

UNIT - 1
THE SOLID STATE
QUESTIONS

1. What are Bravais lattices?
2. Why are amorphous solids isotropic in nature?
3. Why glass is regarded as an amorphous solid?
4. Define the term 'crystal lattice.'
5. Name the crystal system for which all four types of unit cells are possible. [Ans. Orthorhombic]
6. What is the total number of atoms per unit cell in a fcc crystal structure? [Ans. 4]
7. What difference in behaviour between the glass and sodium chloride would you expect to observe, if you break off a piece of either cube?
8. Define the term voids.
9. What type of stoichiometric defect is shown by (i) ZnS and (ii) CsCl?
[Hint. : (i) Frenkel defect (ii) Schottky defect]
- *10. If the formula of a compound is A_2B , which sites would be occupied by A ions?
[Hint. : Number of A atoms is double to B, so it occupied tetrahedral void]
11. What is the coordination number for (a) an octahedral void (b) a tetrahedral void. [Hint. : (a) 6; (b) 4]
- *12. How many octahedral voids are there in 1 mole of a compound having cubic closed packed structure?
13. What does the term 'Coordination number' indicate
14. Arrange simple cubic, bcc and fcc lattice in decreasing order of the fraction of the occupied space.
15. How much space is empty in a hexagonal closed packed solid?
16. An element crystallises separately both in hcp and ccp structure. Will the two structures have the same density? Justify your answer. [Hint : Both crystal structures have same density because the percentage of occupied space is same.]
- *17. Write dimensions and bond angles of match-box type of unit cells. [Hint : Orthorhombic crystal system].
- *18. Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal. [Hint : No. of atoms = $8 \times \frac{1}{8} + 4 \times 2 = 9$]
19. In NaCl crystal, Cl^- ions form the cubic close packing. What sites are occupied by Na^+ ions.
20. In Corundum, O^{2-} ions form hcp and Al^{3+} occupy two third of octahedral voids. Determine the formula of corundum.
[Ans. : Al_2O_3]
21. Why is Frenkel defect not found in pure alkali metal halides?
22. Which point defect is observed in a crystal when a vacancy is created by an atom missing from a lattice site.
23. Define the term 'doping'.
24. Although pure silicon is an insulator then how does it behave as a semiconductor on heating.
25. Name the crystal defect which lowers the density of an ionic crystal. [Ans. : Schottky defect]
26. What makes the crystal of KCl sometimes appear violet? [Hint : F-Centre]
27. Which Point defect in ionic crystal does not alter the density of the relevant solid?
28. Name one solid in which both Frenkel and Schottky defects occur.
29. Fe_3O_4 is ferrimagnetic at room temperature but becomes paramagnetic at 850 K. Why? [Hint : Due to randomization of spins at high temperature]
30. Which type of defects are known as thermodynamic defects? [Ans. : Stoichiometric defects]
31. In a p-type semiconductor the current is said to move through holes. Explain.
32. Solid A is very hard, electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it? [Hint : Covalent solid]

SA (I) TYPE QUESTIONS (2 MARKS)

1. List four distinctions between crystalline and amorphous solids with one example of each.
2. Give suitable reason for, the following—
(a) Ionic solids are hard and brittle
(b) Copper is malleable and ductile
3. Define F-centres. Mention its two consequences.
4. What is packing efficiency. Calculate the packing efficiency in body centered cubic structure.
5. Explain : (a) List two differences between metallic and ionic crystals.
(b) Sodium chloride is hard but sodium metal is soft.
6. Account for the following :
(a) Glass objects from ancient civilizations are found to become milky in appearances.
(b) Window glass panes of old buildings are thicker at the bottom than at the top.

7. Why graphite is soft lubricant and good conductor of electricity?
8. Explain the term "Unit Cell". Name the parameters that characterize a unit cell.
- *9. What do you understand by the following types of stacking sequences :
(a) AB AB (b) A B CABC What kind of lattices do these sequences lead to?
11. Explain how much portion of an atom located at (a) corner (b) body centre (c) face-centre and (d) edge centre of a cubic unit cell, is part of its neighbouring unit cells.
- *12. In a fcc arrangement of A and B atoms. A are present at the corners of the unit cell and B are present at the face centres. If one atom of A is missing from its position at the corners, what is the formula of the compound? *13. A compound made up of elements 'A' and 'B' crystallises in a cubic close packed structure. Atom A are present on the corners as well as face centres, whereas atoms B are present on the edgecentres as well as body centre. What is the formula of the compound? [Ans. A₄B₄ or AB]
14. Explain the terms : (a) Intrinsic semiconductors (b) Extrinsic semiconductor.
15. Pure silicon is an insulator. Silicon doped with phosphorus is a semiconductor. Silicon doper with gallium is also a semiconductor. What is the difference between the two types?
16. Explain how vacancies are introduced in a solid NaCl crystal when a compound containing cation of higher valence is added to it.
17. What is meant by non-stoichiometric defect? Ionic solids which have anionic vacancies due to metal excess defect develop colour. Explain with the help of suitable example.
18. Define the term 'point defects' Mention are main difference between stoichiometric and nonstoichiometric point defects.

SA(II) TYPE QUESTIONS (3 MARKS)

1. Write the relationship between atomic radius (r) and edge length (a) of cubic unit cell for
(a) Simple cubic unit cell (b) Body centred cubic unit cell (c) Face centred cubic unit cell
2. Write and explain three differences between Schottky and Frenkel defects under the heads :
(i) Effect on density (ii) Effect on electrical conductivity (iii) Effect on stability of the crystal
3. What is a semiconductor? Describe the two main types of semiconductors on the basis of their conductance mechanism.
4. Explain the following with one examples each : (a) Ferrimagnetism (b) Antiferromagnetism (c) 13-15 compounds

NUMERICALS

1. Sodium crystallises in a bcc unit cell. What is the approximate number of unit cells in 4.6 g of sodium? Given that the atomic mass of sodium is 23 g mol⁻¹. [Ans. : 6.022×10^{22}]
- *2. In a crystalline solid anions 'C' are arranged in cubic close packing, cation 'A' occupy 50% of tetrahedral voids and cations 'B' occupy 50% of octahedral voids. What is the formula of the solid? [Ans. : A₂BC₂]
- *3. Magnetite, a magnetic oxide of iron used on recording tapes, crystallises with iron atoms occupying 1/8 of the tetrahedral holes and 1/2 of the octahedral holes in a closed packed array of oxides ions. What is the formula of magnetite? [Ans. : Fe₃O₄]
4. A metal crystallises into two cubic lattices fcc and bcc, whose edge length are 3.5Å and 3.0Å respectively. Calculate the ratio of the densities of fcc and bcc lattices. [Ans. : 1.26]
5. An element of atomic mass 98.5 g mol⁻¹ occurs in fcc structure. If its unit cell edge length is 500 pm and its density is 5.22 g cm⁻³. Calculate the value of Avogadro constant. [Ans. : 6.03×10^{23} mol⁻¹]
6. An element crystallises in a cubic close packed structure having a fcc unit cell of an edge 200 pm. Calculate the density if 200 g of this element contain 24×10^{23} atoms. [Ans. : 41.6 g cm⁻³]
7. A fcc unit cell containing atoms of element (molar mass 60.4 g mol⁻¹) has cell edge 4×10^{-8} cm. Calculate the density of unit cell. [Ans. : 6.23 g/cm³]
8. The metal calcium (atomic mass = 40 gm mol⁻¹) crystallises in a fcc unit cell with a = 0.556 nm. Calculate the density of the metal if (i) It contains 0.2% Frenkel defect. (ii) It contains 0.1% schottky defect. [Ans. : (i) 1.5463 g/cm³; (ii) 1.5448g/cm³]
9. Analysis shows that a metal oxide has a empirical formula M_{0.96}O. Calculate the percentage of M²⁺ and M³⁺ ions in this crystal. [Ans. : M²⁺ = 91.7%, M³⁺ = 8.3%]
10. AgCl is doped with 10⁻² mol% of CdCl₂, find the concentration of cation vacancies. [Ans. : 6.02×10^{19} mol]
11. A metallic element has a body centered cubic lattice. Edge length of unit cell is 2.88×10^{-8} cm. The density of the metal is 7.20 gcm⁻³. Calculate (a) The volume of unit cell. (b) Mass of unit cell.
(c) Number of atoms in 100 g of metal. [Ans. : (a) 2.39×10^{-23} cm³ (b) 1.72×10^{-22} g, (c) 1.162×10^{24} atoms]
12. KF has NaCl structure. It's density is 2.48 g/cm³. Calculate edge length of crystal lattice. (Given At. mass of K = 39 g mol⁻¹, F = 19 g mol⁻¹ and N_A = 6.002×10^{23} mol⁻¹) [Ans. : 538 pm]

13. Molybdenum has atomic mass 96 g mol⁻¹ with density 10.3 g/cm³. The edge length of unit cell is 314 pm. Determine lattice structure whether simple cubic, bcc or fcc.

(Given $N_A = 6.022 \times 10^{23}$ mol⁻¹) [**Ans. : Z = 2, bcc type**]

*14. The density of copper metal is 8.95 g cm⁻³. If the radius of copper atom is 127 pm, is the copper unit cell a simple cubic, a body-centred cubic or a face centred cubic structure?

(Given at. mass of Cu = 63.54 g mol⁻¹ and $N_A = 6.02 \times 10^{23}$ mol⁻¹) [**Ans. : Z = 4 fcc type**]

15. The well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4 Ca²⁺ ions and 8F⁻ ions and that Ca²⁺ ions are arranged in a fcc lattice.

The F⁻ ions fill all the tetrahedral holes in the fcc lattice of Ca²⁺ ions. The edge of the unit cell is 5.46×10^{-8} cm in length. The density of the solid is 3.18 g cm⁻³ use this information to calculate Avogadro's number (Molar mass of CaF₂ = 78.08 g mol⁻¹)

UNIT - 2

SOLUTIONS

QUESTIONS

1. Give an examples of 'liquid in solid' type solution.

2. Which type of solid solution will result by mixing two solid components with large difference in the sizes of their molecules?

3. What is meant by semimolar and decimolar solutions?

4. What will be the mole fraction of water in C₂H₅OH solution containing equal number of moles of water and C₂H₅OH? [**Ans. : 0.5**]

5. Which method is adopted for expressing the concentration of a solution, when the number of components in solution are more than two? [**Hint : Mole fraction**]

6. Which of the following is a dimensionless quantity; molarity, molality or mole fraction? [**Ans. : mole fraction**]

7. 10 gm glucose is dissolved in 400 gm. of solution. Calculate percentage concentration of the solution. [**Ans. : 2.5% w/w**]

8. Gases tend to be less soluble in liquids as the temperature is raised. Why?

9. State the conditions which must be satisfied if an ideal solution is to be formed.

10. A mixture of chlorobenzene and bromobenzene forms nearly ideal solution but a mixture of chloroform and acetone does not. Why?

11. How is the concentration of a solute present in trace amount in a solution expressed?

*12. Which aqueous solution has higher concentration 1 molar or 1 molal solution of the same solute? Given reason. [**Ans. : 1M aqueous solution**]

*13. N₂ and O₂ gases have K_H values 76.48 Kbar and 34.86 kbar respectively at 293 K temperature. Which of these will have more solubility in water?

*14. Under what condition molality and molarity are identical. Explain with suitable reason.

*15. Addition of HgI₂ to KI (aq.) shows decrease in vapour pressure. Why?

16. What will happen to the boiling point of the solution on mixing two miscible liquids showing negative deviation from Raoult's law.

17. Liquid 'Y' has higher Vapour pressure than liquid 'X', which of them will have higher boiling point?

18. When 50 mL of ethanol and 50 mL of water are mixed, predict whether the volume of the solution is equal to, greater than or less than 100 mL. Justify.

19. Which type of deviation is shown by the solution formed by mixing cyclohexane and ethanol?

20. A and B liquids on mixing produce a warm solution. Which type of deviation from Raoult's law is there?

21. Define cryoscopic constant.

22. Mention the unit of ebullioscopic constant.

23. If k_f for water is 1.86 K kg mol⁻¹. What is the freezing point of 0.1 molal solution? [**Hint : $T_f = K_f \cdot m$**]

24. Name the component that separate first when salt solution is frozen.

25. What is reverse osmosis? Give one large scale use of it.

*26. What is the value of Van't Hoff factor (i) for Na₂SO₄ . 10H₂O? [**Ans. : i = 3**]

*27. What colligative property should be measured for (i) thermally unstable compound (ii) compound having very low solubility at room temperature.

28. What is the value of Van't Hoff factor (i) if solute molecules undergo dimerisation. [**Ans. : i = 0.5**]

29. Under what conditions is Van't Hoff factor less than one?

SA (I) - TYPE QUESTIONS (2 MARKS)

1. Explain the following :
 - (a) Solubility of a solid in a liquid involves dynamic equilibrium.
 - (b) Ionic compounds are soluble in water but are insoluble in non-polar solvents.
2. Give two examples each of a solution : (a) showing positive deviation (b) showing negative deviation
3. Some non-ideal solutions show positive deviations while some other negative deviations. Why?
4. Draw Vapour pressure vs composition (in terms of mole fraction) diagram for an ideal solution.
5. Define azeotropes. Mention their important characteristics.
6. Draw the total vapour pressure Vs. mol fraction diagram for a binary solution exhibiting non-ideal behaviour with negative deviation
8. Describe the following by giving a suitable example in each case :
 - (a) minimum boiling azeotropes (b) maximum boiling azeotropes
9. Show that the relative lowering of vapour pressure of a solvent is a colligative property.
10. Benzene and toluene form a nearly ideal solution. At a certain temperature, calculate the vapour pressure of solution containing equal moles of the two substances.
[Given : $P^\circ_{\text{Benzene}} = 150 \text{ mm of Hg}$, $P^\circ_{\text{Toluene}} = 55 \text{ mm of Hg}$]
11. What is meant by abnormal molecular mass? Illustrate it with suitable examples.
- *12. When 1 mole of NaCl is added to 1 litre water the boiling point increases. When 1 mole of CH_3OH is added to 1 litre water, the boiling point decreases. Suggest reason.
13. Can we separate water completely from HNO_3 solution. Justify your answer.
- *14. 1 gram each of two solutes 'A' and 'B' (molar mass of A > molar mass of B) are dissolved separately in 100 gram each of the same solvent. Which solute will show greater elevation in boiling point. Why?

SA (II) TYPE QUESTIONS (3 MARKS)

1. Define molarity and molality. List two main points of difference between molarity and molality of a solution.
2. (a) State and explain Henry's Law.
(b) If O_2 is bubbled through water at 393 K how many millimoles of O_2 gas would be dissolved in 1L of water? Assume that O_2 exerts a pressure of 0.95 bar. (Given K_H for $\text{O}_2 = 46.82 \text{ bar at } 393\text{K}$).
3. Give reason for the following :—
 - (a) Aquatic species are more comfortable in cold water than in warm water.
 - (b) To avoid bends scuba divers use air diluted with helium.
 - (c) Cold drinks bottles are sealed under high pressure.
4. Why should a solution of a non volatile solute boil at a higher temperature? Explain with the help of a diagram. Derive the relationship between molar mass and elevation in boiling point.
5. Account for the following :— (a) CaCl_2 is used to clear snow from roads in hill stations.
(b) Ethylene glycol is used as antifreeze solution in radiators of vehicles in cold countries.
(c) The freezing point depression of 0.01 m NaCl is nearly twice that of 0.01 m glucose solution.
6. Why do colligative properties of solution of a given concentration are found to give abnormal molecular weight of solute. Explain with the help of suitable examples.
7. Give reasons for the following :—
 - (a) RBC swell up and finally burst when placed in 0.1% NaCl solution.
 - (b) When fruits and vegetables that have been dried are placed in water, they slowly swell and return to original form.
 - (c) A person suffering from high blood pressure is advised to take less amount of table salt.
- *8. Glycerine, Ethylene Glycol and methanol sell at the same price per Kg. Which would be cheaper for preparing an antifreeze solution for the radiator of an automobile? [Ans. : Methanol]
- *9. Determine the correct order of the property mentioned against them :
 - (a) 10% glucose (p1), 10% urea (p2), 10% sucrose (p3) [Osmotic pressure]
 - (b) 0.1 m NaCl, 0.1 m urea, 0.1 m MgCl_2 [Elevation in b.pt.]
 - (c) 0.1 m CaCl_2 , 0.1 m sucrose, 0.1 m NaCl [Depression in f.pt.]

LONG ANSWER TYPE QUESTIONS (5 MARKS)

1. (a) What are ideal solutions? Give two examples.
(b) Calculate the osmotic pressure in pasals exerted by a solution prepared by dissolving 1.0g of polymer of mol. mass 185000 in 450 ml of water at 37°C .
2. (a) Describe a method of determining molar mass of a non-volatile solute from vapour pressure lowering. (b) How much urea (mol. mass 60 g mol⁻¹) must be dissolved in 50 g of water so that the vapour pressure at the room temperature is reduced by 25%? Also calculate the molality

of the solution obtained. [Ans. : 55.55 g and 18.5 m]

3. (a) Why is the freezing point depression considered as a colligative property? (b) The cryoscopic constant of water is 1.86 K m^{-1} . Comment on this statement. (c) Calculate the amount of ice that will separate out on cooling solution containing 50 g of ethylene glycol in 200 g H_2O to -9.3°C . (K_f for water = $1.86 \text{ K kg mol}^{-1}$) [Ans. : 38.71g]

4. (a) Define osmotic pressure. Explain how molecular mass of a solute can be determined by osmotic pressure. (b) Why osmotic pressure is preferred over other colligative properties for the determination of molecular mass of macromolecules?

(c) What is the molar concentration of particles in human blood if the osmotic pressure is 7.2 atm. at normal body temperature of 37°C ? [Ans. : 0.283 M]

NUMERICAL PROBLEMS

1. Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4), If 22 g of benzene is dissolved in 122g of carbon tetrachloride. [Ans. : $\text{C}_6\text{H}_6 = 15.3\%$, $\text{CCl}_4 = 84.7\%$]

2. Calculate the molarity of a solution prepared by mixing 500 ml of 2.5 M urea solution and 500 mL of 2M urea solution. [Ans. : 2.25 m]

3. The mole fraction of CH_3OH in an aqueous solution is 0.02 and density of solution 0.994 g cm^{-3} . Determine the molality and molarity. [Ans. : 1.13m, 1.08m]

4. 200 mL of calcium chloride solution contains $3.011 \times 10^{22} \text{ Cl}^-$ ions. Calculate the molarity of the solution. Assume that calcium chloride is completely ionized. [Ans. : 0.125 M]

5. $6 \times 10^{-3} \text{ g}$ oxygen is dissolved per kg of sea water. Calculate the ppm of oxygen in sea water. [Ans. : 6 ppm]

6. The solubility of oxygen in water is $1.35 \times 10^{-3} \text{ mol L}^{-1}$ at 20°C and 1 atm pressure. Calculate the concentration of oxygen at 20°C and 0.2 atm. pressure. [Ans. : $2.7 \times 10^{-4} \text{ mol L}^{-1}$]

7. Two liquids X and Y on mixing form an ideal solution. The vapour pressure of the solution containing 2 mol of X and 1 mol of Y is 550 mm Hg. But when 4 mol of X and 1 mole of Y are mixed, the vapour pressure of solution thus formed is 560 mm Hg. What will be the vapour pressure of pure X and pure Y at this temperature? [Ans. : X = 600 mm Hg; Y = 400 mm Hg]

8. An aqueous solution containing 3.12 g of barium chloride in 250 g of water is found to boil at 100.0832°C . Calculate the degree of dissociation of barium chloride.

[Given molar mass $\text{BaCl}_2 = 208 \text{ g mol}^{-1}$, K_b for water = 0.52 K/m] [Ans. : 83.3%]

9. The degree of dissociation of $\text{Ca}(\text{NO}_3)_2$ in a dilute aqueous solution, containing 7.0 g of salt per 100 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution.

[Ans. : 745.3 mm of Hg]

10. 2g of $\text{C}_6\text{H}_5\text{COOH}$ dissolved in 25g of benzene shows depression in freezing point equal to 1.62K.

Molar freezing point depression constant for benzene is $4.9 \text{ K kg mol}^{-1}$. What is the percentage association of acid if it forms a dimer in solution? [Ans. : 99.2%]

11. Calculate the amount of NaCl which must be added to one kg of water so that the freezing point is depressed by 3K. Given $K_f = 1.86 \text{ K kg mol}^{-1}$, Atomic mass : Na = 23, Cl = 35.5). [Ans. : 47.2 g NaCl]

12. Three molecules of a solute, A associate in benzene to form species A_3 . Calculate the freezing point of 0.25 molal solution. The degree of association of solute A is found to be 0.8. The freezing point of benzene is 5.5°C and its K_f value is 5.13 K m^{-1} . [Ans. : 4.9°C]

13. A 5% solution of sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ is isotonic with 0.877% solution of urea. Calculate the molecular mass of urea. [Ans. : 59.99 g mol^{-1}]

14. Osmotic pressure of a 0.0103 molar solution of an electrolyte was found to be 0.75 atm at 27°C . Calculate Van't Hoff factor. [Ans. : $i = 3$]

*15. The maximum allowable level of nitrates in drinking water as set by U.S. is 45 mg nitrate ions /dm³. Express this level in ppm? [Ans. : 45 ppm]

16. 75.2 g of Phenol ($\text{C}_6\text{H}_5\text{OH}$) is dissolved in 1 kg solvent of $K_f = 14 \text{ K m}^{-1}$, if the depression in freezing point is 7 K, then find the % of Phenol that dimerises. [Ans. : 75%]

*17. An aqueous solution of glucose boils at 100.01°C . The molal boiling point elevation constant for water is $0.5 \text{ K kg mol}^{-1}$. What is the number of glucose molecule in the solution containing 100 g of water.

[Ans. : 1.2×10^{21} molecules]

18. A bottle of commercial H_2SO_4 [density = 1.787 g/mL] is labelled as 86% by mass.

(a) What is the molarity of the acid?

(b) What volume of the acid has to be used to make 1 litre 0.2 M H_2SO_4 ?

(c) What is the molality of the acid? [Ans. : 15.7 M, 12.74 mL, 62.86 m]