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Class: 12
Subject: Chemistry
Topic: Solid state
No. of Questions: 28

1. How can you convert NaCl structure into CsCl structure and vice-versa?

Sol. NaCl structure can be converted into CsCl structure by application of pressure while reverse can be done by heating to 760 K.

2. AgI crystallizes in cubic close packed ZnS structure. What fraction of tetrahedral sites are occupied by Ag^+ ions?

Sol. In the face-centred unit cell, there are eight tetrahedral voids, of these, half are occupied by silver cations.

3. What is Frenkel defect?

Sol. When some ions (usually cations) are missing from the lattice sites and occupy the interstitial sites so that electrical neutrality as well as stoichiometry is maintained, it is called Frenkel defect.

4. What type of crystal defect is produced when sodium chloride is doped with $MgCl_2$?

Sol. It is called impurity defect. A cations vacancy is produced. A substitutional solid solution is formed (because $2Na^+$ ions are replaced by one Mg^{++} ion). This defect is also known as metal deficiency defect.

5. A compound AB_2 possesses the CaF_2 type crystal structure. Write the co-ordination number of A^{++} and B^- ions in its crystals.

Sol. Co-ordination number of A = 8
Co-ordination number of B = 4

6. A solid between A and B has the following arrangement of atoms
(i) Atoms A are arranged in ccp array
(ii) Atoms B occupy all the octahedral voids and half the tetrahedral voids. What is the formula of the compound?

Sol. In a close packing, the number of octahedral voids is equal to the number of atoms and the number of tetrahedral voids is twice the number of atoms
Since all the octahedral voids and half the tetrahedral voids are filled there will be one atom of B in tetrahedral void and one atom in octahedral void corresponding to each A. Thus, there will be two atoms of B corresponding to each A.
Hence, formula of the solid is AB_2

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7. In corundum, oxide ions are arranged in hcp array and the aluminium ions occupy two thirds of octahedral voids. What is the formula of corundum?

Sol. In ccp or hcp packing there is one octahedral void corresponding to each atom constituting the close packing. In corundum only 2/3rd of the octahedral voids are occupied. It means corresponding to each oxide are 2/3 aluminium ions. The whole number ratio of oxide and aluminium ion in corundum is therefore 3:2 Hence formula of corundum is Al_2O_3

8. Calculate the ratio of the alkali metal bromides on the basis of the data given below and predict the form of the crystal structure in each case. Ionic radii (in pm) are given below

$Li^+ = 74$, $Na^+ = 102$, $K^+ = 138$

$Rb^+ = 148$, $Cs^+ = 170$, $Br^- = 195$

Sol. The ratio of cation to that of anion i.e. $\frac{r^+}{r^-}$ gives the clue for crystal structure

$\frac{Li^+}{Br^-} = \frac{74}{195} = 0.379$ (tetrahedral)

$\frac{Na^+}{Br^-} = \frac{102}{195} = 0.523$ (octahedral)

$\frac{K^+}{Br^-} = \frac{138}{195} = 0.708$ (octahedral)

$\frac{Rb^+}{Br^-} = \frac{148}{195} = 0.759$ (Body centered)

$\frac{Cs^+}{Br^-} = \frac{170}{195} = 0.872$ (Body centered)

9. In the close packed cation in an AB type solid have a radius of 75 pm, what would be the maximum and minimum sizes of the anions filling the voids?

Sol. For close packed AB type solid

$\frac{r^+}{r^-} = 0.414 - 0.732$

$\therefore$ Minimum value of $r^- = \frac{r^+}{0.732} = \frac{75}{0.732} = 102.5 \text{ pm}$

Maximum value $r^- = \frac{r^+}{0.414} = \frac{75}{0.414} = 181.2 \text{ pm}$

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10. NH_4Cl crystallizes in a body centered cubic lattice, with a unit cell distance of 387 pm. Calculate (a) the distance between the oppositely charged ions in the lattice, and (b) the radius of the NH_4^+ ion if the radius of the Cl^- ion is 181 pm.

Sol. (a) In a body centered cubic lattice oppositely charged ions touch each other along the cross - diagonal of the cube. Hence, we can write,

$$2r^+ + 2r^- = \sqrt{3}a, \quad r^+ + r^- = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3}}{2}(387\,pm) = 335.15\,pm$$

(b) Now, since $r^- = 181pm$,

we have $r^+ = (335.15 - 181)pm = 154.14pm.$

11. Copper has the fcc crystal structure. Assuming an atomic radius of 130pm for copper atom (Cu = 63.54):

(a) What is the length of unit cell of Cu?
(b) What is the volume of the unit cell?
(c) How many atoms belong to the unit cell?
(d) Find the density of Cu.

Sol. As we know

$$\rho = \frac{n \times M_m}{N_A \times a^3},$$

(a) for fcc structure

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

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

$= 2\sqrt{2} \times 130$ pm = 367.64 pm

(b) volume of unit cell = $a^3 = \left(367.64 \times 10^{-10} cm\right)^3$

$= 4.968 \times 10^{-23}\ cm^3$

(c) n = 4

(d) $\rho = \dfrac{4 \times 63.54}{6.023 \times 10^{23} \times (3.67 \times 10^{-8} cm^3)^3} = 8.54\ gm / cm^3$

12. The density of CaO is 3.35 gm/cm^3. The oxide crystallises in one of the cubic systems with an edge length of 4.80 Å. How many Ca^{++} ions and O^{-2} ions belong to each unit cell, and which type of cubic system is present?

Sol. From equation

ρ(density) = 3.35 gm/cm^3

a = 4.80 Å

M_m of CaO = (40 + 16) gm = 56 gm CaO

$\because \rho = \dfrac{n \times M_m}{a^3 \times N_A}$ where n = no. of molecules per unit cell

$\therefore n = \dfrac{3.35 \times (4.8 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{56} = 3.98$

or $n \approx 4$

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So, 4-molecules of CaO are present in 1 unit cell
So, no. of Ca^{++} ion = 4
No. of O^{--} ion = 4
So, cubic system is fcc type.

13. A metal crystallizes into two cubic system-face centred cubic (fcc) and body centred cubic (bcc) whose unit cell lengths are 3.5 and 3.0Å respectively. Calculate the ratio of densities of fcc and bcc.

Sol. fcc unit cell length = 3.5Å
bcc unit cell length = 3.0Å

$$\text{Density in fcc} = \frac{n_1 \times \text{atomic weight}}{V_1 \times \text{Avogadro number}}$$

$$\text{Density in bcc} = \frac{n_2 \times \text{atomic weight}}{V_2 \times \text{Avogardro number}}$$

$$\frac{D_{fcc}}{D_{bcc}} = \frac{n_1}{n_2} \times \frac{V_2}{V_1}$$

n_1 for fcc = 4; Also $V_1 = a^3 = (3.5 \times 10^{-8})^3$
n_2 for bcc = 2; Also $V_2 = a^3 = (3.0 \times 10^{-8})^3$

$$\frac{D_{fcc}}{D_{bcc}} = \frac{4 \times (3 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3} = 1.259$$

14. Copper crystal has a face centred cubic structure. Atomic radius of copper atom is 128 pm. What is the density of copper metal? Atomic mass of copper is 63.5.

Sol. In face centred cubic arrangement face diagonal is four times the radius of atoms face diagonal = 4×128 = 512 pm

$$\text{Face diagonal} = \sqrt{2} \times \text{edge lengh}$$

$$\text{Edge length} = \frac{512}{\sqrt{2}} = 362 \text{ pm} = 362 \times 10^{-10} \text{ cm}$$

Volume of the unit cell = $(362 \times 10^{-10})^3$ cm^3 = 47.4×10^{-24} cm^3
In a face centred cubic unit cell, there are four atoms per unit cell

$$\text{Mass of unit cell} = \frac{4 \times 63.5}{6.023 \times 10^{23}} g = 4.22 \times 10^{-22} g$$

$$\text{Density} = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{4.22 \times 10^{-22}}{47.4 \times 10^{-24}} = 8.9 \text{ gcm}^{-3}$$

15. The first order reflections of a beam of X – rays of wavelength of 1.54A° from the (100) face of a crystal of the simple cubic type occurs at an angle 11.29°. Calculate the length of the unit cell.

Sol. Applying Bragg's equation
$2 d \sin\theta = n\lambda$
Given $\theta = 11.29°$, $\lambda = 1.54A° = 1.54 \times 10^{-8}$ cm

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n = 1

$$d = \frac{1.54\times10^{-8}}{2\times \text{Sin}11.29^\circ} = \frac{1.54\times10^{-8}}{2\times0.1957} = 3.93\times10^{-8}\text{cm}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} = a$$

a = 3.93×10^{-8} cm (length of the unit cell)

16 In a crystalline solid, having formula AB_2O_4, oxide ions are arranged in cubic close packed lattice while cations A are present in tetrahedral voids and cations B are present in octahedral voids

(i) What percentage of the tetrahedral voids is occupied by A?

(ii) What percentage of the octahedral voids is occupied by B?

Sol: In a cubic close packed lattice of oxide ions there would be two tetrahedral voids and one octahedral void for each oxide ion.

$\therefore$ For four oxide ions there would be 8 tetrahedral and four octahedral voids two are occupied by B.

Percentage of tetrahedral voids occupied by A = $\frac{1}{8}\times100 = 12.5\%$

Percentage of tetrahedral voids occupied by B = $\frac{2}{4}\times100 = 50\%$

17. In a solid, oxide ions are arranged in ccp. Cations A occupy one – sixth of the tetrahedral voids and cations B occupy one third of the octahedral voids. What is the formula of the compound?

Sol: In ccp with each oxide there would be 2 tetrahedral voids and one octahedral voids. 1/3rd octahedral voids are occupied by B and 1/6th tetrahedral void by A. Therefore the compound can be

$A_{2/6}B_{1/3}O$ or ABO_3

18 Br^- ion forms a close packed structure. If the radius of Br^- ions is 195 pm. Calculate the radius of the cation that just fits into the tetrahedral hole. Can a cation A^+ having a radius of 82 pm be slipped into the octahedral hole of the crystal A^+Br^-?

Sol: (i) Radius of the cations just filling into the tetrahedral hole
= Radius of the tetrahedral hole = 0.225×195
= 43.875 pm

(ii) For cation A^+ with radius = 82 pm

Radius ratio $\frac{r^+}{r^-} = \frac{82}{195} = 0.4205$

As it lies in the range 0.414 – 0.732, hence the cation A^+ can be slipped into the octahedral hole of the crystal A^+Br^-.

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19 CsCl has bcc structure with Cs^+ at the centre and Cl^- ion at each corner. If r_{Cs^+} = 1.69Å and r_{Cl^-} = 1.81Å, what is the edge length "a" of the cube?

(A) 3.50Å (B) 3.80Å
(C) 4.04Å (D) 4.50Å

Sol: (C) Assuming the closest approach between Cs^+ and Cl^- ions, the internuclear separation is one–half of the cubic diagonal i.e.

$$1.69 + 1.81 = 3.50 = \frac{a\sqrt{3}}{2}$$

$$\therefore a = \frac{2 \times 3.5}{\sqrt{3}} = 4.04\text{Å}$$

20 A substance has density of 2 kg dm^{-3} & it crystallizes to fcc lattice with edge-length equal to 700pm, then the molar mass of the substance is

(A) 74.50gm mol^{-1} (B) 103.30gm mol^{-1}
(C) 56.02gm mol^{-1} (D) 65.36gm mol^{-1}

Sol: (B) $\rho = \frac{n \times M_m}{N_A \times a^3}$

$$2 = \frac{4 \times M_m}{6.023 \times 10^{23} \times (7 \times 10^{-8})^3}$$

(since, effective number of atoms in unit cell = 4)
On solving we get M_m = 103.03 gm / mol

21 The electrical conductivity of a metal decreases with rise in temperature while that of a semiconductor increases. Explain.

Sol: In metals with increase of temperature, the kernels start vibrating 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.

22 What type of substance would make better permanent magnets, ferromagnetic or ferrimagnetic, why?

Sol: 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.

23 In terms of band theory what is the difference between a conductor, an insulator and a semiconductor?

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Sol: 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.

Q24. 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?

Sol. 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 = $X_{16/3}\ Y_4$
$=X_{16}\ Y_{12}$
$=X_4Y_3$

Q25. $CaCl_2$ will introduce Schottky defect if added to AgCl crystal. Explain

Sol. 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.

Q26.. Classify each of the following as either a p-type semi-conductor or an n-type semiconductor:

A) Ge doped with In
B) B doped with Si

A. Ge is group 14 elements and In is group 13 element. Therefore, an electron deficit hole is created. Thus semi-conductor is p-type.
B. Since B group belong to group 13 element and Si is group 14 elements, there will be a free electron, thus is n-type semi-conductor.

Q27. Gold crystallizes in an FCC unit Cell. What is the length of a side of the cell (r=0.144mm)

Sol: R=0.144nm
A=2*√2r
=2*1.414*0.44nm
=0.407nm

Q28. Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.

Sol: 8 corner *1/8 atom per unit cell = 1atom
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

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