there is small gap of energy between valance band and conduction band. Some of the electron may jump and show some activity. The metal showing this type of activity is known as intrinsic semi-conductors. For example : Silicon and Germanium
- In case of insulator there is a large energy difference between valance band and conduction band



Classification of semi-conductors:

The electrical conductivity of semi-conductors can be increased by adding some electron rich impurity or electron deficient impurity. This is called doping.

n-type semiconductor : When the conductivity of semi-conductor is increased by adding electron rich impurity. It generates n-type semi-conductor. For Example: when Silicon is doped with phosphorus, phosphorus also occupies some lattice site. The covalency of Si is 4 but that of P is 5. So, one electron per atom left unused and it delocalise from its location. This delocalise electron help in increasing conductivity of semi-conductor.

p-type semiconductor : When the conductivity of semi-conductor is increased by adding electron deficient impurity. It generates p-type semi-conductor. For Example: when Silicon is doped with boron, boron also occupies some lattice site. The covalency of Si is 4 but that of B is 3. So, one of the position of electron is left unused. This is called electron hole. The electron from neighbouring atom moves to fill this hole but creates a new hole. This looks like movement of electron hole throughout the system. Electrons moves through theses hole under the influence of electric fields. In this way electrical conductivity increases.



Application of n-type and p-type semiconductors:

By the combination of n-type and p-type semi-conductors many electronic devices are prepared.

- Diode (is a device that allows the current in one direction only) is used as amplifier
- ppp and npn sandwiching is done in making transistors
- As photo diode in solar cells
- In lasers

MAGNETIC PROPERTIES:

Electrons are charged particles and it generates a magnetic field around itself. The magnetic field arises due to the spinning of electron at its own axis and movement of atomic orbital around nucleus. Classification of magnetic properties:

I. Paramagnetism :

- Weakly attracted by magnetic fields
- Alignment of magnetic dipole in the same direction of magnetic field
- Loose magnetism in absence of magnetic field
- They have unpaired electrons
 Ex. Cu 2+, Fe 3+

II. Diamagnetism :

- Weakly repelled by magnetic fields
- Alignment of magnetic dipole in the opposite direction of magnetic field
- They have all the electrons paired Ex. H2O, NaCl

III. Ferromagnetism :

- strongly attracted by magnetic fields
- Permanently magnetised. Ex. Fe, Co, Ni etc.

IV. Anti-Ferromagnetism :

- strongly repelled by magnetic fields
- Alignment of magnetic domains (group of metal ions)in the opposite direction of magnetic field..
 Ex. MnO

V. Ferrimagnetisms :

- Weakly attracted by magnetic fields
- Alignment of magnetic domains (group of metal ions)in the parallel and anti parallel direction with direction of magnetic field and unequal in number.
- Loss magnetic moment on heating.
 Ex. Fe3O4(magnetite)

Ex. Fe₃O₄(magnetite)



PREPARED BY: MR. ARNAB PAUL CHOWDHURY