

1. Define the term 'amorphous'. Give a few examples of amorphous solids.

Sol. Amorphous solids are those substances, in which there is no regular arrangement of its constituent particles (i.e. ions, atoms or molecules). The arrangement of the constituting particles has only short range order, that is a regular and periodically repeating pattern is observed over short distances only (e.g. quartz, glass, rubber and plastics).

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

Sol. Glass is made up of SiO_4 tetrahedral units. These constituent particles have short range order only. Quartz is also made up of SiO_4 tetrahedral units. These constituent particles have short range as well as long range order.

Quartz can be converted into glass by first melting and then rapidly cooling it.

3. Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous:

(a) Tetraphosphorus decoxide (P_4O_{10})

(b) Graphite

(c) Ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$

(d) Brass

(e) SiC

(f) Rb

(g) I_2

(h) LiBr

(i) P_4

(j) Si

(k) Plastics

Sol.

<i>Ionic</i>	<i>Metallic</i>	<i>Molecular</i>	<i>Network (covalent)</i>	<i>Amorphous</i>
$(\text{NH}_4)_3\text{PO}_4$	Brass	P_4O_{10}	Graphite	Plastics
LiBr	Rb	I_2	SiC	
			P_4	Si

4. (a) What is meant by the term 'coordination number'?

(b) What is the coordination number of atom

(i) in a cubic close-packed structure?

(ii) in a body-centred cubic structure?

Sol. (a) The number of nearest neighbours of a particle is called its coordination number.

(b) (i) 12 (ii) 8

5. How can you determine the atomic mass of an unknown metal if you know its density and the dimensions of its unit cell? Explain your answer.

Sol. Let the edge length of a unit cell = a

Density = d

Molar mass = M

Volume of the unit cell = a^3

Mass of the unit cell = No. of atoms in unit cell \times Mass of each atom = $Z \times m$

Mass of an atom present in the unit cell = $m = \frac{M}{N_a}$

$$\therefore d = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{Z \cdot m}{a^3} = \frac{Z \cdot M}{a^3 N_a}$$

$$\therefore \text{Atomic mass, } M = \frac{d \cdot a^3 \cdot N_a}{Z}$$

6. (a) 'Stability of a crystal is reflected in the magnitude of its melting point'. Comment.

(b) The melting points of some compounds are given below:

Water = 273K, Ethyl alcohol = 155.7K, Diethylether = 156.8K, Methane = 90.5K.

What can you say about the intermolecular force between these molecules?

Sol. (a) Higher the melting point, greater are the forces holding the constituent particles together and thus greater is the stability of a crystal.

(b) The intermolecular forces present in case of water and ethyl alcohol are mainly due to the hydrogen bonding which is responsible for their high melting points. Hydrogen bonding is stronger in case of water than ethyl alcohol and hence water has higher melting point than ethyl alcohol.

Dipole-dipole interactions are present in case of diethylether. The only forces present in case of methane is the weak van der Waal's forces (or London dispersion forces).

7. How will you distinguish between the following pairs of terms:

- (a) Cubic close packing and hexagonal close packing.
 (b) Crystal lattice and unit cell.

(c) Tetrahedral void and octahedral void.

- Sol.**
- (a) (i) **Cubic close packing:** When the third layer is placed over the second layer in such a way that the spheres cover the octahedral voids, a layer different from first (A) and second (B) is produced. If we continue packing in this manner, then a packing is obtained where the spheres in every fourth layer will vertically aligned. This pattern of packing spheres is called ABCABC..... pattern or cubic close packing.
- (ii) **Hexagonal close packing:** When a third layer is placed over the second layer in such a manner that the spheres cover the tetrahedral void, a three-dimensional closet packing is obtained where the spheres in every third or alternate layers are vertically aligned. If we continue packing in this manner, then the packing obtained would be called ABAB..... pattern or hexagonal close packing.
- (b) (i) **Crystal lattice:** It is a regular arrangement of the constituent particles (i.e. ions, atoms or molecules) of a crystal in three-dimensional space.
- (ii) **Unit cell:** The smallest three-dimensional portion of a complete space lattice which when repeated over and again in different directions produces the complete crystal lattice is called the unit cell.
- (c) **Tetrahedral void:** A simple triangular void in a crystal is surrounded by four spheres and is called a tetrahedral void.
- Octahedral void:** A double triangular void is surrounded by six spheres and is called an octahedral void.

8. How many lattice points are there in one unit cell of each of the following lattices:

- (a) Face-centred cubic (b) Face-centred tetragonal
(c) Body-centred cubic

Sol. Lattice points in face-centred cubic (a) and face-centred tetragonal (b) = 8 (at corners) + 6 (at face-centres) = 14

$$\text{Particle per unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

(b) Lattice points in body-centred cubic (c) = 8 (at corners) + 1 (at body centre) = 9

$$\text{Particles per unit cell} = 8 \times \frac{1}{8} + 1 = 2.$$

9. Explain:

- The basis of similarities and differences between metallic and ionic crystals.
- Ionic crystals are hard and brittle.

Sol. (a) Metallic and ionic crystals.

Similarities:

- There is electrostatic force of attraction in both metallic and ionic crystals.
- Both have high melting points.
- Bonds are non-directional in both the cases.

Differences:

- Ionic crystals are bad conductors of electricity in solids state as ions are not free to move. They can conduct electricity only in the molten state or in aqueous solution.

Metallic crystals are good conductors of electricity in solid state as electrons are free to flow.

- Ionic bond is strong due to strong electrostatic forces of attraction.

Metallic bond may be strong or weak depending upon the number of valence electrons and the size of the kernels.

- Ionic crystals are hard and brittle.

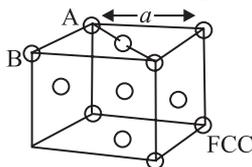
Ionic crystals are hard due to the presence of strong electrostatic forces of attraction.

The brittleness in ionic crystals is due to the non-directional bonds in them.

10. Calculate the efficiency of packing in case of a metal crystal for (a) simple cubic, (b) body-centred cubic and (c) face-centred cubic.

Sol. **Packing efficiency:** It is the percentage of total space filled by the particles.

- In HCP and CCP structures:** Let the edge length of unit cell = a



Let the radius of each sphere = r

$$\therefore AC = 4r$$

From right-angled triangle ABC,

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2}a$$

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

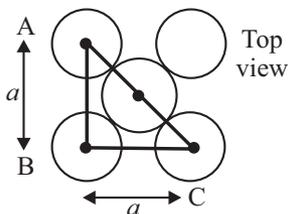


Fig. 1.6 Top view

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

$$\therefore \text{Volume of the unit cell} = a^3 = \left(\frac{4}{\sqrt{2}}r\right)^3 = \frac{64r^3}{2\sqrt{2}} = \frac{32r^3}{\sqrt{2}}$$

No. of unit cell in FCC = 4

$$\therefore \text{Volume of four spheres} = 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$$

$$\therefore \text{Packing efficiency} = \frac{16\pi r^3 / 3}{64r^3 / 3\sqrt{2}} = 0.74, \text{ i.e. } 74\%$$

HCP and CCP are equally efficient, hence packing efficiency of both is 74%.

(b) **In BCC:** $AD = 4r$

From right-angled triangle ABC,

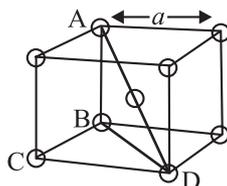


Fig. 1.7 3D view

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

Body diagonal,

$$AD = \sqrt{AC^2 + CD^2} = \sqrt{2a^2 + a^2} = \sqrt{3a^2} = \sqrt{3} a$$

$$\therefore \sqrt{3} a = 4r \quad a = 4r/\sqrt{3}$$

$$\therefore \text{Volume of unit cell} = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$$

No. of spheres per unit cell = 2

$$\therefore \text{Volume of two spheres} = 2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3$$

$$\therefore \text{Packing efficiency} = \frac{8/3 \pi r^3}{64r^3/3\sqrt{3}} = 0.68, \text{ i.e. } 68\%$$

(c) In simple cubic lattice:

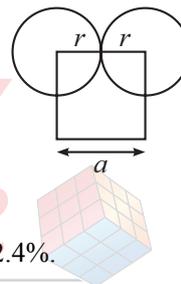
Here $a = 2r$

No. of spheres per unit cell = 1

$$\text{Volume of spheres} = \frac{4}{3} \pi r^3$$

$$\text{Volume of cube} = a^3 = (2r)^3 = 8r^3$$

$$\therefore \text{Packing efficiency} = \frac{4/3 \pi r^3}{8 r^3} = 0.524, \text{ i.e. } 52.4\%$$



- 11.** Silver crystallises in FCC lattice. If the edge length of the cell is 4.077×10^{-8} cm and density is 10.5 g cm^{-3} , calculate the atomic mass of silver.

Sol.
$$M = \frac{d \cdot a^3 \cdot N_a}{Z} = \frac{10.5 \times (4.077 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{4} = 107.09 \text{ g mol}^{-1}.$$

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

Sol. As atoms Q are present at the eight corners of the cube, therefore, the

$$\text{contribution of atoms of Q in the unit cell} = \frac{1}{8} \times 8 = 1.$$

As atom P is present at the body centre, therefore, the contribution of atoms of P in the unit cell = 1.

$$\therefore \text{Ratio of atoms of P : Q} = 1 : 1$$

Hence, the formula of the compound = PQ

The coordination number of each P and Q = 8.

13. Niobium crystallises in a body-centred cubic structure. If density is 8.55 g cm^{-3} , calculate atomic radius of niobium, given that its atomic mass is 92.9 u .

$$\text{Sol.} \quad a^3 = \frac{M \cdot Z}{d \cdot N_a \times 10^{-30}} = \frac{92.9 \times 2}{8.55 \times 6.02 \times 10^{23} \times 10^{-30}} = 3.61 \times 10^7$$

$$\therefore a = (3.61 \times 10^7)^{1/3} = (36.1 \times 10^6)^{1/3} = 3.304 \times 10^2 \text{ pm} = 330.4 \text{ pm}$$

14. If the radius of the octahedral void is r and the radius of the atoms in the close packing is R , derive relationship between r and R .

Sol. A sphere is fitted into the octahedral void as shown in the diagram.

ΔABC is a right-angled triangle.

$$\therefore BC^2 = AB^2 + AC^2$$

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

$$(2R)^2 = 2(R + r)^2 \quad \Rightarrow \quad \frac{(2R)^2}{2} = (R + r)^2$$

$$(\sqrt{2}R)^2 = (R + r)^2 \quad \Rightarrow \quad \sqrt{2}R = R + r$$

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

$$r = R(1.414 - 1)$$

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

$$r = 0.414R$$

15. Copper crystallises into a FCC lattice with edge length $3.61 \times 10^{-8} \text{ cm}$. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3} .

$$\text{Sol.} \quad d = \frac{Z \times M}{a^3 \times N_a} = \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times (6.023 \times 10^{23})}$$

$$\{M = 68.5 \text{ for Cu}\} = 8.97 \text{ g cm}^{-3}$$

This calculated value of density is closest in agreement with its measured value of 8.92 g cm^{-3} .

16. Analysis shows that nickel oxide has the formula $\text{Ni}_{0.98}\text{O}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ions?

Sol. The formula $\text{Ni}_{0.98}\text{O}$ implies that 98 Ni atoms are associated with 100 O atoms.

Let out of 98 Ni atoms present, x atoms are present as Ni^{2+} ions and $(98 - x)$ are present as Ni^{3+} ions.

\therefore Total charge is $x \text{ Ni}^{2+}$ ions and $(100 - x) \text{ Ni}^{3+}$ ions should balance the charge on 100 O^{2-} ions.

$$\text{Hence, } x \times 2 + (98 - x) \times 3 = 100 \times 2$$

$$2x + 294 - 3x = 200$$

$$x = 94.$$

$$\therefore \text{Fraction of Ni atoms present as Ni}^{2+} = \frac{94}{98} \times 100 = 96\%$$

$$\text{and fraction of Ni atoms present as Ni}^{3+} = \frac{4}{98} \times 100 = 4\%.$$

17. What is a semi-conductor? Describe the two main types of semi-conductors and contrast their conduction mechanisms.

Sol. Semi-conductors are those substances whose conductances lie between that of conductors and insulators. Semi-conductor are of two type: (a) *n*-type (b) *p*-type.

- (a) *n*-type: When group 14 elements like silicon and germanium (having four electrons in the valence shells) are doped with group 15 element like phosphorous or arsenic (having five electrons the valence shells), few lattice sites in Si or Ge is substituted by atoms of P or As. As group 15 atoms have five electrons in the valence shell, after forming four covalent bonds with neighbouring Si atoms, fifth extra electron is free and delocalised gets delocalised. These electrons increases the conductivity of Si or Ge. As the increase in conductivity is due to the negatively charged electrons, the silicon or germanium crystals doped with electron-rich impurities are called *n*-type semi-conductor.
- (b) When group 14 elements like silicon or germanium, having four electrons in the valence shell, is doped with group 13 elements like boron, aluminium or gallium, few sites of Si or Ge atoms are substituted by atoms of B, Al or Ga. As group 13 atoms have three electrons in the valence shell, they form three covalent bonds with the neighbouring Si or Ge atoms. Thus, a hole is created at the site where fourth electron is missing (called electron hole or electron vacancy). As electron from the neighbouring atom can jump to fill up this electron hole than a hole is created at the site from where electron has jumped. As this continues, the electron holes will move in a direction opposite to that of the flow of electrons. When electricity in applied, the electrons move towards the positively charged plate and electron holes move towards the negatively charged plate as if they carry positive charge. Hence, electron deficit doped Si or Ge are called *p*-type semi-conductors.

18. Non-stoichiometric cuprous oxide, Cu_2O can be prepared in the 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 semi-conductor?

Sol. The radius ratio slightly less than 2 : 1 in Cu_2O shows that some cuprous (Cu^+) ions have been replaced by cupric (Cu^{2+}) ions. In order to maintain electroneutrality, every two (Cu^+) ions will be replaced by one Cu^{2+} ion thereby creating a hole. As the conduction will be due to the presence of these positive holes, hence it is a p -type semi-conductor.

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

Sol. Let the number of oxide ions (O^{2-}) in the packing = x

\therefore Number of octahedral voids = x

As out of every three octahedral holes, two are occupied by ferric ions,

therefore, the number of ferric ions present = $\frac{2}{3} \times x = \frac{2x}{3}$

\therefore Ratio of $\text{Fe}^{3+} : \text{O}^{2-} = \frac{2x}{3} : x = 2x : 3x = 2 : 3$

Hence, the formula of ferric oxide is Fe_2O_3 .

20. Classify each of the following as being either p -type or n -type semi-conductor:

(a) Ge doped with In (b) B doped with Si.

Sol. (a) In belongs to group 13, hence an electron deficient hole is created and therefore, it is a p -type semi-conductor.

(b) Be belongs to group 15, hence there will be a free electron, therefore, it is a n -type semi-conductor.

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

Sol. In case of FCC, $a = 2\sqrt{2}r = 2 \times 1.414 \times 0.144 \text{ nm} = 0.407 \text{ nm}$.

22. In terms of band theory, what is the difference

(a) between a conductor and an insulator.

(b) between a conductor and a semi-conductor.

Sol. (a) In case of conductor, the energy gap between the valence band and the conduction band is very small or there is overlapping between valence and conduction band whereas in case of insulator the energy gap between the valence band and the conduction band is very large.

(b) In case of conductor, there is very small energy gap or there is overlapping between valence and conduction band; but in a semiconductor, there is always a small energy gap between valence and conduction band.

23. Explain the following terms with suitable example:

- (a) Schottky defect (b) Frenkel defect
(c) Interstitials defect (d) F-centres

Sol. (a) Schottky defect occurs when a pair of ions of opposite charges (i.e. cations and anions), are missing from the ideal lattice. In NaCl, there are approximately 10^6 Schottky pairs per cm^3 at room temperature. There is one Schottky defect for 10^{16} ions. The presence of a large number of Schottky defects in a crystal lowers its density.

(b) Frenkel defects is a combination of two basic types of point defects: Schottky and interstitial. It occurs when an ion leaves its position in the lattice and occupies an interstitial site leaving a gap in the crystal.

(c) Interstitials are the atoms or ions which occupy the normally vacant interstitial sites in a crystal.

(d) When there is an excess of metal ions in non-stoichiometric compounds, the crystal lattice has vacant anion sites. These sites are occupied by electrons. The anion sites occupied by electrons are called F-centres.

24. Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.

- (a) What is the length of the side of the unit cell?
(b) How many unit cells are there in 100 cm^3 of aluminium?

Sol. Aluminium crystallises in CCP structure which is same as FCC structure.

$$\text{For FCC, } a = 2\sqrt{2}r = 2 \times 1.414 \times 125 \text{ pm} = 354 \text{ pm}$$

$$\begin{aligned} \text{Volume of one unit cell} &= a^3 = (354 \times 10^{-12})^3 \\ &= (354 \times 10^{-10} \text{ cm})^3 = 4.44 \times 10^{-23} \text{ cm}^3 \end{aligned}$$

$$\text{Number of unit cells in } 1 \text{ cm}^3 = \frac{1}{4.44 \times 10^{-23}} = 2.25 \times 10^{22}.$$

25. If NaCl is doped with 10^{-3} mol of SrCl_2 , what is the concentration of cation vacancies?

Sol. Doping of NaCl with 10^{-3} mol of SrCl_2 means that 100 moles of NaCl are doped with 10^{-3} mol of SrCl_2 .

\therefore 1 mole of NaCl is doped with $\text{SrCl}_2 = \frac{10^{-3}}{100}$ mole = 10^{-5} mole.

Each Sr^{2+} introduces one cation vacancy, therefore, concentration of cation vacancies

= 10^5 mole/mole of NaCl = $10^{-5} \times 6.023 \times 10^{23} \text{ mol}^{-1} = 6.023 \times 10^{18} \text{ mol}$.

26. Explain the following with suitable examples:

- (a) Ferromagnetism (b) Paramagnetism
(c) Ferrimagnetism (d) Anti-ferromagnetism

- Sol.**
- (a) Ferromagnetism is the phenomenon shown by substances which are strongly attracted by a magnetic field. These substances show magnetism even in the absence of a magnetic field. Examples are Fe, Co, Ni and CrO_2 .
- (b) Paramagnetism is the phenomenon shown by substance which are attracted by a magnetic field but they lose their magnetism in the absence of a magnetic field.
Examples are Cu^{2+} , Fe^{3+} , O_2 , NO and CuO.
- (c) Ferrimagnetism is the phenomenon shown by substances in which the number of magnetic moments oriented in one direction out number those in the other direction.
Examples are Fe_3O_4 and ferrites of formula $\text{M}^{2+} \text{Fe}_3\text{O}_4$, where M = Mg, Cu and Zn.
- (d) Anti-ferromagnetism is the phenomenon shown by substances in which equal number of magnetic moments are aligned in opposite directions so as to give net zero moment.
Examples are MnO, MnO_2 and Mn_2O_3 .