UNIT I

THE SOLID STATE

Points to Remember

1. HCP and CCP have equal efficiency *i.e.,* 74% of space is occupied and coordination number is 12. CCP arrangement has FCC lattice.
2. Coordination number is the number of nearest neighbouring points surrounding a particular lattice point (point may be atom, ions or molecules).
3. Packing efficiency in simple cubic unit cell is 52.4%, in bcc arrangement is 68% and in fcc is 74%.
4. Unoccupied spaces in solids are called interstitial voids or interstitial sites.
5. Two types of interstitial voids are :

   (i) tetrahedral void

   (ii) octahedral void

   * No. of tetrahedral voids = $2 \times N$ (where N is number of closed packed particles).
   * No. of octahedral voids = N.
6. Valency defect lowers the density of a crystal.
7. Interstitial defect increases the density of a crystal.
8. Point defects in the ionic crystal may be classified as :

   (i) Stoichiometric defect also known as intrinsic or thermodynamic defect. Ratio of cations and anions is the same in defective crystal as in ideal crystal.

   (ii) In non-stoichiometric defect ratio of cations to anions is the difference in defective crystal from the ideal crystal.

   (iii) Impurity defect (due to presence of some other ions at the lattice sites).
9. Schottky defect arises due to missing of equal number of cations and anions from lattice sites in the crystalline solid of the type A^+B^- and it lowers and density of alkali metal halides, *e.g.,* NaCl, KCl etc.
10. Frenkel defect is the combination of vacancy and interstitial defects. Cations leave their actual lattice sites and occupy the interstitial space in the solid. Density remains the same in Frenkel defect.

+AgBr is the compound which shows both Schottky defect as well as Frenkel defect.

11. Non-stoichiometric defect

(i) Metal excess defect due to anion vacancies.

(ii) Metal excess defect due to presence of extra cations.

(iii) Metal deficiency due to absence of cations.

12. **F-Center :** In metal excess defect, electrons are trapped in the anion vacancies which act as colour centres, *e.g.,* NaCl gives yellow colour when heated in sodium vapour.

13. Doping is the process of increasing the conductivity of intrinsic semiconductors by adding an appropriate amount of suitable impurity in Si or Ge.

*** n-type semiconductors :** Silicon or Germanium (group 14) doped with electron rich impurity (group 15 element like P or As). Here, conductivity is due to the extra electrons or delocalized electrons.

*** p-type semiconductors :** Silicon or Germanium (group 14) doped with group 13 elements like B or Al. Here, conductivity is due to positively charged electron holes.

* 13-15 group compounds, *e.g.,* InSb, AlP, GaAs.

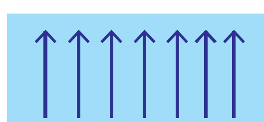
* 12-16 group compounds, *e.g.,* ZnS, CdS, CdSe, HgTe.

* These compounds have average valence of four and are used in semiconductor devices.

14. Magnetic Properties

* **Ferromagnetic substances :** A few substances like iron, cobalt, nickel and CrO_2 etc. are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances.

All molecular domains are arranged permanently in the same direction under influence of magnetic field.



* **Antiferromagnetism :** Substances like MnO showing antiferromagnetism have domain structure similar to ferromagnetism substances, but their domains are oppositely oriented and cancel out each other's magnetic moment and so cannot be attracted towards magnet.

* **Ferrimagnetism :** When the magnetic moments of the domains in the substances are aligned in parallel and antiparallel directions in unequal number.

These are weakly attracted by magnetic field as compared to ferromagnetic substances. For example, Fe_3O_4, MgF_2O_4 etc.

* Paramagnetic substances are weakly attracted by a magnetic field. Examples are O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} which are paramagnetic due to the presence of unpaired one or more electrons. They lose their magnetism in the absence of magnetic field.

* Diamagnetic substances are weakly repelled by a magnetic field. Examples are H_2O, NaCl, C_6H_6 because they have all the electrons paired.

1. Calculation of number of particles/atoms/ions in a unit cell :

Type of unit cell	Number of particles per unit cell	Relationship between edge length (a) and radius (r) of atom/ion
Simple cubic (SC)	1	$a = 2r$
Body centred cubic (BCC)	2	$a = \frac{4}{\sqrt{3}}r$
Face centred cubic (FCC)	4	$a = 2\sqrt{2}r$

2. Density of unit cell :

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

where Z is rank of unit cell (number of atoms per unit cell), M is molar mass/ atomic mass, a is edge length of the cube, a^3 is volume of cubic unit cell and N_A is Avogadro constant.

3. Packing efficiency, $\mathbf{PE} = \dfrac{Z \times \frac{4}{3}\pi r^3}{a^3} \times 100$

Here, M is molar mass, r is radius of atom, d is density and N_A is Avogadro's constant (6.022×10^{23} mol^{-1}).

Rank of unit cell can be computed by packing efficiency value :

Type of unit cell	Packing efficiency	Rank of unit cell (Z)
SC	52.4%	1
BCC	68%	2
FCC	74%	4

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What do you mean by paramagnetic substance ?

Ans. Weakly attracted by magnetic field and these substances are made of atoms or ions with unpaired electrons.

Q. 2. Which substance exhibit both Schottky and Frenkel defects ?

Ans. AgBr.

Q. 3. Name a salt which is added to AgCl so as to produce cationic vacancies.

Ans. $CdCl_2$

Q. 4. Why Frenkel defects not found in pure alkali metal halides ?

Ans. Due to larger size of alkali metal ion, these cannot shift in interstitial space.

Q. 5. What is he use of amorphous silica ?

Ans. Used in photovoltanic cell.

Q. 6. Analysis shows that a metal oxide has the empirical formula $M_{0.98}O_{1.00}$. Calculate the percentage of M^{2+} and M^{3+} ions in the crystal.

Ans. Let the M^{2+} ion in the crystal be x and $M^{3+} = 0.98 - x$

Since, total charge on the compound must be zero,

So, $2x + 3(0.98 - x) - z = 0$

Or $x = 0.94$

$$\% \text{ of } M^{2+} = \frac{0.94}{0.98} \times 100 = 97.9\%$$

$$\% \text{ of } M^{3+} = 100 - 97.9 = 2.1\%$$

Q. 7. What is the co-ordination number of cation and anion in Caesium chloride (bcc arrangement) ?

Ans. 8 and 8.

Q. 8. What is F-centre ?

Ans. It is the anion vacancy occupied by free electron in metal excess defect.

Q. 9. What makes alkali metal halides sometimes coloured, which are otherwise colourless ?

Ans. Due to presence of F-centre.

Q.10. How does silica differ from quartz ?

Ans. Silica is amorphous form, while quartz is crystalline form of SiO_2.

Q.11. Which point defect lowers the density of a crystal ?

Ans. Schottky defect/Vacancy defect.

Q.12. Why glass is called super cooled liquids ?

Ans. *Hint :* Its molecules move under gravity.

Q.13. Some of the very old glass objects appear slightly milky instead of being transparent. Why ?

Ans. Reallignment of molecules takes place due to movement because of constant heating and cooling.

Q.14. What is anisotropy ?

Ans. Physical properties show different values when measured along different axis in crystalline solids.

Q.15. What is the coordination number of atoms in :

(a) fcc structure (b) bcc structure ?

Ans. (a) 12 (b) 8

Q.16. How many lattice points are there in one unit cell of :

(a) fcc

(b) bcc

(c) simple cubic arrangement ?

Ans. (a) 14 (b) 9 (c) 8

Q.17. What are the co-ordination numbers of octahedral voids and tetrahedral voids ?

Ans. 6 and 4 respectively.

Q.18. Why common salt is sometimes yellow instead of being pure white ?

Ans. Due to the presence of electrons in some lattice sites in place of anions these sites act as F-centres. These electrons when excited impart colour to the crystal.

Q.19. A compound is formed by two elements X and Y. The element Y forms ccp arrangement and atoms of X occupy octahedral voids. What is the formula of the compound ?

Ans. No. of Y (ccp) = 4

No. of X (octahedral void) = 4

X : Y = 4 : 4

XY

SA-(I) Type Question (2 Marks)

Q.20. Define F-centres and how it is formed in lattice of crystal ?

Q.21. What type of stoichiometric defect is shown by

(a) ZnS

(b) AgBr

Q.22. What are the differences between Frenkel and Schottky defect ?

Q.23. Define the following terms with suitable examples :

(a) Ferromagnetism

(b) Paramagnetism

(c) Ferrimagnetism

(d) 12-16 and 13-15 group compounds

Q.24. In terms of band theory, what is the difference :

(a) between conductor and an insulator ?

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

Q.25. Explain how electrical neutrality is maintained in compounds showing Frenkel and Schottky defect.

Ans. In compound showing Frenkel defect, ions just get displaced within the lattice, while in compounds showing Schottky defect, equal number of anions and cations are removed from the lattice. Thus, electrical neutrality is maintained in both cases.

Q.26. Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.

Ans. 8 corner × 1/8 atom per unit cell = 1 atom

There are four body diagonals in a cubic unit cell and each has two body centre atoms.

So, 4 × 2 = 8 atoms therefore, total number of atoms per unit cell = 1 + 8 = 9.

Q.27. Gold crystallizes in an FCC unit cell. What is the edge length of unit cell (r = 0.144 mm) ?

Ans.

$$r = 0.144 \text{ nm}$$

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

$$= 2 \times 1.414 \times 0.144 \text{ nm}$$

$$= 0.407 \text{ nm}$$

Q.28. Classify each of the following as either a p-type or n-type semi-conductor :

(a) Ge doped with In

(b) B doped with Si

Ans. *Hint :* (a) Ge is group 14 element and In is group 13 element. Therefore, an electron deficit hole is created. Thus semi-conductor is p-type.

(b) Since B is group 13 element and Si is group 14 element, there will be a free electron, thus, it is n-type semi-conductor.

Q.29. In terms of band theory, what is the difference between a conductor, an insulator and a semi-conductor ?

Ans. The energy gap between the valence band and conduction band in an insulator is very large while in a conductor, the energy gap is very small or there is overlapping between valence band and conduction band.

Q.30. $CaCl_2$ will introduce Schottky defect if added to AgCl crystal. Explain.

Ans. Two Ag^+ ions will be replaced by one Ca^{2+} ion to maintain electrical neutrality. Thus, a hole is created at the lattice site for every Ca^{2+} ion introduced.

Q.31. The electrical conductivity of a metal decreases with rise in temperature while that of a semi-conductor increases. Explain.

Ans. In metals with increase of temperature, the kernels start vibrating at faster rate and thus offer resistance to the flow of electrons. Hence, conductivity decreases. In case of semi-conductors, with increase of temperature, more electrons can shift from valence band to conduction band. Hence conductivity increases.

Q.32. What type of substances would make better permanent magnets – ferromagnetic or ferromagnetic ? Why ?

Ans. Ferromagnetic substances make better permanent magnets. This is because the metal ions of a ferromagnetic substance are grouped into small regions called domains. Each domain acts as tiny magnet and get oriented in the direction of magnetic field in which it is placed. This persists even in the absence of magnetic field.

Q.33. In a crystalline solid, the atoms A and B are arranged as follows :

(a) Atoms A are arranged in ccp array.

(b) Atoms B occupy all the octahedral voids and half of the tetrahedral voids.

What is the formula of the compound ?

Ans. No. of A (ccp) = 4

$$\text{No. of B} = \text{octahedral voids} + \frac{\text{Tetrahedral}}{2}$$

$= 4 + \frac{8}{2}$

$= 8$

A : B therefore, formula of the compound is AB_2

4 : 8

1 : 2

AB_2

Q.34. In compound atoms of element Y forms ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. What is the formula of the compound ?

Ans. No. of Y atoms per unit cell in ccp lattice = 4

No. of tetrahedral voids = 2 × 4 = 8

No. of tetrahedral voids occupied by X = 2/3 × 8 = 16/3

Therefore, Formula of the compound = $X_{16/3}Y_4$

$= X_{16}Y_{12}$

$= X_4Y_3$

Q.35. How many lattice points are there in one unit cell of the following lattices :

(a) FCC (b) BCC (c) SCC

Q.36. A cubic solid is made of two elements X and Y. Atom Y are at the corners of the cube and X at the body centres. What is the formula of the compound ?

Ans. [Hint : XY]

Q.37. Silver forms ccp lattice and X-ray studies of its crystal show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (Atomic wt. = 107.9u).

Ans. [Hint : PQ, 8 and 9]

Q.38. A cubic solid is made up of two elements P and Q. Atoms of the Q are present at the corners of the cube and atoms of P at the body centre. What is the formula of the compound ? What are the co-ordination number of P and Q ?

Ans. [Hint : PQ, 8]

Q.39. What happens when :

(a) CsCl crystal is heated. (Hint : Changes to NaCl type crystal)

(b) Pressure is applied on NaCl crystal. (Hint : Changes to CsCl type crystal)

SA-(II) Question (3 marks)

Q.40. The density of chromium is 7.2 g cm^{-3}. If the unit cell is a cubic with length of 289 pm, determine the type of unit cell. (Atomic mass of Cr = 52 *u* and N_A = 6.022 × 10^{23} atoms mol^{-1}).

Ans. $$d = \frac{ZM}{a^3 \times N_A}$$

Here, $Z = ?$, $a = 289$ pm $= 289 \times 10^{-10}$, M = 52 g mol^{-1}, $d = 7.2$ g cm^{-3}

So, $$Z = \frac{d \times a^3 \times N_A}{M}$$

$$Z = \frac{7.2 \text{ g cm} \times \left(289 \times 10^{-10} \text{ cm}\right)^3 \times 6.022 \times 10^{23} \text{ atom mol}^{-1}}{52 \text{ g mol}^{-1}} = 2.01 \approx 2$$

Hence type of unit cell in BCC.

Q.41. An element crystallizes in FCC structure; 200 g of this element has 4.12×10^{24} atoms. If the density of A is 7.2 g cm^{-3}, calculate the edge length of unit cell.

Q.42. Niobium crystallizes in bcc structure. If its density is 8.55 cm^{-3}, calculate its atomic radius. (Atomic mass of Niobium = 92.9 *u*, $N_A = 6.022 \times 10^{23}$ atoms mol^{-1})

Q.43. Non-stoichiometric cuprous oxide 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 the substance is a p-type semiconductor ?

Q.44. The unit cell of an element of atomic mass 50 *u* has edge length 290 pm. Calculate its density. The element has bcc structure. ($N_A = 6.022 \times 10^{23}$ atoms mol^{-1})

Q.45. Calculate the density of silver which crystallizes in face centred form. The distance between nearest metal atoms is 287 pm. (Ag = 107.87 g mol^{-1}, $N_A = 6.022 \times 10^{23}$ atoms mol^{-1})

Q.46. What is the distance between Na^+ and Cl^- ions in NaCl crystal if its density is 2.165 gm cm^{-3}. NaCl crystallizes in FCC lattice.

Q.47. Analysis shows that Nickel oxide has $Ni_{0.98}O_{1.00}$. What fractions of nickel exist as Ni^{2+} ions and Ni^{3+} ions ?

Q.48. Find the type of lattice for cube having edge length of 400 pm. Atomic weight = 60g mol^{-1} and density = 6.25 g/cc.

Q.49. Aluminium crystallizes in cubic closed pack structure. Its metallic radius is 125 pm.

(a) What is the length of the side of the unit cell ?

(b) How many unit cell are there in 100 cm^3 of Aluminium ?

Q.50. Classify the following as either p-type or n-type semiconductors :

(a) Ge doped with In

(b) B doped with Si

Q.51. Zinc oxide is white but it turns yellow on heating. Explain.

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q.52. A metal has cubic lattice. It is face centered cubic lattice. Edge length of lattice cell is 2 Å. The density of metal is 2.4 g cm^{-3}. How many unit cells are present in 200 g of metal ?

Q.53. A metal crystallizes as face centered cubic lattice with edge length of 450 pm. Molar mass of metal is 50 g mol^{-1}. What is the density of metal ?

Q.54. A compound forms hexagonal close packed structure. What is the total number of voids in 0.5 mol of it ? How many of these are tetrahedral voids ?

Q.55. Copper crystallizes into FCC lattice with edge length 3.61×10^{-8} cm. Show that calculated density is in arrangement with measured value of 8.92 g/cc.

Q.56. Niobium crystallizes in bcc structure with density 8.55 g/cc. Calculate atomic radius using atomic mass *i.e.,* 93 *u*.

Q.57. The compound CuCl has FCC structure like ZnS. Its density is 3.4 g cm^{-3}. What is the length of the edge of unit cell ?

Hint : $d = \dfrac{ZM}{a^3 \times N_A}$

$$a^3 = \frac{4 \times 99}{3.4 \times 6.022 \times 10^{-23}}$$

$a^3 = 193.4 \times 10^{-24}$ cm^3

$a = 5.78 \times 10^{-8}$ cm

Q.58. If NaCl is doped with 10^{-3} mol% $SrCl_2$. What is the concentration of cation valancies ?

Q.59. If the radius of the octahedral void is *r* and the radius of the atom in the close packing is R, derive relationship between *r* and R.

Q.60. The edge length of the unit cell of metal having molecular weight 75 g/mol is A° which crystallizes into cubic lattice. If the density is 2 g/cm^3, then find the radius of metal atom. ($N_A = 6.022 \times 10^{23}$ mol^{-1})

Q.61. The density of KBr is 2.75 g cm^{-3}. The length of edge of the unit cell is 654 pm. Predict the type of cubic lattice to which unit cell of KBr belongs. ($N_A = 6.022 \times 10^{23}$ mol^{-1}, Atomic mass of K = 39 g mol^{-1}, Br = 80g mol^{-1})

Hint : Calculate the value of z = 4 so it has fcc lattice.

Q.62. CsCl has bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance of CsCl.

Ans. 34604 pm

Q.63. The radius of an iron atom is 1.42 Å. It has rock salt structure. Calculate the density of unit cell.

Ans. 5.74 g cm^{-3}

Q.64. What is the distance between Na^+ and Cl^- in a NaCl crystal if its density is 2.165 g cm^{-3} ? NaCl crystallizes in fcc lattice.

Ans. 281 pm

Q.65. Copper crystallizes with fcc unit cell. If the radius of copper atom is 127.8 pm, calculate the density of copper metal. Atomic mass of Cu = 63.55u, $N_A = 6.022 \times 10^{23}$.

Ans. $a = 2\sqrt{2}r$, $a^3 = 4.723 \times 10^{-23}$, $d = 8.95$ g cm^{-3}

Q.66. The density of lead is 11.35 g/cm^3 and the metal crystallizes with fcc unit cell. Estimate the radius of lead atom. (Atomic mass of Pb = 207 g/mol, $N_A = 6.02 \times 10^{23}$)

Ans. 174.95 pm

Q.67. Explain the following with suitable examples :

(a) Ferromagnetic substances

(b) 12-16 group compounds

(c) Paramagnetism

(d) Impurity defects

(e) Diamagnetism

Q.68. The well-known mineral fluonte is chemically calcium fluoride. In one unit of this mineral, there are $4Ca^{2+}$ and BF^- ions arranged in fcc lattice. The F^- ions fill all the tetrahedral void in the fcc lattice. The edge of the unit cell is 5.46×10^{-8} cm. The density of the solid is 3.18 g/cm^3. Calculate Avogadro's number. (Molar mass of CaF_2 = 78.08 g/mol)

Ans. 6.03×10^{23} mol^{-1}

Q.69. Metallic magnetism has a hexagonal close-packed structure and its density is 1.74 g/cm^3. Assuming magnetism atoms to be spherical, calculate the radius of magnetism atom. (Mg = 24.3 amu)

Ans. 1.6×10^{-8} cm

VALUE BASED QUESTIONS (4 Marks)

Q.70. Radha suggested that the conductivity of the semiconductors can be increased by heating. Her friend Mira advised her to dope the semiconductor with either group 13 or group 15 elements to increase the conductivity.

(a) Explain the cause of increase in conductivity by doping.

(b) Which type of semiconductor is formed if it is doped with group 13 or group 15 elements ?

(c) What are intrinsic semiconductors ?

(d) What values are associated with the suggestion of Mira ?

Q.71. Students of class XII Chemistry wanted to prepare magnets. They have substances like iron, cobalt, nickel, CrO_2 and MnO. Kapil tried best to prepare the magnets from MnO but attempt failed. Veena suggested that except MnO, all the above mentioned substances can be used to prepare magnets.

(a) Why did Kapil fail to prepare magnet from MnO ?

(b) What values are associated with the suggestion of Veena ?

(c) Define antiferromagnetism.

(d) How can a ferromagnetic substance be made a permament magnet ?

Q.72. Vinay and Manish are provided with 50 oranges each with a tray. They are asked to arrange them in an ordered manner within 5 minutes. Vinay successfully arranged the oranges with minimum empty space but Manish does not.

(a) What type of crystal packing had Vinay attempted ?

(b) What is the % empty space that remains in such type of arrangement of oranges ?

(c) Name the values associated with the Vinay's attempt for arranging oranges.

(d) How many tetrahedral and octahedral voids are formed in the packing of 50 oranges ?