

SOLID STATE

Solids, amorphous, face centered, body centered, hexagonal close packing, nearest neighbours, simple ionic compounds.

Introduction

Solids are characterised by incompressibility, rigidity and mechanical strength. This indicates that the molecules, atoms or ions that make up a solid are closely packed, they are held together by strong cohesive forces and cannot move at random. Thus, in solids we have well ordered molecular arrangements.

Moreover solids are also characterised by a definite geometrical arrangement. Substances which satisfy all the characteristics of a solid except the definite geometrical arrangement are called amorphous substances (e.g. glass, rubber etc.). The definite geometrical arrangement of atoms, molecules or ions in a solid extends over the entire structure of the solid. This is termed as long range order.

Difference Between Solids And Amorphous Substances

- i) The first major difference between a solid and an amorphous substance is the existence of a definite and orderly arrangement of molecules or atoms in 3 - D space. An amorphous substance, on the other hand, does not have any pattern of arrangement of molecules or atoms i.e, it does not have any geometrical shape. It has been found that even if some orderly arrangement of molecules or atoms exists in a few amorphous substances, it does not extend more than a few Angstrom units. Thus, unlike solids, amorphous substances do not have long range order.
- ii) Due to the definite ordered state, a solid tends to melt at a very short range of temperature (exaggerated to say that it has a sharp melting point). While the amorphous substance melts at larger range of temperature.

- iii) Amorphous substances differ from solids and in fact resemble liquids in an important respect. The properties such as electrical conductivity, thermal conductivity, mechanical strength and refractive index are the same in all directions. Amorphous substances are said to be isotropic. Liquids and gases are also isotropic. Solids, on the other hand are anisotropic, i.e, their physical properties are different in different directions. For example, the velocity

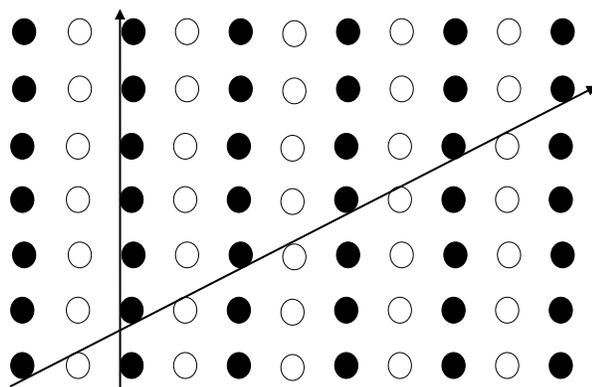


Fig. 1. Anisotropic behaviour of solids

of light passing through a solid varies with the direction in which it is measured. Thus, a ray of light entering such a solid may split up into two components each following a different velocity. This phenomenon is known as double refraction. Thus, anisotropy in itself is a strong evidence for the existence of ordered molecular arrangements in such materials.

Unit Cells

In this topic we would be studying certain properties of a solid which depend only on the constituents of the solid and the pattern of arrangement of these constituents. To study these properties, it would be convenient to take up as small amount of the solid as possible because this would ensure that we deal with only the minimum number of atoms or ions. This smallest amount of the solid whose properties resemble the properties of the entire solid irrespective of the amount taken is called a **unit cell**. It is the smallest repeating unit of the solid. Any amount of the solid can be constructed by simply putting as many unit cells as required.

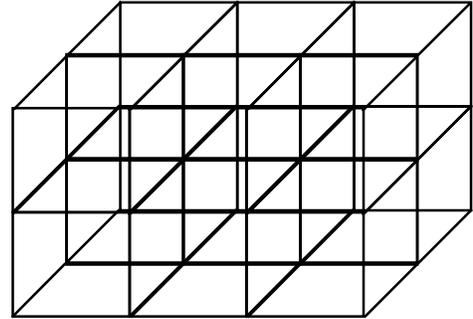


Fig.2. Unit cells arranged together

Bravais Lattices

Bravais (1848) showed from geometrical considerations that there are only seven shapes in which unit cells can exist. These are:

- i) Cubic
- ii) Orthorhombic
- iii) Rhombohedral
- v) Hexagonal
- v) Tetragonal
- vi) Monoclinic and
- vii) Triclinic.

Moreover, he also showed that there are basically four types of unit cells depending on the manner in which they are arranged in a given shape. These are : Primitive, Body Centered, Face Centered and End Centered. He also went on to postulate that out of the possible twenty eight unit cells (i.e. seven shapes \times four types in each shape = 28 possible unit cells), only fourteen actually would exist. These, he postulated, based only on symmetry considerations. These fourteen unit cells that actually exist are called **Bravais Lattices**

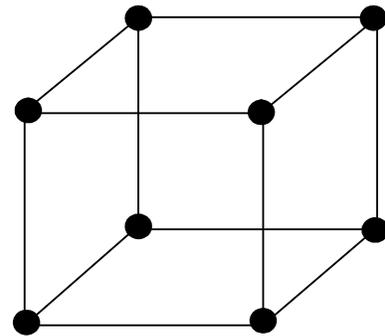


Fig. 3 (a). Primitive unit cell

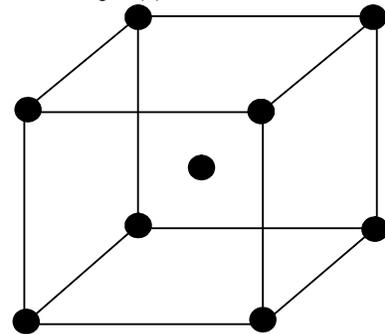


Fig. 3 (b) Body center unit cell

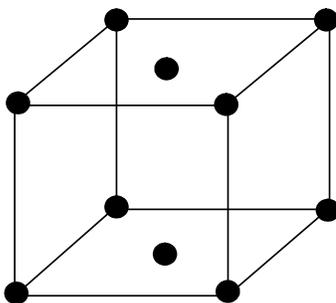


Fig. 3 (d) End Center unit cell.

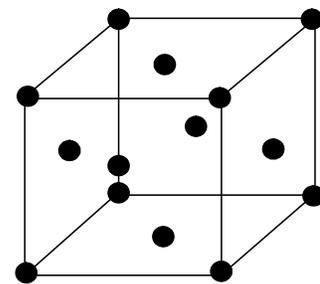
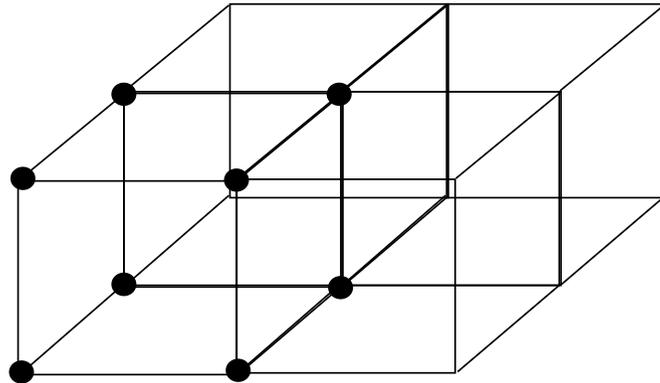


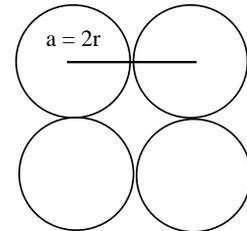
Fig. 3 (c) Face Center unit cell.

Primitive Unit Cell: In a primitive unit cell the same type of atoms are present at all the corners of the unit cell and are not present anywhere else. It can be seen that each atom at the corner of the unit cell is shared by eight unit cells (four on one layer, as shown, and four on top of these). Therefore, the volume occupied by a sphere in a unit cell is just one-eighth of its total volume. Since there are eight such spheres, the total volume occupied by the spheres is one full volume of a sphere. Therefore, a primitive cubic unit cell has effectively one atom.



Each atom is shared by eight unit cells

A primitive unit cell is created in the manner as shown in the figure. Four atoms are present in such a way that the adjacent atoms touch each other. Therefore, if the length of the unit cell is 'a', then it is equal to 2r, where r is the radius of the sphere. Four more spheres are placed on top of these such that they eclipse these spheres.



Exercise 1: How many atoms are present in a primitive cell?

Packing Fraction

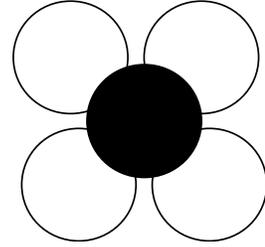
The packing efficiency of a unit cell can be understood by calculating what is called the **packing fraction**. It is defined as ratio of the volume of the unit cell that is occupied by the spheres of a unit cell to the volume of the unit cell.

Therefore, $PF = \frac{4}{3} \frac{\pi r^3}{(2r)^3} \approx 0.52$. (This implies that 52 % of the volume of a unit cell is occupied by the spheres).

Body Center Unit Cell : A Body Center unit cell is an unit cell in which the same atoms are present at all the corners and also at the center of the unit cell and are not present anywhere else. This unit cell is created by placing four atoms which are not touching each other. Then we place an atom on top of these four. Again, four spheres eclipsing the first layer are placed on top of this. The effective number of atoms in Body Center Unit Cell is 2 (One from all the corners and one at the center of the unit cell). Moreover, since in BCC the body centered atom touches the top four and the bottom four atoms, the length of the body

diagonal ($\sqrt{3}a$) is equal to 4r. The packing fraction in this case is $= \frac{2 \times \frac{4}{3} \pi r^3}{(4r / \sqrt{3})^3} \approx 0.68$

Face Center Unit Cell : In an FCC unit cell, the same atoms are present at all the corners of the cube and are also present at the center of each square face and are not present anywhere else. The effective number of atoms in FCC is 4 (one from all the corners, 3 from all the face centers since each face centered atom is shared by two cubes). Since, here each face centered atom touches the four corner atoms, the face diagonal of the cube ($\sqrt{2}a$) is equal to $4r$.



$$\text{packing fraction} = \frac{4 \times \frac{4}{3} \pi r^3}{(4r / \sqrt{2})^3} \approx 0.74$$

Exercise 2: a) What is the void fraction in case of S.C., B.C.C and F.C.C?
 b) Which is most packed structure S.C., B.C.C or F.C.C?

Seven crystal systems : The seven crystal systems are given below:

Crystal System	Bravais Lattices	Parameters of Unit Cell	
		Intercepts	Crystal angle
1. Cubic	Primitive, Face Centered, Body Centered = 3	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
2. Orthorhombic	Primitive, Face Centered, Body Centered, End Centered = 4	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
3. Tetragonal	Primitive, Body Centered = 2	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
4. Monoclinic	Primitive, End Centered = 2	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
5. Triclinic	Primitive = 1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
6. Hexagonal	Primitive = 1	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
7. Rhombohedral	Primitive = 1	$a = b = c$	$\alpha = \gamma = \beta \neq 90^\circ$
Total = 14			

Illustration 1: Iron (II) oxide, FeO, crystal has a cubic structure and each edge of the unit cell is 5\AA . Taking density of the oxide as 4 g/cc , calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell.

Solution: Volume of the unit cell = $(5 \times 10^{-8} \text{ cm})^3 = 1.25 \times 10^{-22} \text{ cm}^3$.
 Density of FeO = 4 g cm^{-3}
 Therefore mass of unit cell = $1.25 \times 10^{-22} \times 4 = 5 \times 10^{-22} \text{ g}$.
 Mass of one molecule of FeO = Molar mass in g./ Avagadro's number

$$= \frac{72 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.195 \times 10^{-22} \text{ g}$$

 Number of FeO molecules per unit cell = $\frac{5 \times 10^{-22}}{1.195 \times 10^{-22}} \approx 4$

Close Packing of Atoms / Ions

Atoms are space filling entities and structures can be described as resulting from the packing of spheres. The most efficient, called Closest Packing, can be achieved in two ways, one of which is called Hexagonal Close Packing (Hexagonal Primitive) and the other, Cubic Close Packing (FCC). Hexagonal close packing can be built up as follows: Place a sphere on a flat surface. Surround it with six equal spheres as close as possible in the same plane. Looking down on the plane, the projection is as shown in Fig. 5 (a). Let us call this layer as the A layer. Now form over the first layer a second layer of equally bunched spheres, Fig 5 (b), so as to nestle into the voids. It will be clearly seen that once a sphere is placed over a void, it blocks the voids which are adjacent to that void. Let us call this layer as the B layer. Now, it can be clearly seen that there are two types of voids created by the B layer of spheres. If a sphere is placed on the x - type of voids, it would resemble the A layer of spheres in the sense that, it eclipses the spheres of the A layer.

On the other hand, if the spheres were to be placed on the y - type of voids, it would neither eclipse the A layer nor the B layer of spheres. This would clearly be a unique layer. Let us call this layer as the C layer. This arrangement (i.e, ABCABC...) is called the Cubic Close Packing (FCC).

Hexagonal Primitive Unit Cell : Each corner atom would be common to 6 other unit cells, therefore their contribution to one unit cell would be 1/6. Therefore, the total number of atoms present per unit cell effectively is 6. The height of the unit cell 'c' is $4r\sqrt{2/3}$ and the length of the unit cell 'a' is $2r$. Therefore the area of the base is equal to the area of six equilateral triangles = $6 \times \frac{\sqrt{3}}{4}(2r)^2$. The volume of the unit cell = $6 \times \frac{\sqrt{3}}{4}(2r)^2 \times 4r\sqrt{2/3}$. Therefore the packing fraction =

$$\frac{6 \times \frac{4}{3} \pi r^3}{6 \times \frac{\sqrt{3}}{4}(2r)^2 \times 4r\sqrt{2/3}} \approx 0.74$$

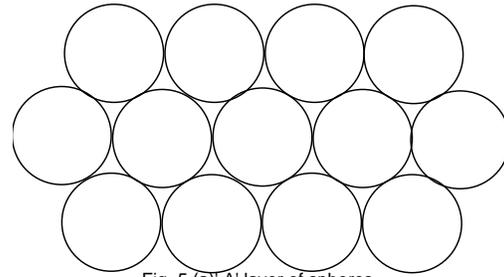
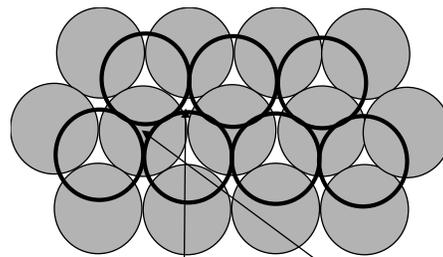


Fig. 5 (a) A' layer of spheres.



y' type of void x' type of void
Fig. 5 (b) A' and 'B' layer of spheres.

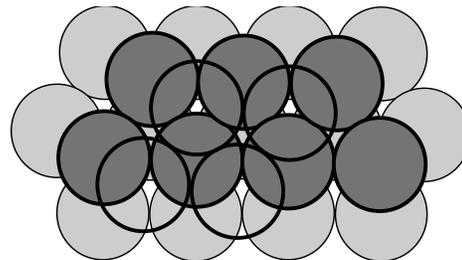
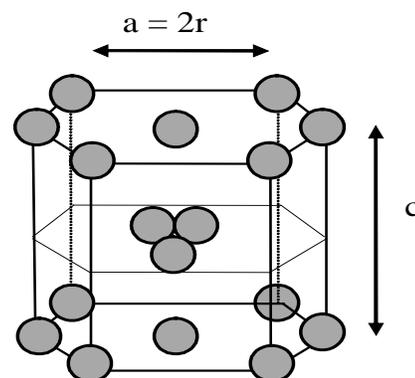


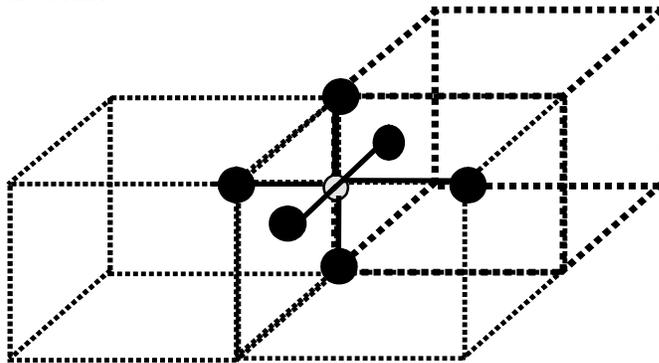
Fig. 5 (c) A' and 'B' layer of



Exercise 3: a) What is the coordination number of the atoms arranged in (ABC ABC ABC...) type structure.
 b) The void fraction of _____ and H.C.P is same.

Tetrahedral Voids and Octahedral Voids

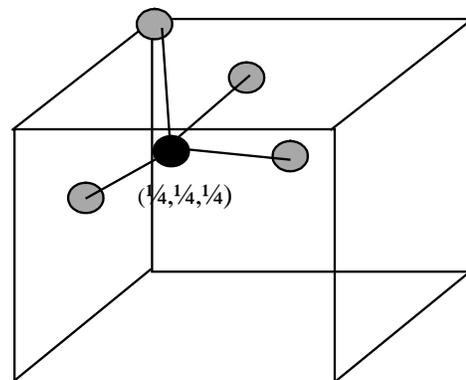
The close packing system involves two kinds of voids - tetrahedral voids and octahedral voids. The former has four spheres adjacent to it while the latter has six spheres adjacent to it. These voids are only found in either FCC or Hexagonal Primitive unit cells. Let us first consider a FCC unit cell (as shown in the figure). Not all the atoms of the unit cell are shown (for convenience). Let us assume that there is an atom (different from the one that forms the FCC) at the center of an edge. Let it be big enough to touch one of the corner atoms of the FCC. In that case, it can be easily understood that it would also touch six other atoms (as shown) at the same distance. Such voids in an FCC unit cell in which if we place an atom it would be in contact with six spheres at equal distance (in the form of an octahedron) are called octahedral voids.



An atom at the center of an edge touches six other atoms in the form of an octahedron

On calculation, it can be found out that a FCC unit cell has four octahedral voids effectively. The number of octahedral voids of a unit cell is equal to the effective number of atoms of that unit cell.

Let us again consider a FCC unit cell. If we assume that one of its corners is an origin, we can locate a point having coordinates $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. If we place an atom (different from the ones that form the FCC) at this point and if it is big enough to touch the corner atom, then it would also touch three other atoms (as shown in the figure) which are at the face centers of all those faces which meet at that corner. Moreover, it would touch all these atoms at the corners of a regular tetrahedron. Such voids are called tetrahedral voids. Since there are eight corners, there are eight tetrahedral voids in a FCC unit cell. The number of tetrahedral voids is double the number of octahedral voids. Therefore, the number of tetrahedral voids in HCP is 12.



An atom occupying a tetrahedral void

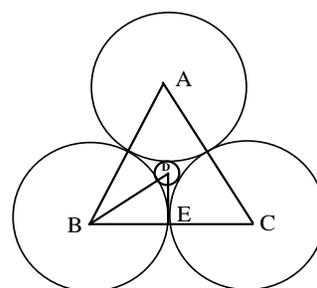
Exercise 4: i) *What is the number of octahedral and tetrahedral voids in case of S.C H.C.P and F.C.C?*
 ii) *True of False*
Number of tetrahedral voids is a whole number multiple of the number of octahedral void where n is any integer.

Radius Ratio Rules

The structure of many ionic solids can be accounted for by considering the relative sizes of the positive and negative ions, and their relative numbers. Simple geometric calculations allow us to work out as to how many ions of a given size can be in contact with a smaller ion. Thus, we can predict the coordination number from the relative sizes of the ions.

Calculation of Some Limiting Radius Ratio Values

- i) **Co - ordination number 3 :** The adjacent figure shows the smaller positive ion of radius r^+ in contact with three larger negative ions of radii r^- . It can be seen that $AB = BC = AC = 2r^-$, $BE = r^- + r^+$. Further, the angle ABC is 60° , and the angle DBE is 30° . By trigonometry $\cos 30^\circ = (BE / BD)$.



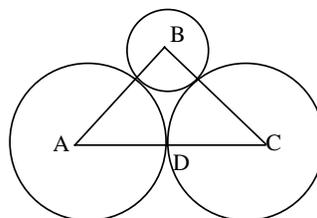
Cross Section Through Planar Triangle Site

$$BD = (BE / \cos 30^\circ), r^+ + r^- = r^- / \cos 30^\circ$$

$$= (r^- / 0.866) = r^- \times 1.155, r^+ = (1.155 r^-) - r^-$$

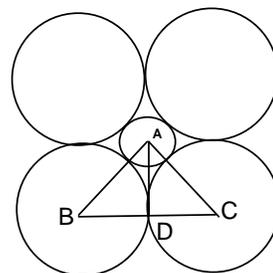
$$= 0.155 r^-, \text{ Hence } (r^+ / r^-) = 0.155.$$

- ii) **Co - ordination number 4 (tetrahedron):** Angle ABC is the tetrahedral angle of $109^\circ 28'$ and hence the angle ABD is half of this, that is $54^\circ 44'$. In the triangle ABD , $\sin ABD = 0.8164 = AD / AB = \frac{r^-}{r^+ + r^-}$. Taking reciprocals,



$$\frac{r^+ + r^-}{r^-} = \frac{1}{0.8164} = 1.225, \text{ rearranging, we get, } \frac{r^+}{r^-} = 0.225.$$

- iii) **Co - ordination number 6 (octahedron):** A cross section through an octahedral site is shown in the adjacent figure and the smaller positive ion (of radius r^+) touches six larger negative ions (of radius r^-). (Note that only four negative ions are shown in this section and one is above and one below the plane of the paper). It is obvious that $AB = r^+ + r^-$ and $BD = r^-$. The angle ABC is 45° in the triangle ABD . $\cos ABD = 0.7071 = (BD / AB)$



$$= \frac{r^-}{r^+ + r^-}. \text{ Rearranging, } \frac{r^+}{r^-} = 0.414.$$

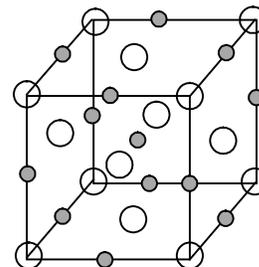
Limiting radius ratio $\frac{r^+}{r^-}$	Co - ordination number	Shape	Example
< 0.155	2	Linear	BeF ₂
0.155 - 0.225	3	Planar Triangle	-
0.225 - 0.414	4	Tetrahedron	ZnS
0.414 - 0.732	4	Square planar	PtCl ₄ ²⁻
0.414 - 0.732	6	Octahedron	NaCl
0.732 - 0.999	8	Body centered cubic Type	CsCl

Exercise-5: The radius of calcium ion is 94 pm and of an oxide ion is 146 pm. The coordination number of calcium is _____

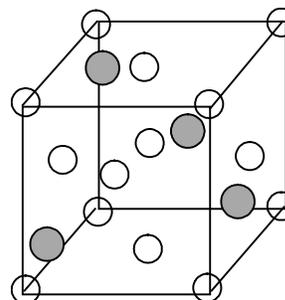
Classification Of Ionic Structures

In the following structures, a black circle would denote a cation and a white circle would denote an anion. In any solid of the type A_xB_y, the ratio of the coordination number of A to that of B would be y : x.

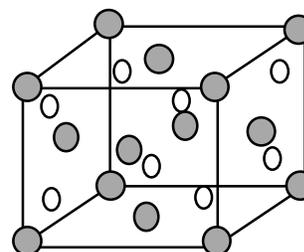
- i) Rock Salt Structure : Cl⁻ is forming a FCC unit cell in which Na⁺ is in the octahedral voids. The coordination number of Na⁺ is 6 and therefore that of Cl⁻ would also be 6. Moreover, there are 4 Na⁺ ions and 4 Cl⁻ ions per unit cell. The formula is Na₄Cl₄ i.e., NaCl. The other substances having this kind of a structure are all halides of alkali metals except cesium halide and all oxides of alkaline earth metals except beryllium oxide.



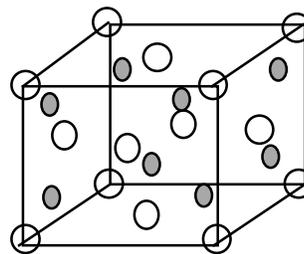
- ii) Zinc Blende Structure (ZnS) : Sulphide ions are face centered and zinc is present in alternate tetrahedral voids. Formula is Zn₄S₄, i.e., ZnS. Coordination number of Zn is 4 and that of sulphide is also 4. Other substance that exists in this kind of a structure is BeO.



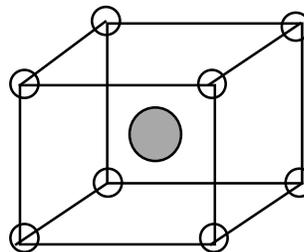
- iii) Fluorite structure (CaF₂) : Calcium ions are face centered and fluoride ions are present in all the tetrahedral voids. There are four calcium ions and eight fluoride ions per unit cell. Therefore the formula is Ca₄F₈, (i.e., CaF₂). The coordination number of fluoride ions is four (tetrahedral voids) and thus the coordination number of calcium ions is eight. Other substances which exist in this kind of structure are UO₂, and ThO₂.



- v) Antifluorite structure (Li_2O) : Oxide ions are face centered and lithium ions are present in all the tetrahedral voids. There are four oxide ions and eight lithium ions per unit cell. As it can be seen, this unit cell is just the reverse of Fluorite structure, in the sense that, the positions of cations and anions is interchanged. Other substances which exist in this kind of a structure are Na_2O , K_2O and Rb_2O .



- v) Cesium halide structure (CsCl) : Chloride ions are primitive cubic while the cesium ion occupies the center of the unit cell. There is one chloride ion and one cesium ion per unit cell. Therefore the formula is CsCl . The coordination number of cesium is eight and that of chloride ions is also eight. Other substances which exist in this kind of a structure are all halides of cesium.



Exercise 6: *MgO has a structure of NaCl and TlCl has the structure of CsCl . What are the coordination numbers of ions in each?*

Answers to Exercises

Exercise 1: One

Exercise 2: (a) 48%, 32%, 26%, (b) f.c.c.

Exercise 3: (a) 12, (b) f.c.c.

Exercise 4: (b) false

Exercise 5: 4

Exercise 6: 6, 8

Solved Problems

Subjective

Problem 1: An element 'X' (atomic mass 150) having fcc structures has unit cell edge 400 pm. Calculate the density of 'X' and the number of unit cell for 15g of X.

Solution: Length of the unit cell edge = 400 pm = 400×10^{-10} cm
Volume of unit cell = $(400 \times 10^{-10})^3 = 6.4 \times 10^{-23}$ cm³
Since structure is fcc the number of atoms will be 4
Density = $\frac{nM_m}{N_A \times V} = \frac{4 \times 150}{6.023 \times 10^{23} \times 6.4 \times 10^{-23}} = 15.56$ g/cc
Volume of 15g of X = $\frac{\text{Mass}}{\text{density}} = \frac{15}{15.56} = 0.9640$ cc
No. of unit cells in 0.9640 cm³ = $\frac{\text{Volume of Substance}}{\text{Unit cell volume}}$
 $= \frac{0.9640}{6.4 \times 10^{-23}} = 1.506 \times 10^{22}$ unit cells

Problem 2: The compound A₂B has ZnS structure. Its density is 3.4 g/cc. What is the edge length of unit cell? (Molecular weight of A = 32, B = 35)

Solution: For ZnS structure, n = 4
Molar mass of A₂B (M_m) = 2 × 32 + 35 = 99
ρ = 3.4 g/cc
 $\therefore \rho = \frac{n \times M_m}{a^3 \times N_A}$
 $a = \left(\frac{4 \times 99}{3.4 \times 6.023 \times 10^{23}} \right)^{1/3}$
a = 5.78×10^{-8} cm = 5.78 Å

Problem 3: The unit cell in a crystal of diamond belongs to a cubic crystal system but doesn't correspond to the Bravais lattice. The volume of unit cell of diamond is 0.0454 nm³ and the density of diamond is 3.52 g/cc. Find the number of carbon atoms in a unit cell of diamond?

Solution: Atomic mass of carbon = 12 g/mol
Volume of the unit cell of diamond = 0.0454 nm³
Density = $\frac{\text{Atomic mass} \times n}{\text{Unit cell volume} \times \text{Avogadro's no.}}$
 $3.52 = \frac{12 \times n}{0.0454 \times 10^{-21} \times 6.023 \times 10^{23}}$
n = 8 atoms/unit cell

Problem 4: Iron occurs as BCC as well as FCC unit cell. If the effective radius of an atom of iron is 124 pm, compute the density of iron in both these structures.

Solution: In a body centered unit cell, atoms touch each other along the cross diagonal. Hence,

$$4r = \sqrt{3}a, a = \frac{4}{\sqrt{3}}r = \frac{4}{\sqrt{3}}(124\text{pm}) = 286.4\text{pm}$$

for this unit cell, $N = 2$. Hence,

$$\rho = \frac{n}{a^3} \left(\frac{M_m}{N_a} \right) = \frac{2}{(286.4 \times 10^{-12})^3} \left[\frac{55.8}{6.023 \times 10^{23}} \right] = 7.887 \times 10^6 \text{gm}^{-3} = 7.887 \text{gcm}^{-3}$$

In a face centered unit cell, atoms touch each other along the face diagonals. Hence,

$$4r = \sqrt{2}a, a = \frac{4}{\sqrt{2}}r = \frac{4}{\sqrt{2}}(124\text{pm}) = 350.7\text{pm}.$$

For this unit cell, $N = 4$. Hence,

$$\rho = \frac{4}{350.7 \times 10^{-12}} \left[\frac{55.8}{6.023 \times 10^{23}} \right] = 8.59 \times 10^6 \text{gm}^{-3} = 8.59 \text{gcm}^{-3}$$

Problem 5: *NH₄Cl crystallizes in a body centered cubic lattice, with a unit cell distance of 387 pm. Calculate (a) the distance between the oppositely charged ions in the lattice, and (b) the radius of the NH₄⁺ ion if the radius of the Cl⁻ ion is 181 pm.*

Solution: a) In a body centered cubic lattice oppositely charged ions touch each other along the cross - diagonal of the cube. Hence, we can write,

$$2r^+ + 2r^- = \sqrt{3}a, r^+ + r^- = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3}}{2}(387\text{pm}) = 335.15\text{pm}$$

b) Now, since $r^- = 181\text{pm}$, we have $r^+ = (335.15 - 181)\text{pm} = 154.15\text{pm}$.

Problem 6: *KCl crystallizes in the same type of lattice as does NaCl. Given that,*

$$\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.5, \quad \frac{r_{\text{Na}^+}}{r_{\text{K}^+}} = 0.7$$

Calculate (a) the ratio of the side of the unit cell for KCl to that for NaCl, and (b) the ratio of density of NaCl to that for KCl.

Solution: NaCl crystallizes in the face centered cubic unit cell such that $r_{\text{Na}^+} + r_{\text{Cl}^-} = \frac{a}{2}$

, where a is the edge length of unit cell. Now since, $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.5$, $\frac{r_{\text{Na}^+}}{r_{\text{K}^+}} = 0.7$

$$\text{we will have, } \frac{r_{\text{Na}^+} + r_{\text{Cl}^-}}{r_{\text{Cl}^-}} = 1.5 \quad \text{or} \quad \frac{r_{\text{K}^+}}{r_{\text{Cl}^-}} = \frac{r_{\text{K}^+}}{r_{\text{Na}^+}} \times \frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = \frac{0.5}{0.7} \times \frac{0.5}{0.7}$$

$$\frac{r_{\text{K}^+} + r_{\text{Cl}^-}}{r_{\text{Cl}^-}} = \frac{1.2}{0.7}, \quad \text{Hence, } \frac{r_{\text{K}^+} + r_{\text{Cl}^-}}{r_{\text{Na}^+} + r_{\text{Cl}^-}} = \frac{1.2}{0.7} \times \frac{1}{1.5}$$

$$\frac{\frac{a_{\text{KCl}}}{2}}{\frac{a_{\text{NaCl}}}{2}} = \frac{1.2}{0.7 \times 1.5} = \frac{a_{\text{KCl}}}{a_{\text{NaCl}}} = 1.143$$

Now since, $\rho = \frac{N}{a^3} \left[\frac{M}{N_A} \right]$

We will have, $\frac{\rho_{NaCl}}{\rho_{KCl}} = \left(\frac{a_{KCl}}{a_{NaCl}} \right)^3 \left(\frac{M_{NaCl}}{M_{KCl}} \right) = (1.143)^3 \left(\frac{58.5}{74.5} \right) = 1.172$

Problem 7: *In the cubic solid of CsCl ($d = 3.97 \text{ g cm}^{-3}$) the eight corners are occupied by Cl⁻ with a Cs⁺ at the center and vice versa. Calculate the distance between the neighbouring Cs⁺ and Cl⁻ ions. What is the radius ratio of the two ions ?*

Solution: In a unit cell, there are one Cs⁺ and one Cl⁻, i.e, one CsCl ion pair.

$$\text{Density} = \frac{n \times \text{mol.wt.}}{a^3 \times \text{Av.number}}$$

$$3.97 = \frac{1 \times 168.36}{a^3 \times 6.023 \times 10^{23}}$$

$$a = 4.13 \times 10^{-8} \text{ cm.}$$

$$a = 4.13 \text{ \AA}$$

For a cube of side length 4.13 \AA, diagonal = $\sqrt{3} \times 4.13 = 7.15 \text{ \AA}$.

As it is a BCC with Cs⁺ at center (radius r^+) and Cl⁻ at corners (radius r^-) so,

$$2r^+ + 2r^- = 7.15 \text{ \AA} \quad \text{or} \quad r^+ + r^- = 3.57 \text{ \AA}$$

that is, distance between neighbouring Cs⁺ and Cl⁻ = 3.57 \AA

Now assume, two Cl⁻ ions touch each other so,

$$\text{length of unit cell} = 2r^- = 4.13 \text{ \AA}$$

$$r^- = 2.06 \text{ \AA}, \quad r^+ = (3.57 - 2.06) = 1.51 \text{ \AA}$$

$$\frac{r^+}{r^-} = \frac{1.51}{2.06} = 0.73 \text{ \AA}$$

Problem 8: *The unit cell cube length for LiCl is 5.14 \AA. Assuming anion cation contact, calculate the ionic radius for chloride ion.*

Solution: The distance between Li⁺ and Cl⁻ ion can be derived as half of the edge length of cube.

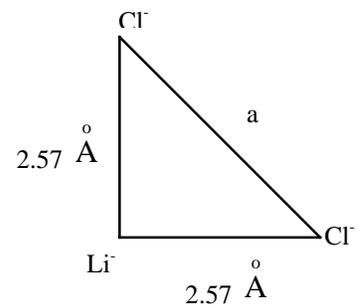
$$d_{Li^+-Cl^-} = \frac{5.14}{2} = 2.57 \text{ \AA}$$

$$d_{Cl^- - Cl^-} = \sqrt{(2.57)^2 + (2.57)^2}$$

$$= 3.63 \text{ \AA}$$

The radius of Cl⁻

$$= \frac{d_{Cl^- - Cl^-}}{2} = \frac{3.63}{2} = 1.815 \text{ \AA}$$



Solution: The distance between Li^+ and Cl^- ion can be derived as half of the edge length of cube.

$$d_{\text{Li}^+ - \text{Cl}^-} = \frac{5.14}{2} = 2.57 \text{ \AA}$$

Problem 9: In fcc arrangement of A & B atoms, where A atoms are at corners of the unit cell, B atoms at the face-centers, one of the atoms are missing from the corner in each unit cell then find the percentage of void space in the unit cell.

Solution: There are $\frac{7}{8}$ A atoms and 3 B atoms per unit cell

$$\text{Also, } 2 r_A + 2 r_B = \sqrt{2}a$$

$$\text{or, } a = \sqrt{2}r_A + \sqrt{2}r_B$$

$$\text{Volume of unit cell} = a^3 = (\sqrt{2}r_A + \sqrt{2}r_B)^3$$

$$= 2\sqrt{2}(r_A + r_B)^3$$

Fraction of volume occupied per unit volume of the unit cell is given by

$$\text{PF} = \frac{\frac{7}{8} \times \left(\frac{4}{3}\pi r_A^3\right) + \left(3 \times \frac{4}{3}\pi r_B^3\right)}{2\sqrt{2}(r_A + r_B)^3} = \frac{\frac{7}{6}\pi r_A^3 + 4\pi r_B^3}{2\sqrt{2}(r_A + r_B)^3}$$

$$\text{Q } \frac{r_A}{r_B} = 0.414$$

$$= \frac{\pi \left[\frac{7}{6}r_A^3 + 4(0.414r_A)^3 \right]}{2\sqrt{2}(r_A + 0.414r_A)^3} = \frac{\pi r_A^3 \times \frac{7}{6} + 4\pi(0.414)^3 r_A^3}{2\sqrt{2} r_A^3 (1 + 0.414)^3}$$

$$= \frac{\pi \left[\frac{7}{6} + (4 \times 0.414)^3 \right]}{2\sqrt{2} (1 + 0.414)^3} = 0.570$$

So, void space = 1 – packing fraction

$$= 1 - 0.570$$

$$= 0.430/\text{unit volume of unit cell}$$

\therefore percentage of void space = 43%

Problem 10: Prove that the void space percentage in zinc blende structure is 25%.

Solution: Anions are in fcc positions and half of the tetrahedral holes are occupied by cations. There are 4 anions and eight tetrahedral holes per unit cell.

$$\text{Here, face-diagonal} = \sqrt{2}a$$

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

$$\text{or, } a = 2\sqrt{2}r_-$$

r_- = radius of anion

r_+ = radius of cation

a = edge length of the cell

Volume of unit cell = a^3

$$= (2\sqrt{2}r_-)^3$$

$$= 16\sqrt{2}r_-^3$$

$$\therefore \text{Packing Fraction} = \frac{4 \times \left(\frac{4}{3}\pi r_-^3\right) + \frac{1}{2} \times 8 \times \left(\frac{4}{3}\pi r_+^3\right)}{16\sqrt{2}r_-^3} = \frac{\pi}{3\sqrt{2}} \left\{ 1 + \left(\frac{r_+}{r_-}\right)^3 \right\}$$

Since, for tetrahedral holes

$$\frac{r_+}{r_-} = 0.225$$

$$\therefore \text{PF} = \frac{\pi}{3\sqrt{2}} [1 + (0.225)^3]$$

= 0.7496 / unit volume of unit cell

\therefore void space = 1 – 0.7496

= 0.2504/unit volume of unit cell

\therefore percentage of void space = 25.04%

\approx **25%**

Objective

Problem 1: An ionic compound AB has ZnS type of structure, if the radius A^+ is 22.5pm, then the ideal radius of B^- is

(A) 54.35pm

(B) 100pm

(C) 145.16pm

(D) None

Solution: Since ionic compound AB has ZnS type of structure, therefore it has tetrahedral holes, for which

$$\frac{\text{radius of cation}}{\text{radius of anion}} = 0.225$$

$$\frac{r_+}{r_-} = 0.225$$

$$\frac{22.5}{r_-} = 0.225$$

Hence, $r_- = 100$ pm

\therefore (B)

Problem 2: In a cubic packed structure of mixed oxides, the lattice is made up of oxide ions, one fifth of tetrahedral voids are occupied by divalent (X^{2+}) ions, while one-half of the octahedral voids are occupied by trivalent ions (Y^{3+}), then the formula of the oxide is.

(A) XY_2O_4

(B) X_2YO_4

(C) $X_4Y_5O_{10}$

(D) $X_5Y_4O_{10}$

Solution: In ccp anions occupy primitives of the cube while cations occupied voids. In ccp there are two tetrahedral voids and one octahedral holes.

For one oxygen atom there are two tetrahedral holes and one octahedral hole.

Since one fifth of the tetrahedral voids are occupied by divalent cations (X^{2+})

$$\therefore \text{number of divalent cations in tetrahedral voids} = 2 \times \frac{1}{5}$$

Since half of the octahedral voids are occupied by trivalent cations (Y^{3+})

$$\therefore \text{number of trivalent cations} = 1 \times \frac{1}{2}$$

So the formula of the compound is $(X)_{\frac{2}{5}} (Y)_{\frac{1}{2}} (O)_1$

$$\text{or } X_{\frac{2}{5}} Y_{\frac{1}{2}} O_1,$$

$$\text{or } X_4 Y_5 O_{10}$$

\therefore (C)

Problem 3: *If three elements X, Y & Z crystallized in cubic solid lattice with X atoms at corners, Y atoms at cube centre & Z-atoms at the edges, then the formula of the compound is:*

(A) XYZ

(B) XY_3Z

(C) XYZ_3

(D) X_3YZ_3

Solution: Atom X is shared by 8 corners
1 atoms of Z is shared by 4 unit cells
Atom Y is present at centre of the unit cell

$$\text{Hence, effective number of atoms of X per unit cell} = 8 \times \frac{1}{8} = 1$$

$$\text{Effective number of atoms of Z per unit cell} = \frac{12}{4} = 3$$

Effective number of atoms of Y per unit cell = 1

Hence, the formula of the compound is XYZ_3

\therefore (C)

Problem 4: *A compound XY crystallizes in bcc lattice with unit cell edge-length of 480pm, if the radius of Y is 225 pm, then the radius of X^+ is*

(A) 190.70pm

(B) 225pm

(C) 127.5pm

(D) None

Solution: For bcc structure,

$$2(r_+ + r_-) = \sqrt{3} a$$

$$\text{or } r_+ + 225 = \frac{\sqrt{3}}{2} \times 480 \therefore r_+ = 190.7 \text{ pm}$$

\therefore (A)

Problem 5: *If the edge-length of the unit cell of Sodium chloride is 600pm, and the ionic radius of Cl^- ion is 190pm, then the ionic radius of Na^+ ion is*

(A) 310pm

(B) 110pm

(C) 220pm

(D) None

Solution: $r_{Na^+} + r_{Cl^-} = 600/2 = 300$

$$r_{Na^+} = 300 - 190 = 110 \text{ pm}$$

\therefore (B)

- Problem 6:** A substance has density of 2 kg dm^{-3} & it crystallizes to fcc lattice with edge-length equal to 700 pm , then the molar mass of the substance is
 (A) $74.50 \text{ gm mol}^{-1}$ (B) $103.30 \text{ gm mol}^{-1}$
 (C) $56.02 \text{ gm mol}^{-1}$ (D) $65.36 \text{ gm mol}^{-1}$

Solution:

$$\rho = \frac{n \times M_m}{N_A \times a^3}$$

$$2 = \frac{4 \times M_m}{6.023 \times 10^{23} \times (7 \times 10^{-8})^3}$$

(since, effective number of atoms in unit cell = 4)
 on solving we get $M_m = 103.03 \text{ gm / mol}$
 \therefore (B)

- Problem 7:** If the unit cell length of sodium chloride crystal is 600 pm , then its density will be
 (A) 2.165 gm/cm^3 (B) 3.247 gm/cm^3
 (C) 1.79 gm/cm^3 (D) 1.082 gm/cm^3

Solution:

$$\rho = \frac{n \times M_m}{N_A a^3}$$

$$= \frac{4 \times 58.5}{6.023 \times 10^{23} \times (6 \times 10^{-8})^3} = 1.79 \text{ g/cc}$$

\therefore (C)

- Problem 8:** Select the correct statements:-

- (A) For CsCl unit cell (edge-length = a), $r_c + r_a = \frac{\sqrt{3}}{2} a$
 (B) For NaCl unit cell (edge-length = l), $r_c + r_a = \frac{l}{2}$
 (C) The void space in a b.c.c. unit cell is 0.68
 (D) The void space % in a face-centered unit cell is 26%

Solution: In bcc structure are $r_+ + r_- = \frac{\sqrt{3}}{2} a$
 Hence, for CsCl, $r_c + r_a = \frac{\sqrt{3}}{2} a$
 \therefore (A) is correct
 Since, NaCl crystalise in fcc structure
 $\therefore 2r_c + 2r_a = \text{edge length of the unit cell}$
 Hence, $r_c + r_a = \frac{l}{2}$
 \therefore (B) is correct
 Since packing fraction of a bcc unit cell is 0.68
 \therefore void space = $1 - 0.68 = 0.32$
 \therefore (C) is incorrect

In fcc unit cell PF = 74%
 \therefore VF = 100–74 = 26%
 \therefore (D) is correct

Problem 9: Select the correct statements:-

- (A) In closest packing of x -atoms, there are $2x$ tetrahedral holes, & x -octahedral holes.
- (B) The co-ordination no. of U:O in UO_2 is 8:4
- (C) In hexagonal packing of oxide ion Sapphire (the aluminium oxide) Al^{3+} ions crystallize in $2/3^{\text{rd}}$ of the Octahedral hole, then the formula of Sapphire is Al_2O_3
- (D) If anion B constitutes ccp and all the octahedral voids are occupied by cation (A), the crystal has the same molecular formula AB, if the cation (A) occupies the alternate tetrahedral voids.

Solution: In a closest packing number of tetrahedral holes is twice of number of octahedral voids.

\therefore A & B are correct

For an oxide ion there is one octahedral hole whose $2/3^{\text{rd}}$ part is occupied by Al^{3+} ions.

\therefore number of Al^{3+} ions per unit cell = $1 \times 2/3 = 2/3$

Hence, the formula of the compound is $Al_{2/3}O_1$ or Al_2O_3

\therefore (C) is correct

In ccp structure, there are 2 tetrahedral holes and one octahedral holes.

Anion B occupy primitives of ccp unit cell

If all octahedral holes are occupied by cation A then number of cations per unit cell = 1.

Hence, the formula of the compound is AB

And if cation A occupies tetrahedral holes,

Number of cations (A) per unit cell = $2 \times 1/2 = 1$

Hence, the formula of the compound is AB

\therefore (D) is correct

Problem 10: In closest packing of atoms

- (A) The size of tetrahedral void is greater than that of the octahedral void.
- (B) The size of the tetrahedral void is smaller than that of the octahedral void.
- (C) The size of tetrahedral void is equal to that of the octahedral void.
- (D) The size of tetrahedral void may be larger or smaller or equal to that of the octahedral void depending upon the size of atoms.

Solution: For tetrahedral voids

$$\frac{r_+}{r_-} = 0.225, \quad r_+ = 0.225 r_- \quad \dots(i)$$

Similarly for octahedral voids

$$r_+ = 0.414 r_- \quad \dots(ii)$$

From equation (i) and (ii) it is clear that size of octahedral void is larger than that of tetrahedral voids.

\therefore (B)

Assignments

Subjective

LEVEL - I

1. A compound formed by element A and B crystallises in cubic structure, where A atoms are at the corners of a cube and B atoms are at the face center. What is the formula of the compound?
2. A solid has a structure in which W atoms are located at the cube corners of the unit cell, O atoms are located at the cube edges, and Na atoms at the centers. What is the formula of the compound ?
3. Calculate the number of atoms in a cubic based unit cell having one atom on each corner and two atoms on each body diagonal.
4. The density of CaF_2 is 3.18 gm/cm^3 at 20°C . Calculate the dimensions of the unit cube of the substance.
5. Potassium metal crystallizes in a face-centered arrangement of atoms where the edge of the unit cell is 0.574 nm . What is the shortest separation of any two nuclei?
6. The coordination number of the Barium ions, Ba^{2+} , in Barium Fluoride (BaF_2) is 8. What must be the coordination number of the fluoride ions, F^- .
7. Aluminium forms face centered cubic crystals. The density of Al is 2.7 g/cm^3 . Calculate the length of the side of the unit cell of Al. (At.wt. of Al = 27).
8. Polonium crystallises in a simple cubic unit cell. It has an atomic mass = 209 and density = 91.5 Kg m^{-3} . What is the edge length of its unit cell ?
9. KF has NaCl structure. What is the distance between K^+ and F^- in KF if the density of KF is 2.48 g cm^{-3} ?
10. Compute the packing fraction for spheres occupying (a) a body centered cubic and (b) a simple cubic structure, where closest neighbours in both cases are in contact.

LEVEL - II

1. A compound formed by element X and Y crystallises in the cubic structure, where X is at the corners of a cube and Y is at the face center. What is the formula of the compound. If side length is 5 \AA , estimate the density of the solid assuming at. wt. of X and Y as 60 and 90 respectively.
2. An element occurs in BCC structure with a cell length of 288 pm. The density of the element is 7.2 g cm^{-3} . How many atoms of the element does 208 g. of the element contain ?
3. An element crystallises into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two atoms on one of its diagonals. If volume of this unit cell is $24 \times 10^{-24} \text{ cm}^3$ and density of the element is 7.2 g/cm^3 , calculate the number of atoms present in 200 g of the element.
4. In LiI crystal, I⁻ ions form a cubical closest packed arrangement, and Li⁺ ions occupy octahedral holes. What is the relationship between the edge length of the unit cells and the radii of the I⁻ ions ? Calculate the limiting ionic radii of Li⁺ and I⁻ ions if $a = 600 \text{ pm}$.
5. Tungsten has body centered cubic lattice and each lattice point is occupied by one atom. Calculate the radius of metallic tungsten if density of tungsten is 19.03 g cm^{-3} and at.wt. is 183.9.
6. If the density of crystalline CsCl is 3.988 g/cm^3 , (a) calculate the volume effectively occupied by a single CsCl ion pair in the crystal (b) calculate the smallest Cs-Cs inter nuclear distance.
7. Calculate the value of Avagadro number from the internuclear distance of adjacent ions in NaCl, 0.282 nm, and the density of solid NaCl, $2.17 \times 10^3 \text{ Kg/m}^3$.
8. An element 'A' (At.wt = 100) having BCC structure has unit cell edge 400 pm. Calculate the density of A and the number of unit cells and the number of atoms in 10 g. of A.
9. Iron crystallises in several modifications. At about 910°C , the body centered cubic α form undergoes a transition to the face centered cubic γ form. Assuming that the distance between nearest neighbours is the same in the two forms at the transition temperature, calculate the ratio of density of γ iron to that of α iron at the transition temperature.
10. If NaCl is doped with 10^{-3} mole % of SrCl_2 , what is the concentration of cation vacancy?

LEVEL – III

1. The unit cell of tungsten is a face centered cubic having a volume of 31.699 \AA^3 . The atom at the centre of each face just touches the atoms at the corners. Calculate the radius and atomic volume of tungsten.
2. A certain compound, whose density is 4.56 gm/cm^3 , crystallizes in the tetragonal system with unit cell distances of $a = b = 658 \text{ pm}$ and $c = 593 \text{ pm}$. If the unit lattice contains four molecules, calculate the molar mass of the compound.
3. Metallic gold crystallises in the face centered lattice. The length of the cubic unit cell is
 $a = 4.070 \text{ \AA}$.
 - a) What is the closest distance between gold atoms ?
 - b) How many " nearest neighbours" does each gold atom have at the distance calculated in (a)
 - c) What is the density of gold ?
 - d) Prove that the packing factor for gold is 0.74.
4. Potassium crystallises in body centered cubic lattice with a unit cell length
 $a = 5.2 \text{ \AA}$.
 - a) What is the distance between nearest neighbours ?
 - b) What is the distance between next - nearest neighbours ?
 - c) How many nearest neighbours does each K atom have ?
 - d) How many next nearest neighbours does each K have ?
 - e) What is the calculated density of crystalline potassium ?
5. BaTiO_3 crystallises in the perovskite structure. This structure may be described as a cubic lattice, with barium ions occupying the corners of the unit cell, oxide ions occupying the face centers and titanium ions occupying the centers of the unit cells.
 - a) If titanium is described as occupying holes in the BaO lattice, what type of hole does it occupy ?
 - b) What fraction of the holes of this type does it occupy ?
6. The ZnS structure is cubic. The unit cell may be described as a face centered sulphide ion sublattice with nine ions in the centers of alternating minicubes made by partitioning the main cube into eight equal parts.
 - a) How many nearest neighbours does each Zn^{2+} have ?
 - b) How many nearest neighbours does each S^{2-} have ?
 - c) What angle is made by the lines connecting any Zn^{2+} to any two of its nearest neighbour?
 - d) What minimum (r^+/r^-) ratio is needed to avoid anion-anion contact ? Closest cation-anion pairs are assumed to touch.
7. Cesium chloride, bromide and iodide form interpenetrating simple cubic crystals like the other alkali halides. The length of the side of the unit cell of CsCl is 412.1 ± 0.3 . Determine

- a) density of CsCl
b) Ion radius of Cs^+ , assuming that the ions touch along a diagonal through the unit cell and that the ion radius of Cl^- is 181 pm.
8. Calculate the value of Avogadro's number from the internuclear distance of adjacent ions in NaCl, 0.282 nm and the density of solid NaCl is $2.17 \times 10^3 \text{ kg/m}^3$.
9. A compound formed by element X and Y crystallises in the cubic structure, where X is at the corners of a cube and Y is at the face center. What is the formula of the compound. If side length is 5\AA , estimate the density of the solid assuming at. wt. of X and Y as 60 and 90 respectively.
10. An unknown metal is found to have a specific gravity of 10.2 at 25°C . It is found to crystallize in a body-centered cubic lattice with a unit cell edge length of 3.147\AA . Calculate the atomic weight.

Objective

LEVEL - I

- The number of tetrahedral and octahedral voids in hexagonal primitive unit cell are
(A) 8,4 (B) 2,1
(C) 12,6 (D) 6,12
- An element with molecular weight of 200 gm/mole crystallizes in a simple cubic cell. If the unit cell length is 3\AA and Avogadro's no. is $6 \times 10^{23} \text{ mole}^{-1}$, the density of the element is
(A) 15 g/cc (B) 13.12 g/cc
(C) 12.34 g/cc (D) 15.9 g/cc
- If a be the edge-length of the unit cell, r be the radius of an atom, then for face centered cubic lattice, the correct relation is
(A) $4r = \sqrt{3}a$ (B) $4r = \sqrt{2}a$
(C) $4a = \sqrt{3}r$ (D) None
- The rank of atoms in the hexagonal unit cell is
(A) 4 (B) 3
(C) 5 (D) 6
- A solid is made of two elements P&Q. Atoms P are in ccp arrangement and atoms Q occupy all the octahedral voids and half of the tetrahedral voids, then the simplest formula of the compound is
(A) PQ_2 (B) P_2Q
(C) PQ (D) P_2Q_2
- The arrangement of Cl^- ions in CsCl structure is
(A) hcp (B) fcc
(C) bcc (D) Simple cubic
- The structure of CsCl Crystal is
(A) bcc lattice (B) fcc lattice
(D) Octahedral (D) None
- Close packing is maximum in the Crystal which is
(A) Simple cube (B) bcc
(C) fcc (D) none
- In hexagonal primitive unit cell, the Corner is shared by
(A) 4 Unit cells (B) 6-unit cells
(C) 3 unit cells (D) 3 unit cells
- In fluorite structure (CaF_2)
(A) Ca^{++} ions are ccp & F^- ions are present in all the tetrahedral voids
(B) Ca^{++} ions are ccp & F^- ions are present in all the octahedral voids
(C) Ca^{++} ions are ccp & F^- ions are present in all the octahedral voids and half of ions are
(D) None

11. CsBr has bcc Lattice with the edge length 9.4\AA , the shortest inter-ionic distance in between Cs^+ & Br^- is
(A) 8.14\AA (B) 7.14\AA
(C) 7.50\AA (D) 4.07\AA
12. The mass of unit cell of CaF_2 (fluorite structure) corresponds to
(A) mass of 8Ca^{++} ions & 4F^- ions (B) mass of 4Ca^{++} ions & 8F^- ions
(C) mass of 4Ca^{++} ions & 4F^- ions (D) mass of 1Ca^{++} ions & 2F^- ions
13. Fe_3O_4 is
(A) Ferromagnetic (B) Diamagnetic
(C) Paramagnetic (D) Ferrimagnetic
14. When an ion leaves its correct lattice site and occupies interstitial sites in its crystal lattice, it is called
(A) Crystal defect (B) Frenkel defect
(C) Schottky defect (D) None
15. The 8 : 8 type of packing is present in ?
(A) CsCl (B) KCl
(C) NaCl (D) MgF_2

LEVEL - II

1. Select the correct statement(s)
 - (A) The C.N. of cation occupying a tetrahedral hole is 4
 - (B) The C.N. of cation occupying an octahedral hole is 6
 - (C) In Schottky defects, density of the lattice decreases.
 - (D) In Frenkel defects, density of the lattice increases.

2. A solid X^+Y^- has a bcc structure. If the distance of closest approach between the two atoms is 1.73\AA . The edge length of the cell is

(A) $\sqrt{2}$ pm	(B) $\sqrt{3}/2$ pm
(C) 100 pm	(D) 142.2 pm

3. The edge length of a cube is 400 pm. Its body diagonal would be

(A) 600 pm	(B) 566 pm
(C) 693 pm	(D) 500 pm

4. Select the correct statement(s):-
 - (A) Schottky defect is shown by CsCl
 - (B) Frenkel defect is shown by ZnS
 - (C) Hexagonal close packing (hcp) & Cubic close packing (ccp) structure has same co-ordination no. 12
 - (D) At high pressure, the co-ordination number increases.

5. Select the correct statement(s)
 - (A) At high pressure, the co-ordination no. increases from 6:6 to 8:8
 - (B) At high pressure, the co-ordination no. decreases from 8:8 to 6:6
 - (C) At high temperature, co-ordination number decreases
 - (D) AT 760K temperature, CsCl structure changes into NaCl.

6. A corner atom in the hexagonal unit cell structure is shared with

(A) 4-unit cells	(B) 3-unit cells
(C) 6-unit cells	(D) None

7. The interstitial hole is called tetrahedral hole because
 - (A) It is formed by 4 spheres
 - (B) It is tetrahedral in shape
 - (C) It is formed by 4 spheres the centre of which form a regular tetrahedron.
 - (D) None of these

8. Fraction of total volume occupied by atoms in a simple cube is

(A) $\frac{\pi}{2}$	(B) $\frac{\sqrt{3}\pi}{8}$
(C) $\frac{\sqrt{2}\pi}{6}$	(D) $\frac{\pi}{6}$

9. KBr shows, which of the following defects?

(A) Frenkel defect	(B) Schottky defect
(C) Metal excess defect	(D) Metal deficiency

10. If in diamond, there is a unit cell of carbon atoms as fcc and if carbon atom is sp^3 what fractions of void are occupied by carbon atom.
(A) 25% Tetrahedral (B) 50% Tetrahedral
(C) 25% Octahedral (D) 50% Octahedral
11. The limiting radius ratio of the complex $[\text{Ni}(\text{CN})_4]^{2-}$ is
(A) 0.225 – 0.414 (B) 0.414 – 0.732
(C) 0.155 – 0.225 (D) None
12. If the ratio of co-ordination no. P to that of Q be Y:Z, then the formula of the solid is
(A) P_yQ_z (B) P_zQ_y
(C) $\text{P}_{1/y}\text{Q}_{1/z}$ (D) None
13. Xenon crystallizes in face centre cubic lattice and the edge of the unit cell is 620 pm, then the radius of xenon-atom is.
(A) 438.5pm (B) 219.25pm
(C) 536.94pm (D) 265.5pm
14. Which of the following doesn't crystallize in the rock-salt structure?
(A) NaCl (B) KCl
(C) MgO (D) CsCl
15. In closet packing of A type of atoms (radius, r_A), the radius of atom B that can be fitted into octahedral void is
(A) $0.155r_A$ (B) $0.125r_A$
(C) $0.414r_A$ (D) $0.732r_A$

Answers

Subjective

LEVEL - I

- | | |
|--------------------------------------|--------------------------------------|
| 1. AB_3 | 2. $NaWO_3$ |
| 3. 9 | 4. 5.46\AA |
| 5. 95.7 | 6. 4 |
| 7. $4.054 \times 10^{-8} \text{ cm}$ | 8. $15.59 \times 10^{-8} \text{ cm}$ |
| 9. 2.68×10^{-8} | 10. a) 0.68; b) 0.52 |

LEVEL - II

- | | |
|-------------------------------------|--|
| 1. $XY_3, 4.38 \text{ g cm}^{-3}$ | 2. 24.16×10^{23} |
| 3. 4722×10^{24} atoms | 4. $r^- = 212.132 \text{ pm}, r^+ = 86.8679 \text{ pm}$ |
| 5. $1.37 \overset{\circ}{\text{A}}$ | 6. a) $7.014 \times 10^{-23} \text{ cm}^3$; (b) $4.125 \overset{\circ}{\text{A}}$ |
| 7. 6.04×10^{23} | 8. $5.188 \text{ g/cc}, 3 \times 10^{22}$ unit cells,
6×10^{22} atom |
| 9. 1.09 | 10. 6.023×10^{18} cationic vacancies |

LEVEL - III

- | | |
|---|---|
| 1. 6.3697\AA^3 | 2. 175.8 gm |
| 3. a) 2.878\AA ,
b) 12
c) 194 g/cc | 4. a) 4.5\AA b) 5.2\AA
c) 8 d) 6
e) 0.925 g/cc |
| 5. a) Octahedral holes
b) $\frac{1}{4}$ | 6. a) 4 b) 4
c) $109^\circ 28'$ d) 0.225 |
| 7. a) 3.99 g/cc b) 176.13 pm | 8. 6.04×10^{23} |
| 9. $X_2Y; 1.115 \times 10^{-7} \text{ g/cc}$ | 10. 0.406 nm |

Answers

Objective

LEVEL - I

- | | | | |
|-----|----------|-----|----------|
| 1. | C | 2. | B |
| 3. | B | 4. | D |
| 5. | A | 6. | C |
| 7. | A | 8. | C |
| 9. | B | 10. | A |
| 11. | B | 12. | B |
| 13. | A | 14. | B |
| 15. | A | | |

LEVEL - II

- | | | | |
|-----|--------------|-----|----------------|
| 1. | A,B,C | 2. | C |
| 3. | C | 4. | A,B,C,D |
| 5. | A,C,D | 6. | C |
| 7. | C | 8. | D |
| 9. | B | 10. | B |
| 11. | B | 12. | B |
| 13. | A | 14. | D |
| 15. | C | | |

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