

Ranjan Singh Chemistry Classes

JEE (Main & Advanced)• NEET• XI• XII

Study Package



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M.Sc. Bio-Chemistry(P.U) Ex-Faculty : Narayana & Goal

# **PHYSICAL** CHEMISTRY

SOLID STATE



Chemistry plays a central and important role in all competitive examinations as well as in day to day life. For last so many years, I have constantly been in touch with students, guiding them in Chemistry and looking into their difficulties for them to succeed in their board as well as competitive examinations JEE(Mains & Advance) | NEET.

I have felt a need for a good coaching centre to fulfil the requirements of students. Students need a highly experienced and qualified faculty in chemistry, who can guide them well, clear their doubts, provide them the effective & tricky notes, and make them do much needed practice. More importantly they should also be provided Classroom Monitoring, Periodical & Surprise Tests to guide them in the proper direction. I realize that, it is very important to diagnose the basic weaknesses and problems of students not succeeding in JEE(Mains & Advance) | NEET and Board exams. In fact, as question patterns are changing, now they need to have a different approach for these Examinations.

At RANJAN SINGH CHEMISTRY CLASSES, we have our own way to prepare students for Competitive Examinations as well as Board Examination at a time so they can crack the entrance exam like JEE(Mains & Advance) and NEET as well as 12th Board simultaneously. We act as a medium to provide the simplest, easiest and a comfortable way to make students achieve their target. At RANJAN SINGH CHEMISTRY CLASSES(RSCC), we guide our students with the best motivational classes so weak students are also able to believe that, They can do it.

When you join RANJAN SINGH CHEMISTRY CLASSES you become a part of the powerful force which propels you towards your goal and if you get a position among the rankers with my excellent guidance, I will think that our efforts have borne fruits.

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#### <u>Solids</u>

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**

In solid state the particles are not able to move randomly.

**Crystalline Solids** 

- They have definite shape and volume.
- Solids have high density.
- Solids have high and sharp melting point which depend on the strength or value of binding energy.
- They are very low compressible.
- They show very slow diffusion.
  - Types of Solids

Solids

Amorphous Solids

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#### **Crystalline solids**

- In this type of solids the atoms or molecules are arranged in a regular pattern in the three dimensional network.
- They have well defined geometrical pattern, sharp melting point, definite heat of fusion and anisotropic nature.
- Anisotropic means they exhibit different physical properties in all directions, eq. The electrical and thermal conductivities are different in different directions.
- They are generally incompressible.
- The general examples of crystalline solids are as Quartz, diamond etc.
   Amorphous Solids
- In this type of solids, the arrangement of building constituents is not regular.
- 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.
- They do not have sharp melting points.
- They are isotropic as they exhibit same physical properties in all the directions.
- The general examples of this solids are as glass, Rubber, plastics etc.

#### Study of Cyrstals

- Crystal A crystal is a homogenous 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 intersecting faces called interfacial angles.
- Plane of symmetry

It is an imaginary plane which passes through the centre of a crystal & can divide it into two equal portions which are exactly the mirror images to each other.



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#### Axis of symmetry

- It is an imaginary line about which the crystal may be rotated so that it presents the same appearance more than once in a complete rotation through 360°.
- The axes of symmetry are called diad, triad, tetrad and hexad respectively. It is the original appearance and is repeated twice (180°), thrice (120°), four times (90°) and six times (60°) in one rotation.
- These axes of symmetry are also called as two fold, three fold, four fold and six fold respectively.
- Five fold symmetry is not found in crystals.



(i) Axis of two fold symmetry



(ii) Axis of three fold symmetry



(iii) Axis of four fold symmetry Centre of symmetry

(iv) Axis of six fold symmetry

• It is a point in the crystal so that any line drawn through it intersects the surface of the crystal at equal distance on either side.

**Note :** Only simple cubic system have one centre of symmetry. Other system do not have centre of symmetry.

#### **ELEMENTS OF SYMMETRY**

Total symmetry

- The total number of planes, axes and centre of symmetries possessed by a crystal is termed as elements of symmetry.
- A cubic crystal possess total 23 elements of symmetry

(i)	Plane of symmetry	(3 + 6)	=	9
(ii)	Axes of symmetry	(3 + 4 + 6)	=	13
(iii)	Centre of symmetry	(1)	=	1



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Study of Structure of Crystalline Solids To study crystalline solids we need some mathematical and geometrical tools.Lets get familier with them.

- **Space lattice :** It is the regular arrangement of points in space and forms the basis of classification of all structures. This regular arrangement spread over whole space in the **long range order**.
- **Unit cell:** Unit cell is the smallest arrangement of points which on repetition generates the whole space lattice. It is the *building block* of the whole structure.

(a) Unit cell contains the *minimum information* in terms of edge lengths and angles sufficient to determine the structure of the lattice.

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(b) Generally unit cell is the smallest element of the space lattice. But sometimes a slightly bigger Various types of unit cells can be chosen within a particular lattice:

(i) *<u>Primitive</u>*: When lattice points are found only at the corners of the unit cell.

(ii) <u>Centered/Non-primitive</u>: When lattice points are found at the corners and as well as inside the unit cell.



#### ♦ <u>1-DIMENSIONAL SPACE LATTICE</u>

Uniformly separated lattice points in 1-dimension will represent 1-D lattice.Only one parameter is needed to describe it.

#### **2 DIMENSIONAL SPACE LATTICE**

d

It is the regular arrangement of points in a plane. Only **three parameters** are needed to describe the lattice. Two sides a and b and angle between them( $\gamma$ ).

(i) Square unit cell: a = b,  $\gamma = 90^{\circ}$ 



(ii) **Rectangle:**  $a \neq b$ ,  $\gamma = 90^{\circ}$ 



(iii) **Hexagonal unit cell:** a = b,  $\gamma = 60^{\circ}$ Unit cell can be chosen in more than one way.



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Crystal System	Axial distances	Axial angles	Examples	Type of Unit cells
Cubic	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$	Cu, ZnS, KCl	S,BC,FC
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	$Sn(white tin), SnO_2, TiO_2$	S,BC
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$	Rhombic sulphur, CaCO <sub>3</sub>	S,BC,FC,EC
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Monoclinic sulphur, PbCrO <sub>2</sub>	S,BC
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^{\circ}; \gamma = 120^{\circ}$	Graphite, ZnO	S
Rhombohedral	a = b = c	$\alpha = \beta = \gamma \neq 90^{\circ}$	CaCO <sub>3</sub> (Calcite), HgS(Cinnabar)	S
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , CuSO <sub>4</sub> .5H <sub>2</sub> O	S

#### Ways of choosing unit cells in 3-dimensions:

1. Primitive /Simple: lattice points only at the corners only.



Found in **all** crystal systems.

2. Body centered: Lattice points at corners & at the body center.



Found only in **Cubic, Tetragonal, Orthorhombic** and **Monoclinic** systems.

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3. Face centered : Lattice points at corners & at each of the face centre.



Found only in **Cubic** and **Orthorhombic** systems.

4. End centered: Lattice point at corners & only at two oppsosite faces.



Total number of lattice arrangements in three dimensions = 14.These are called 14 BRAVAIS LATTICES

#### Contribution of different lattice points in one unit cell (CUBIC SYSTEM)

**Corner atom**: Since eight cubes meet at one corner, each atom at the corner gives 1/8th contribution to each cube. This means 1/8th of the electron density, 1/8th of the nuclear density(in case of atoms), 1/8th of the molecule are found completely inside one unit cell due to corner.

**Face Center**:Since each face is shared by two cubes, each atom/molecule is equally divided between them. Hence it contributes 1/2 to each cube

Body Centre: Whole of the atom/molecule is found inside and contributes 1 to each cube.

**Edge Centre**: Each edge is shared by four cubes, each atom/molecule at the cube contributes 1/4th to each cube.





#### Structure of Solids

#### (a) Solids having only one type of particles : e.g. metallic, molecular, covalent network solids.

The particle of the solid will be represented by a sphere of radius r. We assume that there is only attraction force existing between those spheres. Hence in order to to get maximum stable arrangement of these particles the seperation between the particles should be minimum.

#### Arrangement in 1-D :

In one dimension it is possible to arrange the spheres in only one stable way. This is the position with minimum separation and minimum potential energy of the system(most stable)



1-D close packing stable arrangement

#### Arrangement in two dimension :

**1. Square arangement(poor arrangement) :** If the one dimensional arrays are placed on top of one another, we get the square packing in twio dimensions.



unit cell

One sphere will be in constant contact with 4 other spheres.

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

**Packing fraction**, fraction of area occupied by spheres =  $\frac{\pi r^2}{4r^2} = \frac{\pi}{4} = 0.78(78\%)$ 

**2. Hexagonal arrangement(better arrangement) :** If each 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 ×  $\frac{\sqrt{3}}{4}$  a<sup>2</sup> = 6 ×  $\frac{\sqrt{3}}{4}$  × 4r<sup>2</sup> ; area of atoms =  $\pi$ r<sup>2</sup> +  $\frac{1}{3}$  × 6 $\pi$ r<sup>2</sup> = 3 $\pi$ r<sup>2</sup>

fraction of area occupied =  $\frac{3\pi r^2}{6\sqrt{3}r^2} = \frac{\sqrt{3}\pi}{6} \simeq 0.91 (91\%)$ 

#### 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.





cubic

(Note that  $\begin{array}{c} a = b = c \\ \alpha = \beta = r = 90^{\circ} \end{array}$ , 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:

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

(iii) packing fraction :

volume occupied by atoms / unit cell

volume of unit cell

$$=\frac{\frac{4}{3}\pi r^{3}}{a^{3}}=\frac{4}{3(2r)^{3}}\pi r^{3}=\frac{4\pi r^{3}}{3\times 8r^{3}}=0.52(52\%)$$

#### (iv) Coordination Number, CN:

It is defined as the number of atoms touching any one particular atom = 6 for simple cubic



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

- (ii) Effective no-of atoms (Z) =  $1 + \frac{1}{8} \times 8 = 2$ .
- (iii) Packing fraction =  $\frac{2 \times \frac{4}{3} \pi r^3}{4 \times 4 \times 4 r^3} \sqrt{3} \times \sqrt{3} \times \sqrt{3} = \frac{\pi \sqrt{3}}{8} \approx 0.68 \ (68\%)$
- (iv) Coordination number CN: 8 (the sphere at the body centre will be touching the spheres at the eight corners)

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



**Close Packing In Three Dimensions :** This is the arrangements in which metallic crystals are generally found. To generate close packing we must start with best possible arrangements in two dimensions i.e., the hexagonal arranged sheets and spheres of IInd sheet must rest depressions/voids of 1st sheet hexagonal close packed

**NOTE:** All the voids of 1st sheet canot be occupied by spheres of 2nd sheet (because of same size of spheres) Only 50% of the viods can be occupied. Out of six voids around any sphere only three atternate voids can be occupied by 2nd sheet of spheres. This arrangements is shown below.







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.

#### Hexagonal Close Packing (HCP)

If spheres of III<sup>rd</sup> layer are placed in voids of II<sup>nd</sup> layer which are lying exactly above the spheres of Ist layer i.e., voids of type 'a' then Ist layer and IIIrd layer will become exactly identical and this generates ABABAB pattern or the hexagonal close packing (HCP)



Exploded view

#### Calculations

1. For '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.



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2. Effective no. of atoms/unit cell, Z :

Z= 3 + 2 × 
$$\frac{1}{2}$$
 + 12 ×  $\frac{1}{6}$  = 3 + 1 + 2 = 6 [z = 6]

The three atoms at the centre of the hexagonal structure is not completely inside the unit cell. A part of it lies in the unit cell, but a part of other atoms in the same plane whose centre is not in the unit cell is included inside the unit cell.

Hence eff. no. = 3.

- 3. Packing fraction : =  $\frac{\text{volume of the atoms}}{\text{volume of unit cell}} = \frac{6 \times \frac{4}{3} \pi r^3}{24 \sqrt{2} r^2} = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$
- 4. Coordination number CN= 12 (each spheres touches 6 spheres in its layer, 3 above and 3 below)
- 5. Density =  $\frac{Mass}{Volume}$  =  $\frac{ZM}{N_A (volume)}$  =  $\frac{6M}{N_A (volume)}$

**NOTE:** In closest packings, whenever two consecutive layers are of different kind then packing efficiency will always be 74%

#### ABC-ABC Arrangement/Cubic Close Packing( ccp ):

If the third layer spheres are placed in those voids of IInd 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 or also as the Face Centred Cubic structure(FCC).



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.



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1. Relation between 'a' and 'r' :

 $a \neq 2r$ 

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

2. Effective no. of atoms per unit cell, Z :

$$Z = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$$

3. Packing fraction :

p.f. = 
$$\frac{4 \times \frac{4}{3} \pi r^3}{4 \times 4 \times 4 r^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = .74(74\%)$$

**4. Coordination number, CN = 12 (** each corner sphere touches three spheres per cube(each of them being shared by two of the eight cubes surrounding that sphere) **)** 

5. Density = $\frac{Z \times M}{N_{\Delta} \cdot a^3}$	Cilles an a	
Type of neighbour	Distance	no. of neighbours
nearest	$\frac{a}{\sqrt{2}}$	$12 = \left(\frac{3 \times 8}{2}\right)$
(next) <sup>1</sup>	а	$6 = \left(\frac{3 \times 8}{4}\right)$
(next) <sup>2</sup>	$a\sqrt{\frac{3}{2}}$	24
(next) <sup>3</sup>	$a\sqrt{2}$	12
(next)⁴	$a\sqrt{\frac{5}{2}}$	24

Types of voids Found in Close packings :

(VOID IN TWO DIMENSIONS)
 Triangular void (2-Dimensional 3-coordinate void) The triangular voids are found in the planes of the close packed structures, whenever three speres are in contact in such a fashion.







 $\cos 30^\circ = \frac{R}{R+r} \Rightarrow \frac{\sqrt{3}}{2} = \frac{R}{R+r} \Rightarrow \frac{2}{\sqrt{3}} = \frac{R+r}{R} \Rightarrow r = 0.155 R$ 

where, **R**= Radius of the sphere, **r** = maximum radius of a sphere that can be placed inside the void. *(VOIDS IN THREE DIMENSIONS)* 

Tetrahedral void (3-Dimensional 4-coordinate) :

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



 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. This can also be obtained by placing two THREE-BALL arrangements on the top of each other such that a hexagonal view is obtained.



 $2\sqrt{3}R = 2(R + r)$ 

 $r = (\sqrt{3} - 1) R$ 

 $r = (\sqrt{3} - 1) R \Rightarrow r = 0.732 R$ 

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.



#### FCC/CCP unit cell: (with the help of model)

(A) Tetrahedral voids : The FCC unit cell has **eight** tetrahedral voids per unit cell. Just below every corner of the unit cell, there is one Tetrahedral void. As there are eight corners, there are eight tetrahedral voids.



The spheres 1, 2, 3, 4 form a tetrahedral void.

(B) Octahedral voids : In an 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 is

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

edge centres body centre

+ (1)

#### HCP unit cell :(with the help of model)

(A) Tetrahedral voids:

Tetrahedral voids are found between any two spheres of alternate sheets that lie perpendicular to the plane of the sheets.

8 are completely inside and 12 are shared

Effective number of tetrahedral voids in hcp unit cell :

effectively 
$$\rightarrow 8 + 12 \times \frac{1}{3} = 12$$

(B) Octahedral Voids: Total 6 octahedral voids completely inside the unit cell.

#### VOIDS PER SPHERE IN CLOSED PACKING

1.Tetrahedral Voids

In HCP : Z = 6, tetrahedral voids = 12

In CCP/FCC :Z = 4, tetrahedral voids = 8

number of tetrahedral voids = 2 × Z

no. of tetrahedral voids in close packings = 2 × effective no. of spheres.

HENCE, there are two Tetrahedral Voids per sphere in closed packing arrangements.

(2) Octahedral Voids

In HCP: Z = 6, octahedral voids = 6 In CCP/FCC: Z = 4, octahedral voids = 4

no. of octahedral voids = Z

There is exactly one octahedral void per sphere in close packing.

Void in Simple cubic lattice

Cubical void (eight coordinate void)

along body diagonal,  $2r\sqrt{3} = 2r + 2r_v$ 

$$r_v = r(\sqrt{3} - 1)$$

Triangular void in HCP: It is located in two dimsensional layers of HCP structure.

$$\frac{2r}{\sqrt{3}} = r + r_{v} \implies r_{v} = r \left(\frac{2}{\sqrt{3}} - 1\right) \implies r \left(\frac{3.464}{3} - 1\right)$$
$$\Rightarrow r_{v} \approx 0.155 r.$$





#### Structure of ionic compounds

#### Structure of compounds containing two different types of atoms.

The bigger atom or ion will form the lattice & smaller atom / ion will occupy the voids. Generally, bigger ion is anion and smaller ion is cation. The type of void occupies by the cation is decided by radius ratio.

Radius ratio =  $\left(\frac{r_+}{r_-}\right)$ , this gives the idea about the type of void occupied. Radius ratio Type of void occupied Coordination No.  $\frac{r_+}{r} < 0.155$ 2 linear void  $0.155 \le \frac{r_+}{r} < 0.225$ 3 triangular void  $0.225 \le \frac{r_+}{r} < 0.414$ tetrahedral void 4  $0.414 \le \frac{r_+}{r} < 0.732$ octahedral void 6  $0.732 \le \frac{r_+}{r} < 1$ cubical void 8

#### Structure of some representative ionic compounds

lonic solids form rigid lattice structure.Large amount of energy is released when ions form lattice arrangement form their gaseous states. This is expressed in terms of the Lattice energy(kJ/mol). This much amount of energy is required to separate one mole of ionic-solid into its gaseous ions.

NaCl type( AB-type ) of structure or rock salt structure or 6 : 6 C.N. compound

Experimental:  $\frac{r_{Na^+}}{r_{o-}} = 0.51$ Cl- ions: fcc lattice effective no. of CF ions in a unit cell = 4 Effective no. of Na+ ions in a unit cell must be 4 (: formula  $\rightarrow$  Nacl) Na<sup>+</sup> ions must occupy all the octahedral voids. formula of one unit cell =  $Na_{4}CI_{4}$  = NaCl Effective no. of formula units , Z = 4mass of unit cell =  $\frac{ZM}{N_A}$ M = 58.5 gm/moleEdge length of unit cell : $a(fcc) = 2(r_{Na^{+}} + r_{Cl^{-}})$ density  $\rho = \frac{ZM}{N_A.a_{fcc}^3}$  $C.N._{Na^{+}} = 6$ C.N.<sub>CI</sub> = 6 NaCI = 6 (cation) : 6 (anion) CN compound (2) ZnS type( AB-type ) of unit cell or 4 : 4 CN compound ZnS – fcc (zinc blende) ZnS – hcp (wurtzite) experimental:  $\frac{r_{zn^{2^+}}}{r_{2^-}} \approx 0.3$ 



mass = 
$$\frac{ZM}{N_A}$$
 M = 97 gm/mole  
 $r_{zn^{2+}} + r_{s^{2-}} = \frac{1}{2} \times \left(\sqrt{3} \frac{a_{fcc}}{2}\right) \implies a_{fcc} = \frac{4}{\sqrt{3}} (r_{Zn^{2+}} + r_{s^{2-}})$ 

density  $\rho = \frac{\angle IVI}{N_A a_{fcc}^3}$ C.N. of Zn<sup>2+</sup> ions = 4 C.N. of s<sup>2-</sup> ions = 4

3. CaF, (Flourite structure)(AB,-type) or 8 : 4 coordination no. compound

 $r_{ca^{2+}} > r_{F^-}$  Here Cation is bigger than Anion.

experimental: 0.225 > 
$$\frac{r_{F^-}}{r_{ca^{++}}}$$
 < 0.414

**fcc** lattice position are occupied by Ca<sup>2+</sup> ion Effective no. of ca<sup>2+</sup> ions = 4  $F^-$  ions occupy all the **Tetrahedral** voids Effective no. of  $F^-$  ions = 8 formula = Ca<sub>4</sub>F<sub>8</sub> = CaF<sub>2</sub> effective no. of formula units, **Z** = 4

$$a_{fcc} = \frac{4}{\sqrt{3}} (r_{Ca^{2+}} + r_{F^{-}})$$

C.N. of  $Ca^{2+} = 8$ C.N of  $F^{-} = 4$ 

4. Na<sub>2</sub>O (sodium oxide) (A<sub>2</sub>B-type )or Anti - Fluorite structure or 4 : 8 coordination compound  $O^{2-}$  – fcc lattice

Na<sup>+</sup> – all the **tetrahedral** voids

5. CsCl type of structure or 8 : 8 CN compound

Experimental:  $\frac{|C_{S^+}|}{r} \approx 0.93$ 

Cl<sup>-</sup> forms **Simple cubic** lattice Effective Cl<sup>-</sup> ions = 1 Cs<sup>+</sup> will occupy **cubic** void Effective Cs<sup>+</sup> ion = 1 Formula = CsCl Z = 1

$$\rho = \frac{2M}{Na a_{sc}^3} \qquad a_{sc} = \frac{2}{\sqrt{3}} (r_+ + r_-)$$
  
C.N of Cs<sup>+</sup> = 8 C.N of Cl<sup>-</sup> = 8

Effect of pressure and temperature on coordination number of compound : On increasing pressure  $\rightarrow$  Coordination number tends to increase

On increasing temperature  $\rightarrow$  Coordination number tends to decrease e.g.

$$4:4 \xrightarrow{\mathsf{P}\uparrow} 6:6$$
$$8:8 \xrightarrow{\mathsf{T}\uparrow} 6:6$$



#### Crystal imperfections / defects

Imperfections 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.

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#### **Point Defects**

1. Stoichiometric -The formula of compound remains same even after presence of these defects.

2. Non-stoichiometric -The formula of compound will get modified because of the presece of these defects.

#### **Stoichiometric defects**



**Schottky :** when atoms/point are totally missing from the lattice. net density of crystal will get decressed

$$\rho_{exp} < \rho_{theoritical}$$
  
% missing units =  $\left(\frac{\rho_{th} - \rho_{exp}}{\rho_{th}}\right) \times 100\%$ 

**FRENKEL** : When atoms/ions displaced from normal lattice positions and are present in some interstitial voids.Density remains same

#### **INTERSTITIAL:**

When some small foreign atoms are trapped in interstitial voids of the lattice without any chemical reaction. Formula remains the same

 $\rho_{exp}$  >  $\rho_{theortical}$ 



(a) metal excess or cation excess defect :-

- If no. of missing anion is more than no. of missing cations.

- To maintain electrical neutrality some electron are trapped at anionic vacancies.

Because of these extra electron the electrical and optical (colour) properties of the compound get modified.

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So these locations of electrons are also known as colour centres (F - centres) .

ZnO - white in colour at room temperature.

- on heating some  $O^{2-}$  ions get released in the form of  $O_2$  and electrons are trapped at their locations. because of this it is yellow in colour.

#### (b) metal deficiency (cation deficiency) defects

- no. of missing cations should be more than no. of missing anions.
- oxidation no. of cation will get modified to maintain electrical mentrality.



**Example:** Ferrous oxide (FeO) is experimentally found to have the formula  $Fe_{0.93}O$ . Find the percentage of Fe ions in +3 state.



_			
	Ranjan Singh		[00]
	Chemistry Classes		
		SEN	ACOS
Type	s of Crystal		The maximum nereenters of evolution
<u>1 ype</u>	Which one is called pseudo solid -	11.	volume that can be filled in a face centred
01.	(A) CaE. (B) Glass		cubic system by an atom is-
	(C)  NaCl (D)  All		(A) 74% (B) 68%
02	Cranhite is an example of		(C) 34% (D) 26%
02.	(A) lonic solid	12.	The rank (effective atoms per unit cell) of a
	(B) Covalent solid		cubic unit cell is 4. The type of cell as-
	(C) Vander waal's crystal		(A) Body centred (B) Face centred
	(D) Metallic crystal	40	(C) Primitive (D) None of these
03	Amorphous solids	13.	An element occurring in the BCC structure
05.	(A) Possess sharp melting points		of atoms of the element in these cell will be
	(R) Undergo clean cleavage when cut with		(A) 24 16 x $10^{23}$ (B) 36 18 x $10^{23}$
	(b) Ondergo clean cleavage when cut with		(C) $6.04 \times 10^{23}$ (D) $12.08 \times 10^{23}$
	(C) Do not undergo clean cleavage when cut	14.	The space occupied by B.C.C. arrangement
	with knife		is approx -
	(D) Possess orderly arrangement over long		(A) 50% (B) 68% (C) 74%(D) 56%
	distances	15.	In a close pack array of N spheres, the
04	Wax is an example of -		number of tetranedral noies are-
•	(A) Ionic crystal (B) Covalent crystal	16	(A) 4N (B) N/2 (C) 2N (D) N Transition metals, when they form interstitial
	(C) Molecular crystal (D) Metallic crystal	10.	compounds the non-metals (H B C N) are
05.	Crystals which are good conductor of		accomodated in-
	electricity and heat are known as -		(A) Voids or holes in cubic - packed structure
	(A) Ionic crystals		(B) Tetrahedral voids
	(B) Covalence crystals		(C) Octahedral voids
	(C) Metallic crystals		(D) All of these
	(D) Molecular crystals	Mathe	ematical analysis of Crystal
06.	lodine crystals are -	1/20	$\sim$ Ferrimagnetism is in -
	(A) Metallic solid (B) Ionic solid	18	$(A) \uparrow \uparrow \uparrow \downarrow \downarrow$ $(B) \uparrow \downarrow \downarrow \downarrow$
	(C) Molecular solid (D) Covalent solid	18.	If a is the length of unit cell, then which one
07.	Which among the following will show		is correct relationship-
	anisotropy-		(A) For simple cubic lattice, Radius of metal
	(A) Glass (B) Barium chloride		a
	(C) Wood / (D) Paper /		atom = $\frac{1}{2}$
08.	Which is covalent solid-		(B) For bcc lattice, Radius of metal
	(A) Fe <sub>2</sub> O <sub>3</sub> (B) Diamond		$\sqrt{3}a$
	(C) Graphite (D) All		atom = $\frac{1}{4}$
<u>Pack</u> i	ing in Crystals & Voids		(C) For fcc lattice,Radius of metal
09.	The arrangement ABC ABC is		a
	referred to as-		atom = $\overline{2\sqrt{2}}$
	(A) Octahedral close packing		(D) All
	(B) Hexagonal close packing	19.	The number of atoms present in a simple
	(C) Tetrahedral close packing		cubic unit cell are-
	(D) Cubic close packing		(A) 4 (B) 3 (C) 2 (D) 1
10.	The most malleable metals (Cu, Ag, Au) have	20.	The number of atoms/molecules contained
	close - packing of the type-	_~·	in one face centred cubic unit cell of a
	(A) Hexagonal close - packing		monoatomic substance is-
	(D) Cubic close - packing (C) Body - centred cubic packing		$(\Delta) \Delta$ (B) 6
	(D) Malleability is not related to type of		
	packing		







	Ranjan Singh		[24]
19.	In a solid, oxide ions are arranged in CCP. Cations A occupy one-sixth of the tetrahedral voids and cations B occupy one-third of the octahedral voids. The formula of the	27.	The mass of a unit cell of CsCl corresponds to- (A) $8Cs^+$ and $1Cl^-$ (B) $1Cs^+$ and $6Cl^-$ (C) $1Cs^+$ and $1Cl^-$ (D) $4Cs^+$ and $4Cl^-$
	compound is - (A) $ABO_3$ (B) $AB_2O_3$ (C) $A_2BO_2$ (D) $A_2B_2O_3$	28.	Close packing is maximum in the crystal lattice of- (A) Simple cubic (B) Face centred
20.	A solid AB has rock salt structure. If the edge length is 520 pm and radius of $A^+$ is 80 pm, the radius of anion $B^-$ would be - (A) 440 pm (B) 220 pm (C) 360 pm (D) 180 pm	29.	<ul> <li>(C) Body centred</li> <li>(D) None of these</li> <li>The structure of MgO is similar to NaCl. The co-ordination number of Mg is-</li> <li>(A) 2</li> <li>(B) 6</li> <li>(C) 4</li> <li>(D) 8</li> </ul>
21.	A binary solid $(A^+ B^-)$ has a zinc blende structure with B <sup>-</sup> ions constituting the lattice and A <sup>+</sup> ions occupying 25% tetrahedral holes. The formula of solid is- (A) AB (B) A <sub>2</sub> B (C) AB (D) AB	30. 31.	Each unit cell of NaCl consists of 14 chlorine atoms and- (A) 13 Na atoms (B) 14 Na atoms (C) 6 Na atoms (D) 8 Na atoms Schottky defect is noticed in- (A) NaCl (B) KCl
22.	A certain metal crystallises in a simple cubic structure. At a certain temperature, it arranges to give a body centred structure. In this transition, the density of the metal- (A) Decreases (B) Increases	32.	<ul> <li>(C) CsCl</li> <li>(D) All</li> <li>The structure of sodium chloride crystal is-</li> <li>(A) Body centred cubic lattice</li> <li>(B) Face centred cubic lattice</li> <li>(C) Octahedral</li> <li>(D) Square planar</li> </ul>
23.	<ul> <li>(C) Remain unchanged</li> <li>(D) Changes without a definite pattern</li> <li>For the structure given below the site marked as S is a-</li> </ul>	33. 34.	A crystal of Fe <sub>3</sub> O <sub>4</sub> is- (A) Paramagnetic (B) Diamagnetic (C) Ferrimagnetic (D) None of these A cubic crystal possesses in all elements of symmetry-
	(A) Tetrahedral void (B) Cubic void	35. 36.	<ul> <li>(A) 9</li> <li>(B) 13</li> <li>(C) 1</li> <li>(D) 23</li> <li>The structure of sodium crystal is-</li> <li>(A) Body centred cubic lattice</li> <li>(B) Face centred cubic lattice</li> <li>(C) Octahedral</li> <li>(D) Square planar</li> <li>Extremely pure samples of Ge and Si are</li> </ul>
24.	<ul> <li>(C) Octahedral void (D) None of these</li> <li>ZnS is-</li> <li>(A) Ionic crystal</li> <li>(B) Covalent crystal</li> <li>(C) Metallic crystal</li> <li>(D) Vander Waals' crystal</li> </ul>	37.	non-conductors, but their conductivity increases suddenly on introducing in their crystal lattice- (A) As (B) B (C) Both (A) and (B) (D) None of these The co-ordination number of a body centred
25.	LiF is a/an- (A) lonic crystal (B) Metallic crystal (C) Covalent crystal (D) Molecular crystal	38.	atom is- (A) 4 (B) 6 (C) 8 (D) 12 Which is ferromagnetic- (A) Ni (B) Co
26.	A solid having no definite shape is called- (A) Amorphous solid (B) Crystalline solid (C) Anisotropic solid (D) None of these	39.	(C) $CrO_2$ (D) $All$ Which of the following is ferroelectric compound(A) $BaTiO_3$ (B) $K_4[Fe(CN)_6]$ (C) $Pb_2O_3$ (D) All.

0	An example of boo	dy cubic is -	45.	$\rm NH_4 Cl$ crystallizes in bcc lattice with edge len
	(A) Sodium	(B) Magnesium		of unit cell equal to 387 pm. If radius of CI-
	Sodium crysrallizes	s in cubic lattice with cell edge		181 pm, the radius of $NH_4^+$ will be -
	a=4.29Å. What is	the radius of Na atom -		(A) 174 pm (B) 154 pm
	(A) 1.86 Å	(B) 6.81 Å	40	(C) 116 pm (D) 206 pm
	(C) 8.61 Å	(D) 2.94 Å	46.	6 : 6 on -
•	A binary solid x <sup>+</sup> y <sup>-</sup>	crystallizes in rock structure.		(A) Applying high P
	If the edge lenght i	s 400pm and radius of cation		(B) Increasing temperature
	(A) 325 pm	(B) 250 pm		(C) Both A and B
	(C) 125 pm	(D) 325 pm	47	(D) Can't be changed Point defect which lowers the density
•	A mineral having t	he formula AB <sub>2</sub> crystallize in	47.	materials -
	cubic close packe	ed lattice with the A atoms		(A) schottky (B) Frenkel
	number of atoms	of A atoms of B and the		(C) Both (D) None of these
	fraction of the tetr	ahedral sites occupied by B	48.	At low temperature $O_2$ freezes to form crystall
	are respectively -			(A) Ionic crystal (B) Covalent crysta
	(A) 2, 6, 75%	(B) 8, 4, 100%		(C) Metallic crystal (D) Molecular cryst
	In Corundum oxid	(D) 0, 0, 50% de ions are arranged in hcn	49.	Arrangement of CI <sup>-</sup> in CsCl is -
•	arrangement and	aluminium ion occupy two		(A) HCP (B) Simple cubic
	third of the octahe	dral holes. Its formula is -	50.	The decreasing order of the size of void is
	(A) $Al_2O_3$	(B) Al <sub>2</sub> O <sub>4</sub>		(A) Cubic > Octahedral > Tetrahedral > Trigo
	$(C) Al_3O_4$	(D) AIO <sub>2.</sub>		(B) Trigonal > Tetrahedral > Octahedral > Cu
			110	(C) Trigonal > Octahedral > Tetrahedral > Cu





[26]

**TOPIC WISE MCQS** 

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	В	В	С	С	С	С	В	D	D	В	А	В	А	В	С
Q.No.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	D	С	D	D	А	В	D	А	А	D	В	В	С	С	В
Q.No.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	
Ans.	В	D	D	D	В	В	В	С	С	А	В	D	С	С	

## **MISCELLANEOUS QUESTIONS**

Ques.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	D	С	С	С	D	А	С	В	В	В	C	В	A	А	А
Ques.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	А	А	С	А	D	С	В	C	A	A	A	С	В	В	А
Ques.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	D	В	С	D	А	С	, c	D	A	×A/	A	С	В	А	В
Ques.	46	47	48	49	50			10		/					
Ans.	В	А	D	В	A				M21/	2					



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