विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचितः मानव धर्म प्रणेता
सद्गुरु श्री रणछोड़दासजी महाराज

STUDY PACKAGE

This is TYPE 1 Package please wait for Type 2

Subject : CHEMISTRY

Topic : SOLID STATE

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THE KEY

Crystalline solids:

Crystalline solids are those whose atom, molecules or ions have an ordered arrangement extending over a **Long Range.** example-(Rock salt, NaCl).

Amorphous solids:

Amorphous solids are those whose constitutent particles are randomly arrange and have no ordered long range structure. example: Rubber, Glass ect.

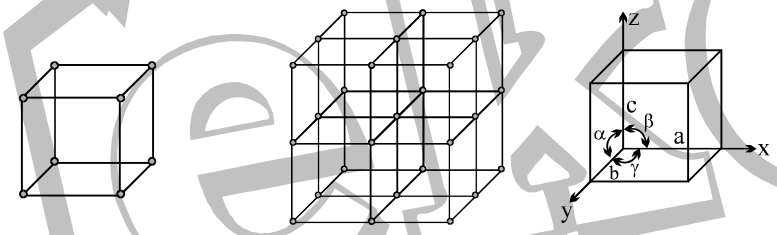
TYPES OF CRYSTALLINE SOLIDS:

Type of Solid	Intermolecular forces	Properties	Examples
Ionic	Ion-Ion forces	Brittle, hard high Melting	NaCl, KCl, $MgCl_2$
Molecular	Dispersion forces/Dipole-Dipole /H-bond	Soft, low melting non-conducting	H_2O, Br_2, CO_2, CH_4
Covalent network	Covalent bonds	Hard: High melting	C-Diamond SiO_2
Metallic	Metallic bonds	Variable hardness and melting point conducting	Na, Zn, Cu, Fe

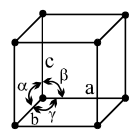
TYPES OF UNIT CELL:

Collection of lattice points, whose repetition produce whole lattice is called a unit cell. The whole lattice can be considered to be made by repetion of unit cell.

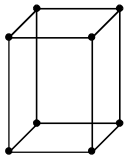
1. Unit Cell:

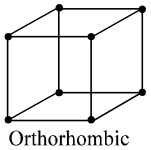


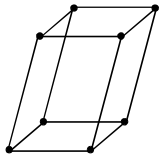
Crystal Systems		Bravais Lattice	Unit Cell Parameters	
			Intercepts	Crystal Angles
1	Cubic	Primitive, Face Centered, Body Centered	a = b = c	$\alpha = \beta = \gamma = 90°$
2	Orthorhombic	Primitive, Face Centered, Body Centered, End Centered	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
3	Rhombohedral	Primitive	a = b = c	$\alpha = \beta = \gamma \neq 90°$
4	Monoclinic	Primitive, End Centered	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$
5	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
6	Tetragonal	Primitive, Body Centered	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
7	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$

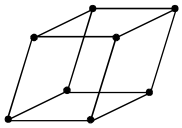


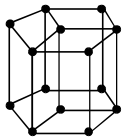
Simple Cubic
a = b = c
$\alpha = \beta = \gamma = 90°$


Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

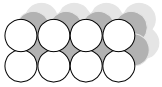

Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

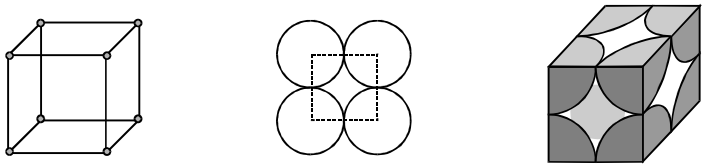

Monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90°, \beta \neq 90°$


Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$


Hexagonal Primitive
$a = b \neq c$
$\alpha = \beta = 90°, \gamma = 120°$

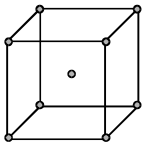
1.1 Primitive or simple cubic (PS/SC) unit cell: Spheres in one layer sitting directly on top of those in previous layer, so that all layers are identical. Each sphere is touched by six other, hence coordination number is 6. 52% of available space occupied by spheres.
Example: Polonium crystallises in simple cubic arrangement.





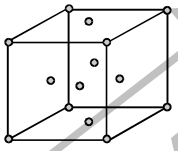
Z = 1 ; C.N. = 6

1.2 Body Centered cubic (BCC) unit cell: Spheres in one layer sit in the depression made by first layer in a-b-a-b manner. Coordination number is 8, and 68% of available space is occupied by atoms.
Example: Iron, sodium and 14 other metal crystallises in this manner.



Z = 2 ; C.N. = 8

1.3 Face centered cubic (FCC) unit cell:
Examples : Al, Ni, Fe, Pd all solid noble gases etc.



Z = 4 ; C.N. = 12

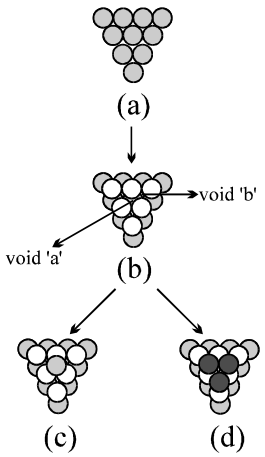
2. Density of cubic crystals:

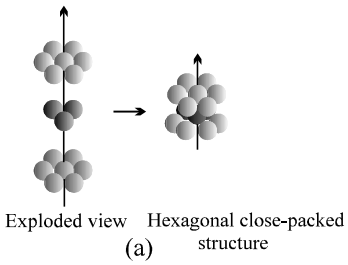
TYPE OF PACKING:

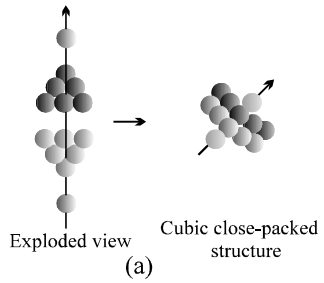
3. Closest packing of atoms: This is the most efficient way of packing 74% of available space is occupied by spheres and coordination number is 12.

(i) ***Hexagonal close pack (A-B-A-B) type packing :*** Each layer has hexagonal arrangement of touching sphere and 3rd layer is similar (exactly on top) of first layer.

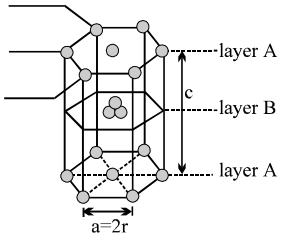
(ii) ***Cubic close pack (A-B-C-A-B-C):*** AB layers are similar to HCP arrangement but third layer is offset from both A and B layers. The fourth layer is exactly on top of first layer.





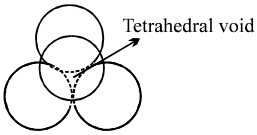


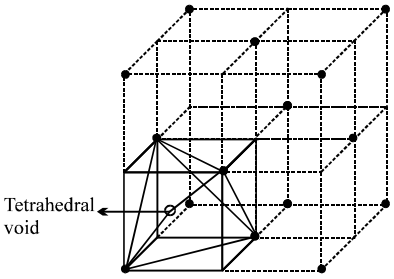
Hexagonal primitive unit cell



4. Types of voids

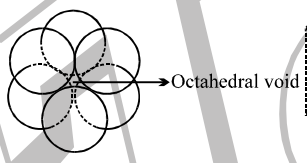
4.1 Tetrahedral void

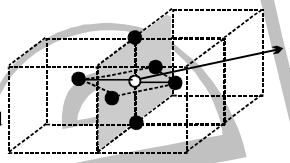




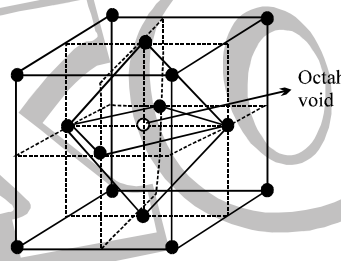
Number of tetrahedral voids per FCC unit cell

4.2 Octahedral void



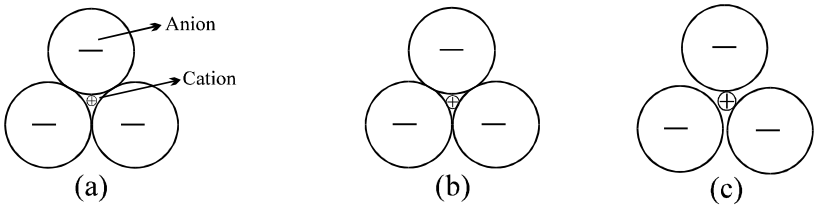


An octahedral void at the centre of an edge in a FCC unit cell.



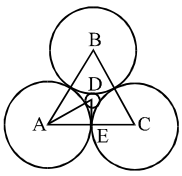
An octahedral void at the body centered position in FCC unit cell

5. Radius ratio



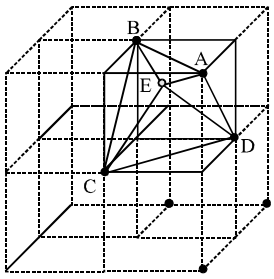
5.1 Radius ratio for co-ordination number 3

(Triangular Arrangement): $r^+ + r^- = \frac{2}{3}\sqrt{3}\, r^-$; $\frac{r^+}{r^-} = \frac{2-\sqrt{3}}{\sqrt{3}} = 0.155$



5.2 Radius ratio for coordination number 4

(Tetrahedral arrangement): $r^+ + r^- = \frac{\sqrt{3}a}{4}$; $4r^- = \sqrt{2}\,a = \frac{\sqrt{3}}{\sqrt{2}}r^-$

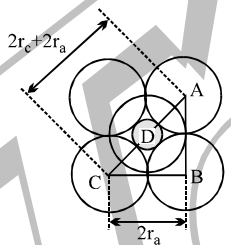


$$\frac{r^+}{r^-} = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}} = 0.225$$

5.3 Radius ratio for coordination number 6: $r^+ + r^- = \sqrt{2}\ r^-$

(Octahedral Arrangement) or $\frac{r^+}{r^-} = \sqrt{2} - 1 = 0.414$

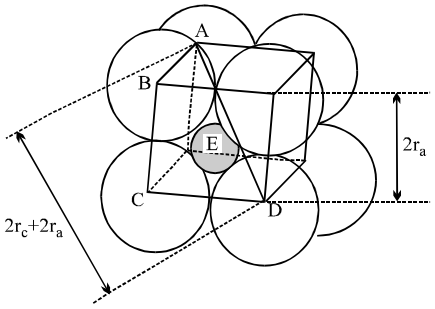
Radius ratio for coordination number 4
(Square plannar arrangement)



Top view of octahedral arrangement

5.4 Radius ratio for coordination number 8 : $r^+ + r^- = \frac{\sqrt{3}}{2}\ a$

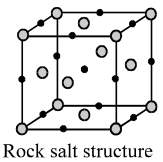
(Body centered cubic crystal) $r^+ + r^- = \sqrt{3}\ r^-$



$$\frac{r^+}{r^-} = \sqrt{3} - 1 = 0.732$$

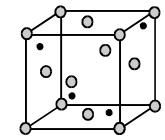
6. Types of ionic structures

6.1 Rock salt structure: (NaCl) Larger atom formic ccp arrangement and smaller atom filling all octahedral voids.

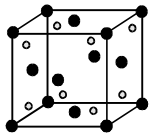


Rock salt structure

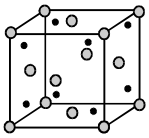
6.2 Zinc blende (sphalerite) structure:(ZnS) Larger atom formic ccp arrangement and smaller atom filling half of alternate tetrahedral voids


Zinc blende structure

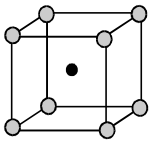
6.3 Fluorite structure:(CaF_2) Ca^{2+} forming ccp arrangement and F^- filling all tetrahedral voids.


Fluorite structure

6.4 Antifluorite structure :(Li_2O) O^{2-} ion forming ccp and Li^+ taking all tetrahedral voids.


Antifluorite structure

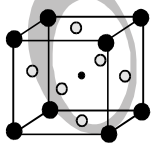
6.5 Cesium halide structure: (CsCl) Cl^- at the corners of cube and Cs^+ in the center.


Cesium chloride structure

6.6 Corundum Structure: (Al_2O_3) O^{2-} forming hcp and Al^{3+} filling 2/3 octahedral voids.

6.7 Rutile structure: (TiO_2) O^{2-} forming hcp while Ti^{4+} ions occupy half of the octahedral voids.

6.8 Pervoskite structure:($CaTiO_3$) Ca^{2+} in the corner of cube O^{2-} at the face center and Ti^{4+} at the centre of cube.


Pervoskite structure

6.9 Spinel and inverse spinel structure: ($MgAl_2O_4$)O^{2-} forming fcc, Mg^{2+} filling 1/8 of tetrahedral voids and Al^{3+} taking half of octahedral voids.In an inverse spinel structure, O^{2-} ion form FCC lattice, A^{2+} ions occupy 1/8 of the tetrahedral voids and trivalent cation occupies 1/8 of the tetrahedral voids and 1/4 of the octahedral voids.

7. Crystal defects:

Point defects: When ions or atoms do not hold the theoretical position, this is called point defect. Point defects are of two types:

(I) ***Stoichiometric defects***:

(a) **Schottky defect:** Due to missing of ions from lattice point in pairs.

(b) **Frenkel defect:** It is caused due to the creation of lattice vacancy as a result of misplaced ion in interstitial site.

✶ Schottky defect common in ionic solid with high coordination number. NaCl, KCl, KBr

✶ Frenkel defect :- Solid with low coordination number ZnS, AgBr.

(II) ***Non-Stoichiometric defects***: Ratio of positive and negative ion differ from that indicated by chemical formula.

✶ **Metal-excess defect :**

(a) A negative ion replaced by electron. (F-centre)

(b) Extra metal ion present in lattice and electron also present in interstitial site.

✶ **Metal-deficiency defect caused by :** Cation missing from lattice point, electroneutrality maintained by metal ions with higher oxidation state as $Fe_{0.94}{}^{\circ}O$.

THE ATLAS

TYPES OF SOLIDS

Crystalline Solids

Crystalline solids have long range order i.e. the constituent particles are arranged in a regular fashion and this symmetrical arrangement extends throughout the crystal length.

Amorphous Solids

Lattice - Unit Cells

(i) A unit cell is the smallest repeating structural unit the crystalline solid. Bravais has predicted that there are only 14 unit cells that exists in nature.

(ii)The relation between the edge length (a) and the radius of atom (r) forming lattice are as follows. PC :a=2r, BCC: $\sqrt{3}a=4$;FCC:$\sqrt{2}a=4r$& HP:a=2r height(c) =4r $\sqrt{\frac{2}{3}}$

Packing fraction and density determination

(i) The ratio of volume occupied by the effective atoms to the volume of the unit cell is called packing fraction. Its values for various unit cells are PC = 0.52, BCC = 0.68, FCC & HP = 0.74.

(ii)Density (ρ) of cubic crystal is calculated using the relation $\rho = \frac{n \times M}{N_{AV} \times a^3}$ where

n=number of effective atoms, M=Atomic mass,N_{AV}=Avogadro's number and a= Edge length.

Type of void and radius ratio rule

(i) Tetrahedral & octahedral voids are present only inclosest packed structures. The effective number of octahedral voids in a unit cell is equal to the effective number of atoms in the unit cell & effective number of tetrahedral voids is equal to double the number of effective atoms in the unit cell.

(ii)The sum of radius of the atom of host lattice (r_h) and the radius of atom occupying void($r_{f(t)}$or $r_{f(o)}$) is given by

For octahedral void, $r_h + r_{f(o)} = \frac{a}{2}$& for tetrahedral void,$r_h + r_{f(t)} = \frac{\sqrt{3}a}{4}$

(iii)Limiting radius is defined as the minimum ratio of cation to anion radius. It is defined when cation is in contact with anions and anions are also in contact with each other.

(iv)Radius ratio depends on the co-ordination number. The limiting radius ratio for the various co-ordination numbers are

C.N.3 : 0.155, C.N.4 (Tetrahedral) : 0.225, C.N.4(Square planar) : 0.414, C.N.6 (Octahedral) : 0.414, C.N.8 (BCC) : 0.732, C.N.12 (Ideal FCC) : 1

Defects in Solids

Ionic lattice has 2 major defects. Schottky defect occurs due to the cation-anion pair vacancy, which decreases the density of crystal. Frenkel defect occurs when an ion leaves its lattice site and fits into an interstitial space. Due to Frenkel defect, density of crystal remains unaffected.

EXERCISE I

Formula of ionic solid from unit cell description

Q.1 A cubic solid is made up of two elements A and B. Atoms B are at the corners of the cube and A at the body centre. What is the formula of compound.

Q.2 A compound alloy of gold and copper crystallizes in a cubic lattice in which gold occupy that lattice point at corners of the cube and copper atom occupy the centres of each of the cube faces. What is the formula of this compound.

Q.3 A cubic solid is made by atoms A forming close pack arrangement, B occupying one. Fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound.

Q.4 What is the percent by mass of titanium in rutile, a mineral that contain Titanium and oxygen, if structure can be described as a closet packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium?

Q.5 Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eight of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by Zn^{2+}, Al^{3+} and O^{2-}, with Zn^{2+} in the tetrahedral holes. Give the formulae of spinel.

Edge length, density and number of atoms per unit cell

Q.6 KF crystallizes in the NaCl type structure. If the radius of K^+ ions 132 pm and that of F^- ion is 135 pm, what is the shortest K–F distance? What is the edge length of the unit cell? What is the closet K–K distance?

Q.7 A closed packed structure of uniform spheres has the edge length of 534 pm. Calculate the radius of sphere, if it exist in
(a) simple cubic lattice (b) BCC lattice (c) FCC lattice

Q.8 Calculate the density of diamond from the fact that it has face centered cubic structure with two atoms per lattice point and unit cell edge length of 3.569 Å.

Q.9 An element crystallizes 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 body diagonals. If the volume of this unit cell is 24×10^{-24} cm^3 and density of element is 7.2 g cm^{-3}, calculate the number of atoms present in 200 g of element.

Q.10 Silver has an atomic radius of 144 pm and the density of silver is 10.6 g cm^{-3}. To which type of cubic crystal, silver belongs?

Q.11 AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be 555 pm and the density of AgCl is 5.561 g cm^{-3}. Find the percentage of sites that are unoccupied.

Q.12 Xenon crystallises in the face-centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom?

Q.13 The two ions A^+ and B^- have radii 88 and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of A^+.

Q.14 CsCl has the bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.

Q.15 Gold crystallizes in a face centered cubic lattice. If the length of the edge of the unit cell is 407 pm, calculate the density of gold as well as its atomic radius assuming it to be spherical. Atomic mass of gold = 197 amu.

Q.16 The density of KBr is 2.75 g cm^{-3} . The length of the edge of the unit cell is 654 pm. Show that KBr has face centered cubic structure.
($N = 6.023 \times 10^{23}$ mol^{-1} , At. mass : K = 39, Br = 80)

Q.17 An element crystallizes in a structure having FCC unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains 24×10^{23} atoms.

Q.18 The effective radius of the iron atom is 1.42 Å. It has FCC structure. Calculate its density (Fe = 56 amu)

Q.19 A crystal of lead(II) sulphide has NaCl structure. In this crystal the shortest distance between Pb^{+2} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.

Q.20 If the length of the body diagonal for CsCl which crystallises into a cubic structure with Cl^- ions at the corners and Cs^+ ions at the centre of the unit cells is 7 Å and the radius of the Cs^+ ion is 1.69 Å, what is the radii of Cl^- ion?

PROFICIENCY TEST

1. Crystalline solids are isotropic.
2. Rhombohedral, triclinic and hexagonal are the unit cells, which have only primitive arrangement possible.
3. Packing fraction of FCC and HP units cells are same.
4. The minimum void fraction for any unit cell in any shape having only one type of atom and all voids unfilled is 0.26.
5. Packing fraction of a lattice structure depends on the radius of the atom crystallizing in it.
6. The location of tetrahedral voids in FCC unit cell are the centers of 8 minicubes forming a large cube.
7. Effective number of octahedral voids in a unit cell is equal to the effective number of atoms in the unit cell.
8. Radius ratio for co-ordination number 4 having tetrahedral and square planar geometry is same.
9. The radius ratio value for co-ordination number 4 having square planar geometry and co-ordination number 6 having octahedral geometry is same.
10. A metallic element crystallises into a lattice containing a sequence of layers of AB AB AB ..... . Any packing of spheres leaves out voids in the lattice 26% percent by volume of this lattice is empty space.
11. The relation between edge length (a) and radius of atom (r) for BCC lattice is_____.
12. The relation between edge length (a) and radius of atom (r) for FCC lattice is_____.
13. ABCABC.....layering pattern is called _____ packing, found in _____ lattice.
14. ABABAB.....layering pattern is called _____packing , found in _____ lattice.
15. Height (c) of the hexagonal primitive unit cell in terms of radius of atom (r) is_____.
16. Anions would be in contact with each other only if the cation to anion radius for a given co-ordination number is_____.
17. The number of tetrahedral voids in hexagonal primitive unit cell is_____.
18. The limiting radius for co-ordination number 8 is_____.
19. For cesium chloride structure, the interionic distance (in terms of edge length, a) is equal to _____.
20. Density of a crystal ___due to Schottky defect and _____due to Frankel defect.

EXERCISE II

Q.1 Iron has body centered cubic lattice structure. The edge length of the unit cell is found to be 286 pm. What is the radius of an iron atom?

Q.2 Cesium chloride forms a body centered cubic lattice. Cesium and chloride ions are in contact along the body diagonal of the unit cell. The length of the side of the unit cell is 412 pm and Cl^- ion has a radius of 181 pm. Calculate the radius of Cs^+ ion.

Q.3 In a cubic closed packed structure of mixed oxides the lattice is made up of oxide ions, one eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids occupied trivalent ions (B^{3+}). What is the formula of the oxide?

Q.4 A solid A^+ and B^- had NaCl type closed packed structure. If the anion has a radius of 250 pm, what should be the ideal radius of the cation? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal of A^+B^- ? Give reasons for your answer.

Q.5 Calculate the value of Avogadro's number from the following data:
Density of NaCl = 2.165 cm^{-3}
Distance between Na^+ and Cl^- in NaCl = 281 pm.

Q.6 If the radius of Mg^{2+} ion, Cs^+ ion, O^{2-} ion, S^{2-} ion and Cl^- ion are 0.65 Å , 1.69 Å, 1.40 Å, 1.84 Å, and 1.81 Å respectively. Calculate the co-ordination numbers of the cations in the crystals of MgS, MgO and CsCl.

Q.7 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.

Q.8 KCl crystallizes in the same type of lattice as does NaCl. Given that $\frac{r_{Na^+}}{r_{Cl^-}}=0.5$ and $\frac{r_{Na^+}}{r_{K^+}}=0.7$ Calculate:
(a) The ratio of the sides of unit cell for KCl to that for NaCl and
(b) The ratio of densities of NaCl to that for KCl.

Q.9 An element A (Atomic weight = 100) having bcc structure has unit cell edge length 400 pm. Calculate the density of A and number of unit cells and number of atoms in 10 gm of A.

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

Q.11 A unit cell of sodium chloride has four formula units. The edge of length of the unit cell is 0.564 nm. What is the density of sodium chloride.

Q.12 In a cubic crystal of CsCl (density = 3.97 gm/cm^3) the eight corners are occupied by Cl^- ions with Cs^+ ions at the centre. Calculate the distance between the neighbouring Cs^+ and Cl^- ions.

Q.13 KF has NaCl structure. What is the distance between K^+ and F^- in KF if density of KF is 2.48 gm/cm^3.

Q.14 The composition of a sample of wustite is $Fe_{0.93}O_{1.0}$. What percentage of iron is present in the form of Fe(III)?

Q.15 $BaTiO_3$ crystallizes in the prevoskite structure. This structure may be described as a cubic lattice with barium ions occupying the corner of the unit cell, oxide ions occupying the face-centers and titanium ion occupying the center of the unit cell.
(a) If titanium is described as occupying holes in BaO lattice, what type of holes does it occupy?
(b) What fraction of this type hole does it occupy?

Q.16 RbI crystallizes in bcc structure in which each Rb^+ is surrounded by eight iodide ions each of radius 2.17 Å. Find the length of one side of RbI unit cell.

Q.17 If NaCl is dopped with 10^{-3} mol % $SrCl_2$, what is the numbers of cation vacancies?

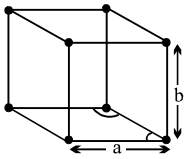
Q.18 Find the size of largest sphere that will fit in octahedral void in an ideal FCC crystal as a function of atomic radius 'r'. The insertion of this sphere into void does not distort the FCC lattice. Calculate the packing fraction of FCC lattice when all the octahedral voids are filled by this sphere.

Q.19 A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.
(a) What is the empirical formula of the compound?
(b) What is the co-ordination number of the Mn ion?
(c) Calculate the edge length of the unit cell, if the radius of Mn ion is 0.65 Å and that of F^- ion is 1.36 Å.

Q.20 NaH crystallizes in the same structure as that of NaCl. The edge length of the cubic unit cell of NaH is 4.88 Å.
(a) Calculate the ionic radius of H^-, provided the ionic radius of Na^+ is 0.95 Å.
(b) Calculate the density of NaH.

Q.21 Metallic gold crystallises in fcc lattice. The length of the cubic unit cell is a = 4.07 Å.
(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 fraction of gold is 0.74.

Q.22 Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants were a = 4.53 Å, and b = 7.60 Å(see figure). How many molecules are contained in a given unit cell? [density (ice) = 0.92 gm/cm^3)]



Q.23 Using the data given below, find the type of cubic lattice to which the crystal belongs.

	Fe	V	Pd
a in pm	286	301	388
ρ in gm cm^{-3}	7.86	5.96	12.16

Q.24 Potassium crystallizes in a body-centered cubic lattice with edge length, a = 5.2 Å.
(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 atom have?
(e) What is the calculated density of crystalline potassium?

Q.25 Prove that void space in fluorite structure per unit volume of unit cell is 0.243.

Q.26 A compound formed by elements X & Y, Crystallizes in a cubic structure, where X is at the corners of the cube and Y is at six face centers. What is the formula of the compound? If side length is 5Å, estimate the density of the solid assuming atomic weight of X and Y as 60 and 90 respectively.

Q.27 The metal nickel crystallizes in a face centred cubic structure. Its density is 8.9 gm/cm^3. Calculate
(a) the length of the edge of the unit cell.
(b) the radius of the nickel atom. [Atomic weight of Ni = 58.89]

Q.28 The olivine series of minerals consists of crystals in which Fe and Mg ions may substitute for each other causing substitutional impurity defect without changing the volume of the unit cell. In olivine series of minerals, oxide ion exist as FCC with Si^{4+} occupying $\frac{1}{4}^{th}$ of octahedral voids and divalent ions occupying $\frac{1}{4}^{th}$ of tetrahedral voids. The density of forsterite (magnesium silicate) is 3.21 g/cc and that of fayalite (ferrous silicate)is 4.34 g/cc. Find the formula of forsterite and fayalite minerals and the percentage of fayalite in an olivine with a density of 3.88 g/cc.

Q.29 The mineral hawleyite, one form of CdS, crystallizes in one of the cubic lattices, with edge length 5.87Å. The density of hawleyite is 4.63 g cm^{-3}.
(i) In which cubic lattice does hawleyite crystallize?
(ii) Find the Schottky defect in g cm^{-3}.

Q.30 A strong current of trivalent gaseous boron passed through a germanium crystal decreases the density of the crystal due to part replacement of germanium by boron and due to interstitial vacancies created by missing Ge atoms. In one such experiment, one gram of germanium is taken and the boron atoms are found to be 150 ppm by weight, when the density of the Ge crystal decreases by 4%. Calculate the percentage of missing vacancies due to germanium, which are filled up by boron atoms.
Atomic wt. Ge = 72.6, B = 11

EXERCISE III

Q.1 A solid has a structure in which W atoms are located at the corners of a cubic lattice, O atom at the centre of the edges and Na atom at centre of the cubic. The formula for the compound is
(A) $NaWO_2$ (B) $NaWO_3$ (C) Na_2WO_3 (D) $NaWO_4$

Q.2 The density of CaF_2 (fluorite structure) is 3.18 g/cm^3. The length of the side of the unit cell is
(A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm

Q.3 Which of the following statements is correct in the rock-salt structure of an ionic compounds?
(A) coordination number of cation is four whereas that of anion is six.
(B) coordination number of cation is six whereas that of anion is four.
(C) coordination number of each cation and anion is four.
(D) coordination number of each cation and anion is six.

Q.4 The coordination number of cation and anion in Fluorite CaF_2 and CsCl are respectively
(A) 8:4 and 6:3 (B) 6:3 and 4:4 (C) 8:4 and 8:8 (D) 4:2 and 2:4

Q.5 The interstitial hole is called tetrahedral because
(A) It is formed by four spheres.
(B) Partly same and partly different.
(C) It is formed by four spheres the centres of which form a regular tetrahedron.
(D) None of the above three.

Q.6 The tetrahedral voids formed by ccp arrangement of Cl^- ions in rock salt structure are
(A) Occupied by Na^+ ions (B) Occupied by Cl^- ions
(C) Occupied by either Na^+ or Cl^- ions (D) Vacant

Q.7 The number of nearest neighbours around each particle in a face-centred cubic lattice is
(A) 4 (B) 6 (C) 8 (D) 12

Q.8 If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is
(A) CA (B) CA_2 (C) C_2A_3 (D) C_3A_2

Q.9 A solid is formed and it has three types of atoms X, Y, Z. X forms a FCC lattice with Y atoms occupying all the tetrahedral voids and Z atoms occupying half the octrahedral voids. The formula of the solid is:
(A) X_2Y_4Z (B) XY_2Z_4 (C) X_4Y_2Z (D) X_4YZ_2

Q.10 The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. The crystal class is
(A) Simple cubic (B) Body centred cubic (C) Face centred cubic (D) None

Q.11 A compound XY crystallizes in BCC lattice with unit cell edge lenght of 480 pm. If the radius of Y^- is 225 pm, then the radius of X^+ is
(A) 127.5 pm (B) 190.68 pm (C) 225 pm (D) 255 pm

Q.12 The mass of a unit cell of CsCl corresponds to
(A) 1 Cs^+ and 1 Cl^- (B) 1 Cs^+ and 6 Cl^- (C) 4 Cs^+ and 4 Cl^- (D) 8 Cs^+ and 1 Cl^-

Q.13 In the closest packing of atoms A (radius : r_a), the radius of atom B that can be fitted into tetrahedral voids is
(A) 0.155 r_a (B) 0.225 r_a (C) 0.414 r_a (D) 0.732 r_a

Q.14 Which one of the following schemes of ordering closed packed sheets of equal sized spheres do not generate close packed lattice.
(A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC

Q.15 An ionic compound AB has ZnS type structure. If the radius A^+ is 22.5 pm, then the ideal radius of B^- would be
(A) 54.35 pm (B) 100 pm (C) 145.16 pm (D) none of these

Q.16 NH_4Cl crystallizes in a body-centered cubic type lattice with a unit cell edge length of 387 pm. The distance between the oppositively charged ions in the lattice is
(A) 335.1 pm (B) 83.77 pm (C) 274.46 pm (D) 137.23 pm

Q.17 r_{Na^+} = 95 pm and r_{Cl^-} =181 pm in NaCl (rock salt) structure. What is the shortest distance between Na^+ ions?
(A) 778.3 pm (B) 276 pm (C) 195.7 pm (D) 390.3 pm

Q.18 In diamond, carbon atom occupy FCC lattice points as well as alternate tetrahedral voids. If edge length of the unit cell is 356 pm, then radius of carbon atom is
(A) 77.07 pm (B) 154.14 pm (C) 251.7 pm (D) 89 pm

Q.19 Which of the following will show schottky defect
(A) CaF_2 (B) ZnS (C) AgCl (D) CsCl

Q.20 Give the correct order of initials **T** (true) or **F** (false) for following statements.
I. In an anti-fluorite structure anions form FCC lattice and cations occupy all tetrahedral voids.
II. If the radius of cations and anions are 0.2 Å and 0.95 Å then coordinate number of cation in the crystal is 4.
III An atom/ion is transferred from a lattice site to an interstitial position in Frenkel defect.
IV. Density of crystal always increases due to substitutinal impurity defect.
(A) TFFF (B) FTTF (C) TFFT (D) TFTF

EXERCISE IV

Q.1 The edge length of unit cell of a metal having atomic weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ($N_A = 6 \times 10^{23}$). Give the answer in pm. **[JEE 2006]**

Q.2 An element crystallises in FCC lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstital sites without disturbing the structure. **[JEE 2005]**

Q.3 Which of the following FCC structure contains cations in alternate tetrahedral voids?
(A) NaCl (B) ZnS (C) Na_2O (D) CaF_2 **[JEE 2005]**

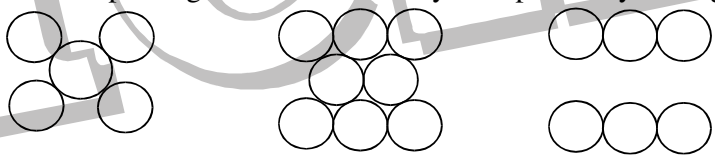
Q.4(i) AB crystallizes in a rock salt structure with A : B = 1 : 1. The shortest distance between A and B is $Y^{1/3}$ nm. The formula mass of AB is 6.023 Y amu where Y is any arbitrary constant. Find the density in kg m^{-3}.

(ii) If measured density is 20 kg m^{-3}. Identify the type of point defect. **[JEE–2004]**

Q.5 Marbles of diameter 10 mm each are to be arranged on a flat surface so that their centres lie within the area enclosed by four lines of length each 40 mm. Sketch the arrangement that will give the maximum number of marbles per unit area, that can be enclosed in this manner and deduce the expression to calculate it. **[JEE–2003]**

Q.6 A substance A_xB_y crystallises in a FCC lattice in which atoms "A" occupy each corner of the cube and atoms "B" occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y.
(A) AB_3 (B) A_4B_3
(C) A_3B (D) composition cannot be specified **[JEE-2002]**

Q.7 The figures given below show the location of atoms in three crystallographic planes in FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. **[JEE-2000]**



Q.8 In a solid "AB" having NaCl structure "A" atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is
(A) AB_2 (B) A_2B (C) A_4B_3 (D) A_3B_4 **[JEE-2000]**

Q.9 In any ionic solid [MX] with schottky defects , the number of positive and negative ions are same.**[T/F]** **[JEE-2000]**

Q.10 The coordination number of a metal crystallising in a hcp structure is **[JEE-2000]**
(A) 12 (B) 4 (C) 8 (D) 6

Q.11 A metal cryatallises into two cubic phases, FCC and BCC whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of FCC and BCC. **[JEE-1999]**

Q.12 Which of the following statements are correct :
(A) The coordination number of each type of ion in CsCl is 8.
(B) A metal that crystallises in BCC structure has a coordination number 12.
(C) A unit cell of an ionic crystal shares some of its ions with other unit cells
(D) The length of the unit cell in NaCl is 552 pm.
[r_{Na^+} = 95 pm ; r_{Cl^-} = 181 pm] **[JEE-1998]**

Q.13 In the sodium chloride structure, each Na^+ ion is surrounded by six Cl^- nearest neighbours and _____ Na^+ ions next nearest neighbours. **[JEE-1997]**

Q.14 A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sod. chloride. **[JEE-1997]**

Q.15 Chromium crystallises with bcc lattice. The unit cell length is 287 pm. Calculate atomic rad. What would be the density of chromium. **[JEE-1997]**

ANSWER KEY

EXERCISE I

Q.1	A-B	Q.2	$AuCu_3$	Q.3	$A_4B_2C_2$	Q.4	59.95%, +4
Q.5	$ZnAl_2O_4$	Q.6	267 pm, 534 pm, 378 pm			Q.7	267 pm, 231.2 pm, 188.8 pm
Q.8	3.5 g cm^{-3}	Q.9	3.472×10^{24} atoms			Q.10	FCC
Q.11	0.24%	Q.12	438.5 pm, 219.25 pm			Q.13	6
Q.14	346.4 pm	Q.15	19.4g/cm^3 , 143.9 pm			Q.17	41.67 g cm^{-3}
Q.18	5.74 g cm^{-3}	Q.19	a =5.94×10^{-8}cm, V=2.096×10^{-22} cm^{-3}			Q.20	1.81Å

PROFICIENCY TEST

1.	F	2.	T	3.	T	4.	T
5.	F	6.	T	7.	T	8.	F
9.	T	10.	T	11.	$\sqrt{3}$ a = 4r	12.	$\sqrt{2}$ a = 4r]
13.	cubic close, FCC			14.	hexagonal close, HP		
15.	$c = 4r\sqrt{\frac{2}{3}}$	16.	least or minimum			17.	12
18.	0.732	19.	$\frac{\sqrt{3}a}{2}$	20.	decreases, remains constant		

EXERCISE II

Q.1	123.84 pm	Q.2	175.8 pm	Q.3	AB_2O_4	Q.4	103.4 pm, No
Q.5	6.01×10^{23}	Q.6	4, 6, 8	Q.7	7.887 g/cc , 8.59 gm/cm^3		
Q.8	**(a)** 1.143, **(b)** 1.172						
Q.9	5.188 gm/cm^3, 6.023×10^{22} atoms of A, 3.0115×10^{22} unit cells						
Q.11	2.16 gm/cm^3	Q.12	3.57 Å	Q.13	2.685 Å	Q.14	15.053
Q.15	**(a)** octahedral, **(b)** 1/4			Q.16	4.34 Å		
Q.17	6.02×10^{18} mol^{-1}			Q.18	0.414 r, 79.3%		
Q.19	(a) MnF_3, (b) 6, (c) 4.02Å			Q.20	(a) 1.49 Å, (b) 1.37 g/cm^3		

Q.21 **(a)** 2.88 Å, **(b)** 12 , **(c)** 19.4 g/cc

Q.22 4 molecules of H_2O

Q.23 for Fe is bcc, for V is bcc, for Pd is face centered

Q.24 (a) 4.5 Å, (b) 5.2 Å, (c) 8, (d) 6, (e) 0.92 g/cm^3

Q.26 XY_3, 4.38 g/cm^3

Q.27 **(a)** 3.52 Å,**(b)** 1.24 Å

Q.28 Mg_2SiO_4, Fe_2SiO_4, 59%

Q.29 (i) 3.90, (ii) 0.120 g/cc

Q.30 2.376%

EXERCISE III

Q.1	B	Q.2	C	Q.3	D	Q.4	C	Q.5	C	Q.6	D	Q.7	D
Q.8	C	Q.9	A	Q.10	B	Q.11	B	Q.12	A	Q.13	B	Q.14	C
Q.15	B	Q.16	A	Q.17	D	Q.18	A	Q.19	D	Q.20	D		

EXERCISE IV

Q.1 216.5 pm Q.2 117.1 pm Q.3 B

Q.4 (i) = 5 kg m^{-3}
(ii) There is huge difference in theoretically calculated density and observed density. It is only possible if some foreign species occupies interstitial space i.e. substitution defect.

Q.5 Discuss

Q.6	A	Q.7	Discuss	Q.8	D	Q.9	True	Q.10	A
Q.11	1.259	Q.12	A, C, D	Q.13	12	Q.14	2.165 g/cm^3		

Q.15 (i)124.27 pm, (ii) 7.30 g/cm^3