Chapter.1
The Solid State
Class-XII
Subject-Chemistry

1.1 Define the term amorphous. Give a few examples of amorphous solids.

Answer 1.1

Amorphous solids exhibits following properties: -

- Their constituent particles are of irregular shapes and have short range order.

- They are isotropic in nature and melt over a range of temperature. Because of which they are also known as pseudo solids or super cooled liquids.

- When cut with a sharp-edged tool, they cut into two pieces with irregular surfaces.

- They do not have definite heat of fusion.

    Examples - glass, rubber, plastic etc.

1.2 What makes a glass different from a solid such as quartz? Under what conditions quartz could be converted into glass?

Answer 1.2

The arrangement of the constituent particles is different in glass & quartz. In glass, the constituent particles have short range order whereas in quartz, the constituent particles have both long range as well as short range orders.
We can convert Quartz into glass by heating and then cooling it rapidly.

1.3 **Classify each of the following solids as ionic, metallic, molecular, network (covalent)**

1. **Tetra phosphorus decoxide (P_4O_{10})**
2. **Ammonium phosphate ($NH_4)_3PO_4$**
3. **SiC**
4. **I_2**
5. **P_4**
6. **Plastic**
7. **Graphite**
8. **Brass**
9. **Rb**
10. **LiBr**
11. **Si**

Answer 1.3

Type of solids	Examples
Ionic	LiBr , Ammonium phosphate ($NH_4)_3PO_4$
Metallic	Brass, Rb
Molecular	Tetra phosphorus decoxide (P_4O_{10}), I_2, P_4
Covalent	SiC, Graphite, Si
Amorphous	Plastic

1.4
I. What is meant by the term 'coordination number'?
II. What is the coordination number of atoms:
   a) In a cubic close-packed structure?
   b) In a body-centred cubic structure?

Answer 1.4

I.   Coordination number: - it is the total number of surrounding atoms of any constituent particle present in the crystal lattice.

II. The coordination number of atoms

a) in a cubic close-packed structure is 12

b) in a body-centred cubic structure is 8

1.5 How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain.

Answer 1.5

Let the edge length of a unit cell of a crystal = a

The density of the metal=d

The atomic mass of the metal=m

The number of atoms in the unit cell=z

$$d = \frac{zm}{a^3}$$

$$m = \frac{da^3}{z}$$

We know that

$$m = \frac{M}{N_A}$$

From above equations, M will be:

$$M = \frac{da^3 N_A}{z}$$

Thus, we can calculate the atomic mass of the unknown metal.

1.6 Stability of a crystal is reflected in the magnitude of its melting point', Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

Answer 1.6

We know that higher the melting point, greater is the intermolecular force of attraction and greater will be stability.

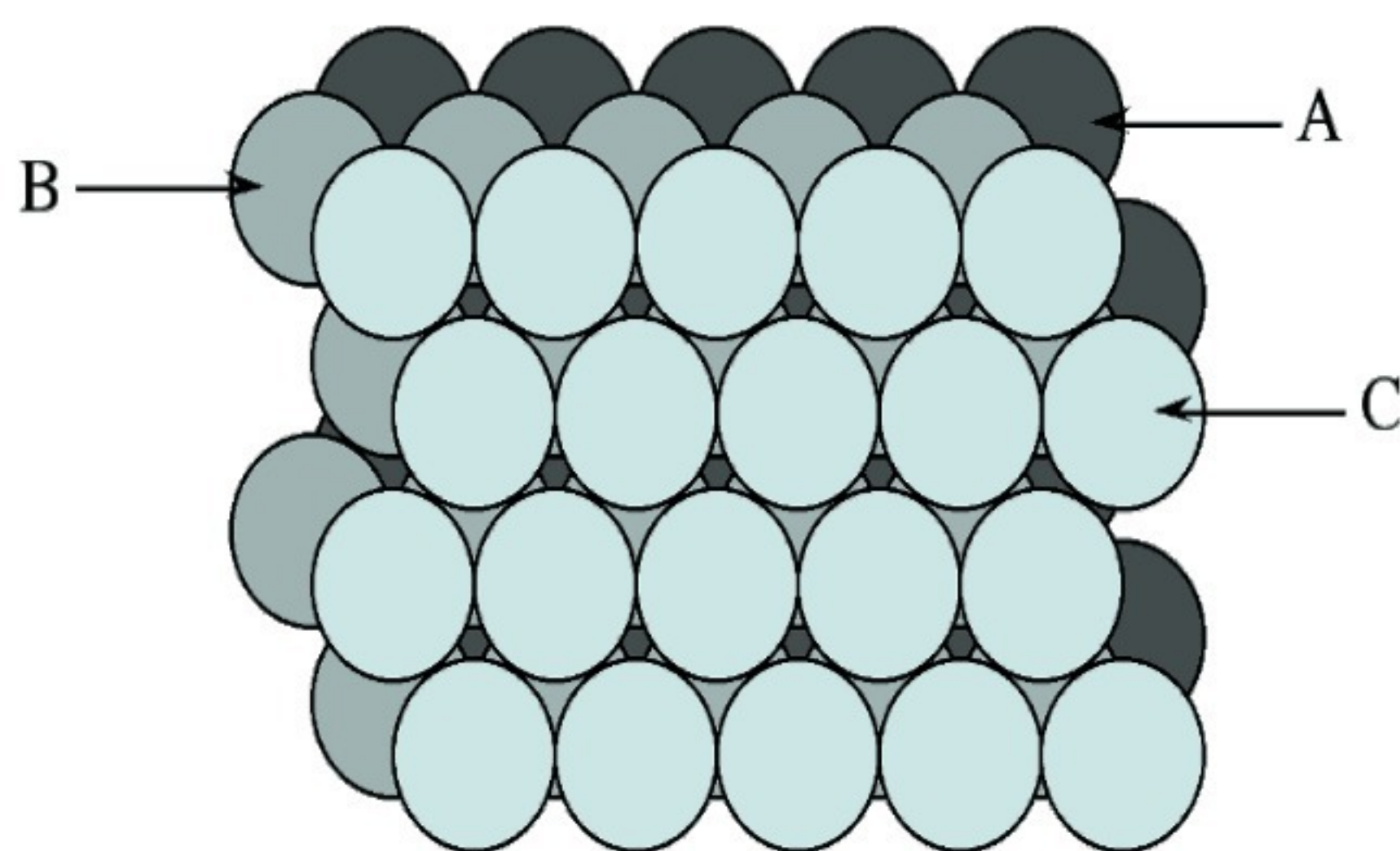| Substance	Melting point
Solid water	273 K
Ethyl alcohol	158.8 K
Diethyl ether	156.85 K
Methane	89.34 K

Now, from above data, we can say that the intermolecular force of solid water is the strongest and that of methane is the weakest.

1.7. How will you distinguish between the following pairs of terms:
   i.   Hexagonal close-packing and cubic close-packing?
   ii.   Crystal lattice and unit cell?
   iii. Tetrahedral void and octahedral void?

Answer 1.7

   i.   Hexagonal close-packing and cubic close-packing:-

Hexagonal close-packing	Cubic close-packing
• In this packing, tetrahedral voids of the second layer are covered. • In this case, the spheres of the third layer are exactly aligned with those of the first layer. • In this, pattern is ABAB .... type. • Examples of this arrangement of atoms are found in many metals like magnesium and zinc.	• In this packing, octahedral voids of the second layer are covered. • In this case, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called "C" type. Only when fourth layer is placed, its spheres are aligned with those of the first layer. • In this, pattern of layers is ABCABC .... type. This structure is also known as face-centred cubic (fcc) structure. • Examples of this arrangement of atoms are copper and silver.

ii.   **Crystal lattice:** - arrangement of the constituent particles of a crystal in a regular three-dimensional network is called crystal lattice.

Unit cell: - it is the smallest three-dimensional part of a crystal lattice. When these cells joined each other they make whole crystal lattice.

iii. **Tetrahedral void:** - it is surrounded by 4 spheres.

Octahedral void: - it is surrounded by 6 spheres.
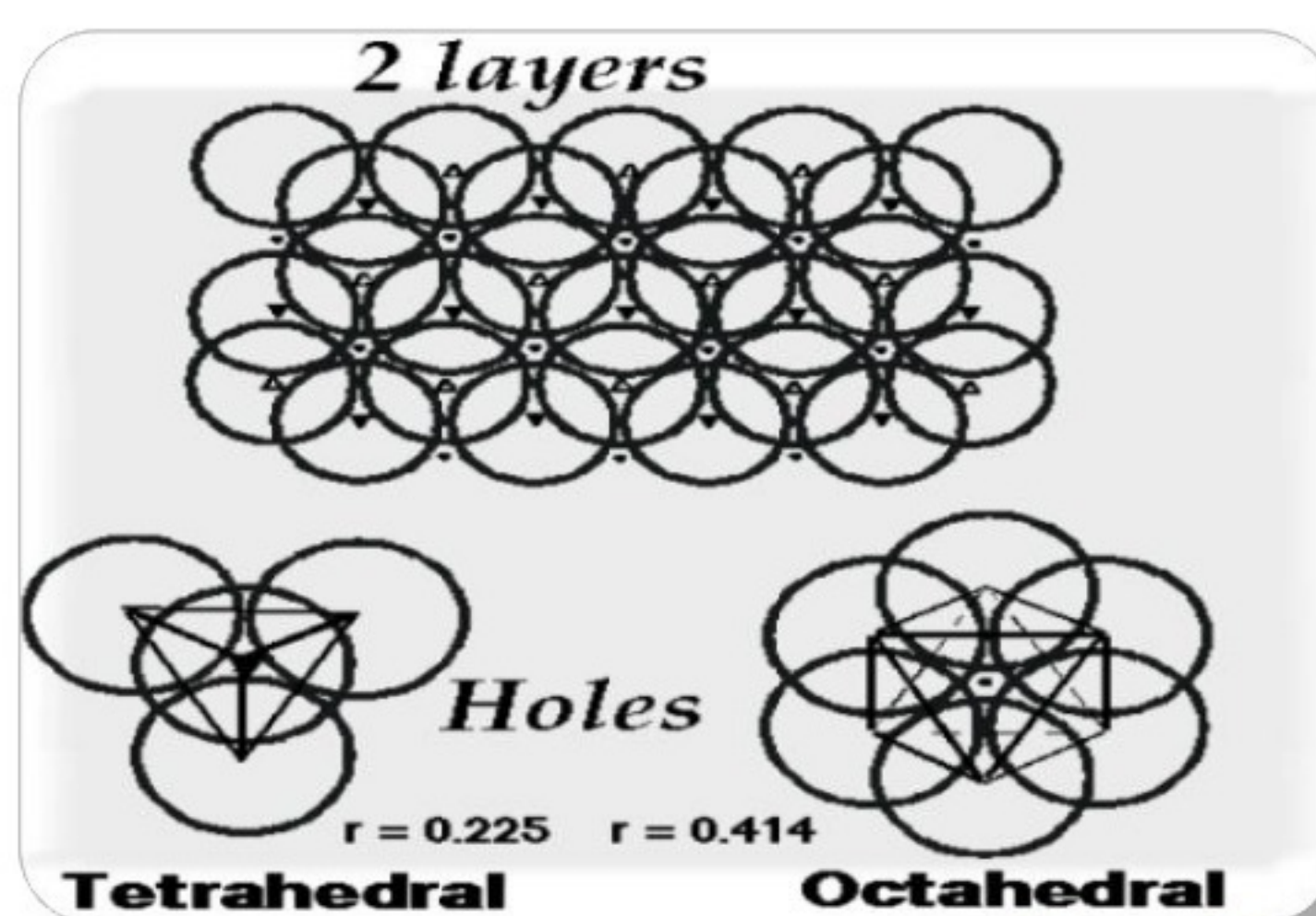
1.8 How many lattice points are there in one unit cell of each of the following lattice?
  i. **Face-centred cubic**
  ii. **Face-centred tetragonal**
  iii. **Body-centred**

Answer 1.8

  i. In face-centred cubic unit cell
     14 lattice points = 8 from the corners + 6 from the faces
  ii. In face-centred tetragonal unit cell
     14 lattice points= 8 from the corners + 6 from the faces
  iii. In body-centred cubic unit cell
     9 lattice points = 1 from the centre + 8 from the corners

1.9 Explain
  i. **The basis of similarities and differences between metallic and ionic crystals.**
  ii. **Ionic solids are hard and brittle.**

Answer 1.9

i. The basis of similarities between metallic and ionic crystals are:
- the electrostatic force of attraction is present in both crystals
- In metallic crystals, forces act between electrons & positive ions whereas in ionic crystals, it acts between the oppositely-charged ions. Thus, both have high melting points.

The basis of differences is:

- In metallic crystals, the electrons are free to move and thus, metallic crystals can conduct electricity. In case of ionic crystals, the ions are fixed they are not free to move. Because of which, they cannot conduct electricity. But, in molten state or in aqueous solution, they do conduct electricity.

ii. Ions are the constituent particles of ionic crystals. These ions are held by the electrostatic force of attraction. Since these forces are very strong, they held these charged ions in fixed positions. That is why ionic crystals are hard and brittle.

1.10. Calculate the efficiency of packing in case of a metal crystal for
  i.   simple cubic
  ii.   body-centred cubic
  iii. Face-centred cubic (with the assumptions that atoms are touching each other).

Answer 1.10

i.   Simple cubic
In this, particles locate only at the corners of the cube and touch each other along the edges.

Let the edge of the cube = a

The radius of a particle = r

Therefore, $a = 2r$

Volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$

We know that,

Number of particles per unit cell = 1

Volume of the occupied unit cell = $\dfrac{4}{3}\pi r^3$

Hence, packing efficiency = $\dfrac{\text{volume of one particle}}{\text{volume of cubic unit cell}} \times 100\%$

$$= \dfrac{\dfrac{4}{3}\pi r^3}{8r^3} \times 100\%$$

$$= \dfrac{\pi}{6} \times 100\%$$

$$= 52.4\%$$

ii. **Body-centred cubic:**

In this type of structure, the atom at the centre is in contact with the other two atoms present diagonally.

From ∆FED, we have:

$b^2 = a^2 + a^2$

$b^2 = 2a^2$

$b = \sqrt{2}\,a$
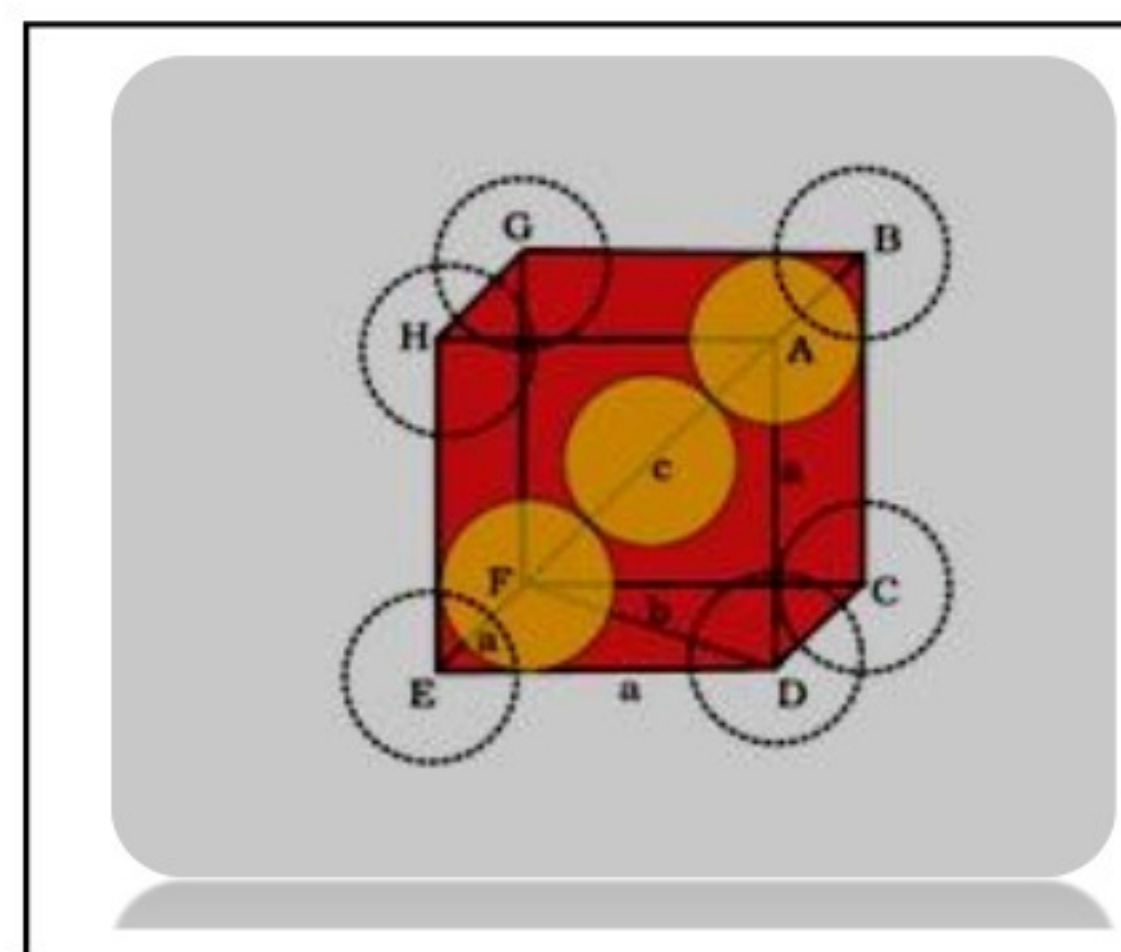
Again, from ∆AFD, we have:

$c^2 = a^2 + b^2$

$b^2 = a^2 + 2a^2 \qquad \left[\because b = \sqrt{2}\,a\right]$

$c = \sqrt{3}\,a$

Let the radius of the atom = r

Length of the body diagonal, $c = 4\pi$

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

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

Volume of the cube, $a^3 = \left(\dfrac{4r}{\sqrt{3}}\right)^3$

The number of atoms per unit cell, $Z = 2$

Therefore, volume of the occupied cubic lattice $= 2\pi \cdot \dfrac{4}{3} r^3 = \dfrac{8}{3}\pi r^3$

$$\text{Packing efficiency} = \frac{\text{volume occupied by 2 spheres in the cell}}{\text{total volume of cell}} \times 100\%$$
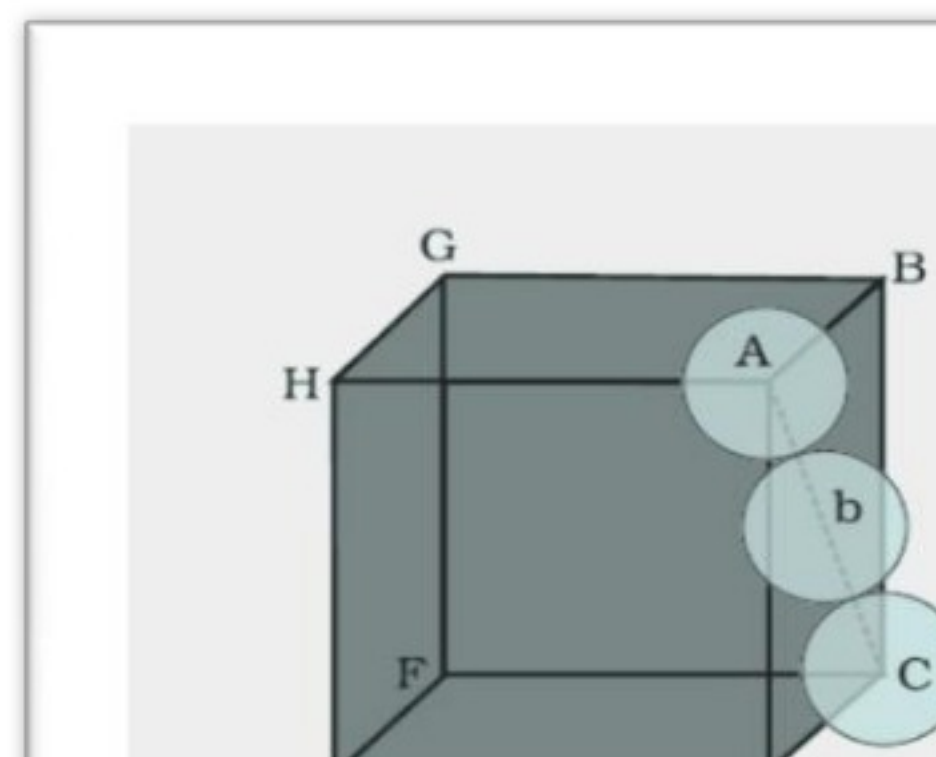
$$= \frac{\dfrac{8}{3}\pi r^3}{\left(\dfrac{4r}{\sqrt{3}}\right)^3} \times 100\%$$

$$= \frac{8}{3}\pi r^3 \times \frac{3\sqrt{3}}{64 r^3} \times 100\%$$

$$= 68\%$$

iii. Face-centred cubic:

Let the edge length of the unit cell = a

The length of the face diagonal AC = b

From ΔABC,

$$\left(AC \right)^2 = \left(BC \right)^2 + \left(AB \right)^2$$

$$b^2 = a^2 + a^2$$

$$b^2 = 2a^2$$

$$b = \sqrt{2}\, a$$

Let the radius of the atom = r

Also,

$$b = 4r$$

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

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

Now, volume of the cube, $a^3 = \left(2\sqrt{2}\, r \right)^3$

The number of atoms per unit cell, $Z = 4$

Therefore, volume of the occupied unit cell $= 4 \times \dfrac{4}{3} \pi r^3$

$$\text{Packing efficiency} = \frac{\text{volume occupied by 4 spheres in the cell}}{\text{total volume of cell}} \times 100\%$$

$$= \frac{4 \left(\dfrac{4}{3} \pi r^3 \right)}{\left(2\sqrt{2}\, r \right)^3} \times 100\%$$

$$= \frac{16}{3 \left(16\sqrt{2}\, r^3 \right)} \pi r^3 \times 100\%$$

$$= \frac{\pi}{3\sqrt{2}} \times 100\%$$

$$= 74\%$$

1.11 Silver crystallises in FCC lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{−3}, calculate the atomic mass of silver.

Answer 1.11

$a = 4.07 \times 10^{-8}$ cm

$d = 10.5$ g cm^{-3}

Lattice is fcc type, $z = 4$

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$$d = \frac{zM}{a^3 N_A}$$

$$\therefore m = \frac{d a^3 N_A}{z} = \frac{10.5 \times 4.077 \times 10^{-8} \times 6.022 \times 10^{23}}{4} = 107.15 \ g/mol$$

Hence, atomic mass of silver = 107.15 u

1.12 A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q?

Answer 1.12

Atoms of Q are present at the corners of the cube.

$\therefore$ No. of atoms of Q in one unit cell $= 8 \times \dfrac{1}{8} = 1$

Atoms of P are present at the body-centre.

$\therefore$ No. of atoms of P in one unit cell $= 1$

P: Q = 1:1

Therefore, the formula of the compound & coordination number of both P and Q is PQ.

1.13 **Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass 93 u.**

Answer 1.13

$d = 8.55$ g cm^{-3}

$M = 93$ gmol^{-1}

Lattice is bcc type, $z = 2$

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$$d = \frac{zM}{a^3 N_A}$$

$$\therefore a^3 = \frac{zM}{dN_A} = \frac{2 \times 93}{8.55 \times 6.022 \times 10^{23}} = 3.61 \times 10^{-23} cm^3$$

$$\Rightarrow a = 3.3 \times 10^{-8} cm$$
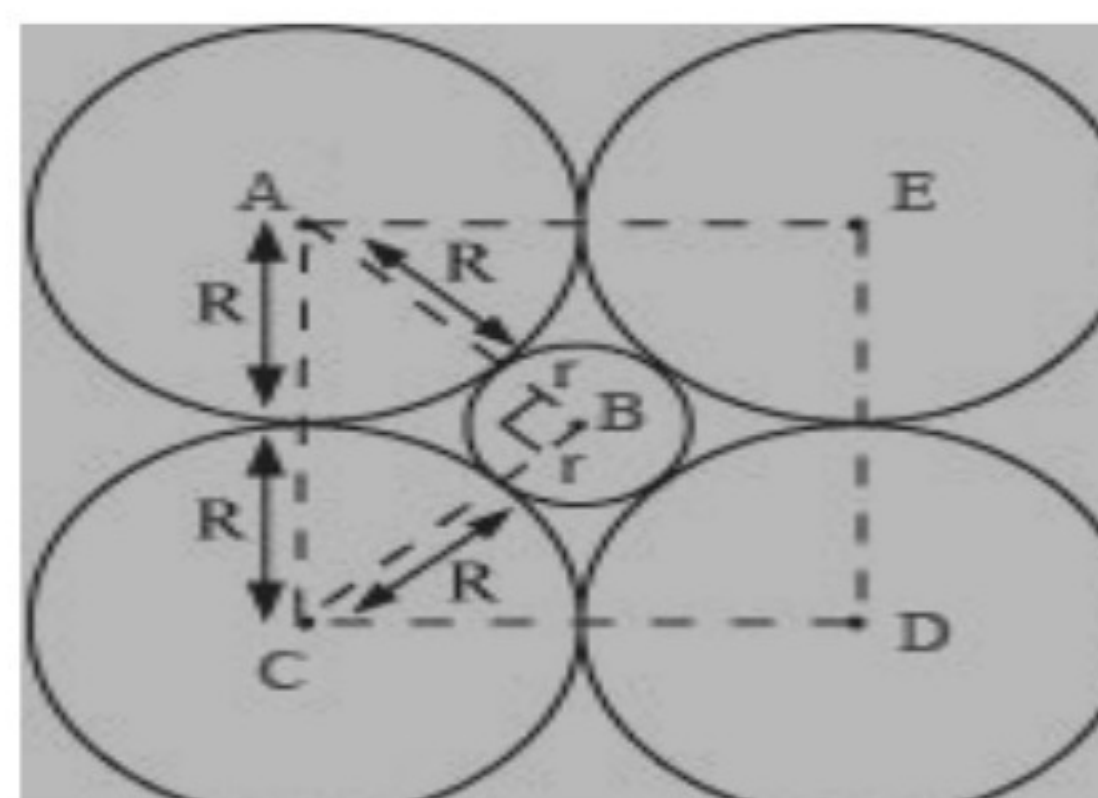
For body-centred cubic unit cell:

$$r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 3.3 \times 10^{-8}}{4} = 14.32 \, nm$$

1.14 **If the radius of the octahedral void is r and radius of the atoms in close packing is R; derive relation between r and R.**

Answer 1.14

$\angle ABC = 90^0$

On applying Pythagoras theorem,

$$(AC)^2 = (AB)^2 + (BC)^2$$

$$(2R)^2 = (R+r)^2 + (R+r)^2$$

$$(2R)^2 = 2(R+r)^2$$

$$2R^2 = (R+r)^2$$

$$R + r = \sqrt{2}R$$

$$r = (\sqrt{2} - 1)R$$

$$r = 0.414R$$

1.15 Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}.

Answer 1.15

$a = 3.61 \times 10^{-8}$ cm

Lattice is fcc type, $z = 4$

$M = 63.5$ g mol^{-1}

$N_A = 6.022 \times 10^{23}$ mol^{-1}

$$d = \frac{zM}{a^3 N_A}$$

$$= \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times 6.022 \times 10^{23}} = 8.97 \ g/cm^3$$

Hence, the calculated density is in agreement with its measured value.

1.16. Analysis shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?

Answer 1.16

The formula of nickel oxide = $Ni_{0.98}O_{1.00}$

Therefore, the ratio of the number of Ni & O atoms will be

$$\frac{Ni}{O} = \frac{0.98}{1.00} = \frac{98}{100}$$

Now, total charge on 100 O^{2-} ions = $100 \times (-2) = -200$

Let the number of Ni^{2+} ions = x

So, the number of Ni^{3+} ions = 98 − x

Now, total charge on Ni^{2+} ions = x (+2) = 2x

And, total charge on Ni^{3+} ions = (98 − x) (+3) = 294 − 3x

Since, the compound is neutral, net charge on the compound will be zero

$2x + (294 - 3x) + (-200) = 0$

X = 94

Hence, number of Ni^{2+} ions = 94

Number of Ni^{3+} ions = 98 − 94 = 4

Fraction of nickel that exists as $Ni^{2+} = \frac{94}{98} = 0.959$

Fraction of nickel that exists as $Ni^{3+} = \frac{4}{98} = 0.041$

1.17 What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism.

Answer 1.17

Semiconductors:-substances which have conductance in the range of 10^{-6} to $10^4 \text{ohm}^{-1}\,\text{m}^{-1}$.

The two types of semiconductors are:

1. N-type semiconductor
2. P-type semiconductor

N-type semiconductor: To increase the conductivity of a semiconductor, we add certain impurities in it. When we add negatively-charged electrons in it, *n*-type semiconductor is formed.

For example- doping of crystal of a group 14 element like Si with a group 15 element like P

Group 14 elements contain four valence electrons each. In their crystals, each atom forms four covalent bonds whereas in case of group 15, they contain five valence electrons each. When Si or Ge is doped with P or As,P or As occupies some of the lattice sites in the crystal. As a result, four out of five electrons are used in the formation of four covalent bonds with four neighbouring Si or Ge atoms. The remaining electron becomes delocalised and increases the conductivity of the doped crystal.

P-type semiconductor: When we add positively-charged electrons in a semiconductor, *p*-type semiconductor is formed.

For example- doping of crystal of a group 14 element like Si with a group13 element like B or Al

Group 14 elements contain four valence electrons each. In their crystals, each atom forms four covalent bonds whereas in case of group 13, they contain three valence electrons each. When Si or Ge is doped with B or Al, B or Al occupies some of the lattice sites in the crystal. As a result, three out of four. electrons are used in the formation of four covalent bonds with four neighbouring Si or Ge atoms and an electron hole is created. An electron from the neighbouring atom can come and fill this electron hole, but in doing so, it would leave an electron hole at its original position. This whole

process appears as if the electron hole is moving in the direction opposite to that of the electron that filled it. Therefore, when an electric field is applied, electrons will move toward the positively-charged plate through electron holes

1.18 Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a *p*-type semiconductor?

Answer 1.18

In the cuprous oxide, Cu_2O prepared in the laboratory, copper to oxygen ratio is slightly less than 2:1. This means that the number of Cu^+ ions is slightly less than twice the number of O^{2-}ions. This happens because some Cu^+ ions are replaced by Cu^{2+} ions. In order to maintain electrical neutrality every Cu^{2+} ion replaces two Cu^+ ions & creates hole. These holes help in conducting electricity in a substance. Therefore, cupric oxide is a *p*-type semiconductor

1.19 Ferric oxide crystallises in a hexagonal close-packed array of oxide ions with two. out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide

Answer 1.19

Let the number of oxide, O^{2-} ions = x
Therefore, number of octahedral voids = x
Two out of every three octahedral holes are occupied by ferric ions.

Therefore, number of ferric, Fe^{3+} ions = $\dfrac{2x}{3}$

Hence, ratio of the number of Fe^{3+} ions to the number of O^{2-} ions will be
$Fe^{3+} : O^{2-} = 2 : 3$
Hence, the formula of the ferric oxide is Fe_2O_3.

1.20 Classify each of the following as being either a *p*-type or an *n*-type semiconductor:

    (i) Ge doped with In   (ii) B doped with Si.

    Answer 1.20

      (i) Ge is an element of group 14 is doped with In which is an element of group 13. It leads to production of a hole and hence, a *p*-type semiconductor will be generated.

      (ii) B is an element of group 13 is doped with Si which is an element of group 14. So, an electron per atom will be free and therefore, an *n*-type semiconductor will be generated.

1.21 Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell?

    Answer 1.21

$r = 0.144$ nm

For a face-centred unit cell,

$$a = 2\sqrt{2}\,r$$
$$= 2 \times 1.414 \times 0.144 \text{ nm}$$
$$= 0.407 \text{ nm}$$

Hence, length of a side of the cell = 0.407 nm

**1.22 In terms of band theory, what is the difference**

    (i) Between a conductor and an insulator

    (ii) Between a conductor and a semiconductor
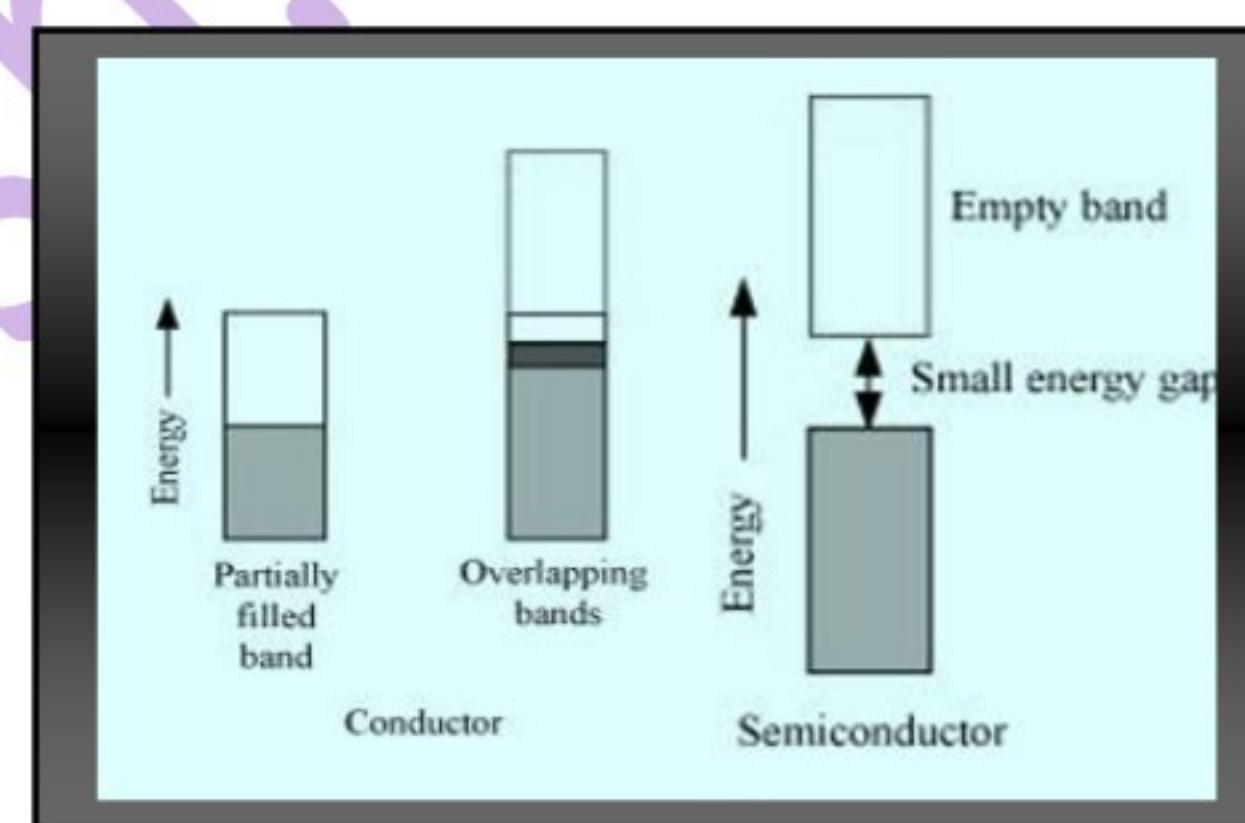
    Answer 1.22

(i) **Conductor:** - valence band of a conductor is partially-filled or it overlaps with a higher unoccupied band known as conduction band. Conduction band is higher energy level.

Insulator: - valence band of an insulator is fully- filled and there is a large gap between its valence and conduction band.
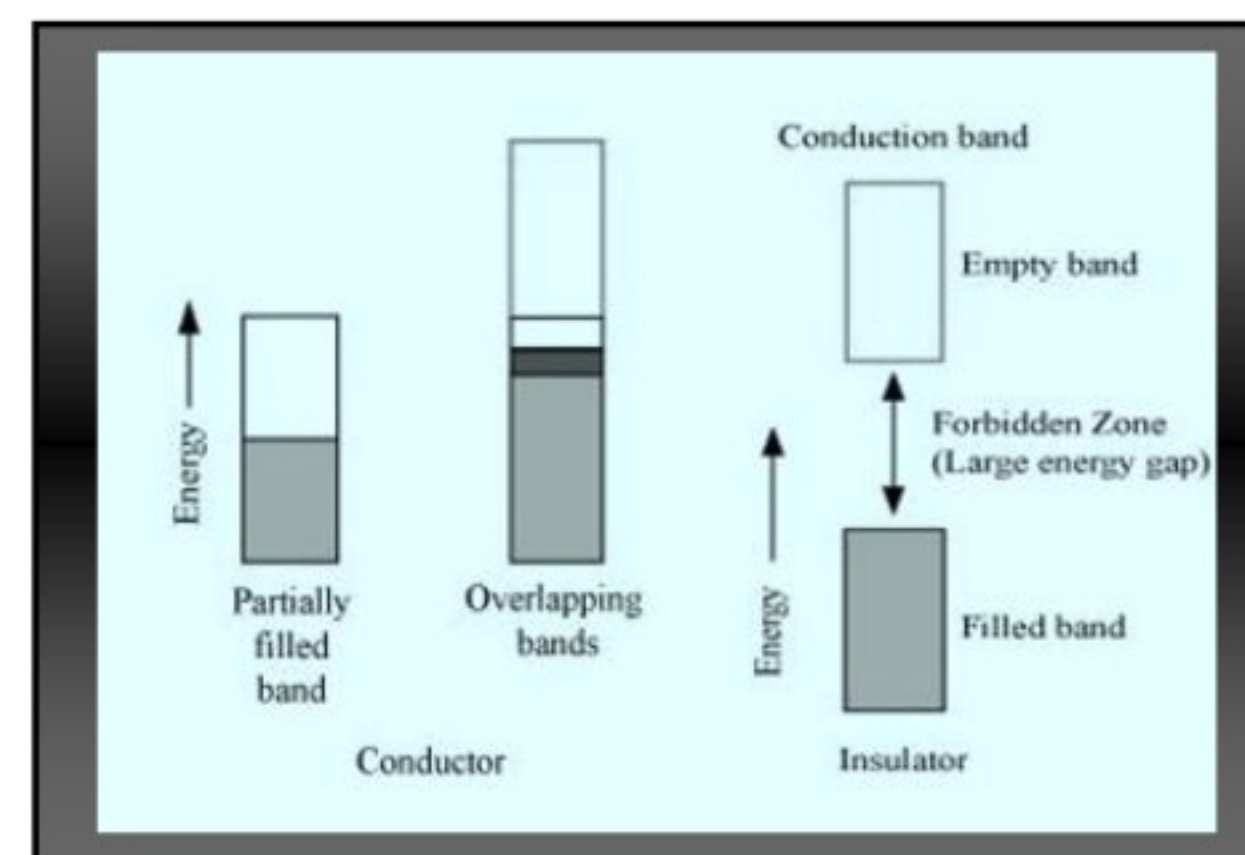
(ii)Conductor: - valence band of a conductor is partially-filled or it overlaps with a higher unoccupied band known as conduction band. Conduction band is higher energy level. So, the electrons can flow easily if we apply an electric field.

Semiconductor: - valence band of a semiconductor is filled and there is a small gap between its valence & conduction band.Therefore, some electrons can jump easily from the valence band to the conduction band and conduct electricity.

1.23 Explain the following terms with suitable examples:

    (i) Schottky defect

    (ii) Frenkel defect

    (iii) Interstitials and

    (iv) F-centres

    Answer 1.23

(i)Schottky defect: it is a vacancy defect which is shown by ionic solids. In this defect, an equal number of cations and anions are missing from their sites to maintain electrical neutrality. This leads to decrease in the density of a substance.

For example- NaCl, KCl, CsCl etc.

(ii)Frenkel defect: this defect is shown by those Ionic solids whose ions have large differences in their sizes of. When the smaller ion is dislocated from its normal site to an interstitial site, this defect is created. It creates a vacancy defect as well as an interstitial defect. This defect is also known as dislocation defect.

For example- Ionic solids such as AgCl, AgBr, ZnS, etc show this type of defect.

(iii)Interstitials: Interstitial defect is shown by non-ionic solids. This defect is produced when some atoms or molecules occupy interstitial sites of the crystal. Because of this defect, density of a substance increases.

(iv)F-centres: When unpaired electrons occupy the anionic sites of a crystal, the ionic sites are called F-centres. These unpaired electrons impart colour to the crystals.

For example, when NaCl crystal is heated in an atmosphere of sodium vapour, the sodium atoms get deposited on the surface of the crystal whereas Cl ions diffuse from the crystal to its surface and combine with Na atoms, forms NaCl. During this whole process, Na atoms lose electrons on the surface of the crystal & these electrons diffuse into the crystal and occupy the vacant anionic sites, which results in formation of F-centres.

1.24 Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.
  (i)   What is the length of the side of the unit cell?
  (ii)   How many unit cells are there in 1.00 cm^3 of aluminium?

  Answer 1.24

  (i)   For cubic close-packed structure:

$$a = 2\sqrt{2}\,r$$
$$= 2\sqrt{2}\,r$$
$$= 2 \times 1.414 \times 125 \text{ pm}$$
$$= 353.55 \text{ pm}$$

(ii)

$$a = 354 \text{ pm}$$
$$\text{volume} = a^3 = (354)^3 \ pm^3$$
$$= 4.4 \times 10^{-23} cm^3$$

$$\therefore No. \text{ of unit cells in } 1.00 \text{ cm}^3 = \frac{1}{4.4 \times 10^{-23}} = 2.27 \times 10^{22}$$

1.25 If NaCl is doped with 10^{-3} mol % of SrCl₂, what is the concentration of cation vacancies?

Answer 1.25

NaCl is doped with 10^{-3} mol% of SrCl₂

Hence, 100 mol of NaCl is doped with= 10^{-3} mol of SrCl₂

1 mol of NaCl is doped with = 10^{-5} mol of SrCl₂

Cation vacancies produced by one Sr²⁺ ion = 1

$$\therefore \ Number \ of \ the \ cation \ vacancies \ produced \ by \ 10^{-5} mol \ of \ Sr^{2+} ions = 10^{-5} \times 6.022 \times 10^{23}$$

$$= 6.022 \times 10^{18} mol^{-1}$$

1.26 Explain the following with suitable examples:
 (i)   **Ferromagnetism**
 (ii)   **Paramagnetism**
 (iii)   **Ferrimagnetism**
 (iv)   **Antiferromagnetism**

   (v)   **12-16 and 13-15 group compounds.**

Answer 1.26

(i)   **Ferromagnetism:** The substances which are strongly attracted towards magnetic field are known as ferromagnetic substances. For examples- iron, cobalt, nickel, etc. These substances can be permanently magnetised even in the absence of a magnetic field.

        In solid state, the metallic ions are grouped together into small group which are known as domains and each domain acts as a tiny magnet. In an un-magnetised ferromagnetic substance, the domains are randomly-oriented; therefore, their magnetic moments get cancelled. But when such substance is placed in a magnetic field, all the domains get oriented in one direction (direction of the magnetic field). Because of which a strong magnetic effect is produced. This ordering of domains remains even after the removal of the magnetic field. Thus, these substances become a permanent magnet.

(ii)   **Paramagnetism**: The substances that are attracted by a magnetic field are called paramagnetic substances. For examples- O_2, Cu^{2+}, Fe^{3+}, etc.

        These substances get magnetised in the direction of magnetic field, but they lose magnetism when the magnetic field is removed.

        To show paramagnetism, a substance should have unpaired electrons.

(iii)   **Ferrimagnetism:** in these substances, magnetic moments of the domains are aligned in parallel and anti-parallel directions but in unequal numbers. For examples magnetite, ferrites, etc.

        These substances are weakly attracted by a magnetic field as compared to ferromagnetic substances but on heating, they become paramagnetic.

(iv)   **Antiferromagnetism:** in these substances domain structures are similar to ferromagnetic substances, but their orientation is opposite. Due to this orientation, domains cancel out each other's magnetic moments.

(v)   **12-16 and 13-15 group compounds:** - 12-16 group compounds are prepared by combining elements of group 12 and group 16. For example- zinc sulphide, cadmium sulphide. 13-15 group compounds are prepared by combining elements of group 13 and group15. Example - gallium arsenide

Bonds of these compounds are not perfectly covalent. Their ionic character depends on the electro negativities of the two atoms.