HINTS & SOLUTIONS

TOPIC : GASEOUS STATE
EXERCISE # 1

Section (A)

1. Intermolecular force are strong.

5. Due to rapid or suddenly cooling of the liquid generate the amorphous solid.
Rubber, Glass, Plastic, starch etc. are examples of amorphous solids.

7. For Tetraagonal crystal system
Features is $a = b \neq c$
$\alpha = \beta = \gamma = 90^o$

8. Refer Theory.

9. Number of Bravais lattice in 2 dimensions are :

11. KCl & $BaCl_2.2H_2O$ are ionic solids and not pseudo solids (amorphous solids).

12. For hexagonal unit cell $\Rightarrow a = b \neq c$; $\alpha = \beta = 90^o$; $\gamma = 120^o$.

Section (B)

8. Density of $P_0 = \frac{1 \times 207}{(3)^3} = \frac{23}{3}$ Amu / $Å^3$

Section (C)

6. P.F. of ABAB arrangement in 3D = 74%.
% of vacant space = 26% = 0.26.

Section (D)

1. In a face centered cubic unit cell has 8 corners i.e.,
(i) Contribution from one corner lattice point = $\frac{1}{8}$ th.
(ii) Contribution from one face centered lattice point = 1/2.

2. Nearest distance between two atoms = $\frac{a}{\sqrt{2}} = \frac{508}{\sqrt{2}}$ = 360 pm

6. for X, $8 \times \frac{1}{8} = 1$ $\Rightarrow$ for Y, $6 \times \frac{1}{2}$ So, AB_3

12. The arrangement of sphere is shown by body diagonal plane.

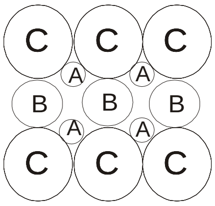
13. $4r = a\sqrt{2}$ $\Rightarrow$ $a = \frac{4r}{\sqrt{2}} = \frac{4 \times 1.28}{\sqrt{2}}$ Å = 3.62 Å

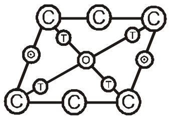
14. In <u>ABB</u> <u>AABB</u> A, there is no close packing as there are repeated planes adjacent to each other.

Section (E)

3. No. of octahedral holes = No. of close packed atoms

& No. of Tetrahedral holes = 2× No. of close packed atoms.

9. 



⊚ → Octahedral void, at edge center & body center.

Ⓣ → Tetrahedral voids on body diagonal.

Section (F)

2.✍ 2(Na^+ + Cl^-) = edge length
2a = edge length

6.✍ It is a fact.

7.✍ In rock salt structure, Cl^- forms fcc (ccp) lattice & Na^+ occupies octahedral voids, So tetrahedral voids are vacant.

8.✍ Coordination number of Zn^{2+} ion in Zinc blende = 4.
Zn^{2+} ion present in half of tetrahedral void formed by S^{2-} in fcc unit cells.

9. $SrCl_2$ is AB_2 type in which cation is of large size.

10. A → $\frac{1}{8}$ × 8 = 1 , B → 4 × $\frac{1}{2}$ = 2 and O^{2-} = 4 so formula of spinal = AB_2O_4

11. Only two tetrahedral holes are occupied in diamond.

Section (G)

1. Equal no. of Na^+ & Cl^- are missing completely ⇒ Schottky defect.

7.✍ Since Ag^+ (cation) is smaller than Cl^- (anion) & hence cation is present in voids.
In CaF_2 , F^-_{anion} is smaller.

EXERCISE # 2

2. Iodine crystal are molecular solid. I_2 is non-polar and having dispersion force.

5. Wax is an example of molecular crystal.

9.✍ density = $\frac{Z \times M}{N_A \times a^3} = \frac{2 \times 100}{6 \times 10^{23} \times (400 \times 10^{-10})^3}$ = 5.2 g/cm³

10. d = $\frac{ZM}{N_A a^3}$ = 2 × $\frac{100}{6.02 \times 10^{23}}$ × $\frac{1}{(4 \times 10^{-8})^3}$ = 5.188 g/cc.

11. $\sqrt{3}$ a = 4r
a = $\frac{4 \times 75 \ \text{pm}}{\sqrt{3}}$ = $\frac{4 \times 75 \ \text{pm}}{1.73}$ = 173.2 pm

12. 8 – 2 = 6

20.✍ $\sqrt{2}$a = 4r
a = $\frac{4R}{1.41}$ = $\frac{4 \times 500}{1.414}$ =1414 Pm

25. It is a octahedral void.

27. 100% octahedral voids are occupied.

32. In cubic close packing no. of tetrahedral void = 2 × no of atom. As there are 4 S^{2-} ions at lattice point and they need 4 Zn^{+2}, which adjusted in alternate tetrahedral void ($0.225 < \frac{r^+}{r^-} < 0.414$).

33. No. of M atoms = $\frac{1}{4} \times 4 + 1 = 1 + 1 = 2$

No. of X atoms = $\frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 3 + 1 = 4$ So, formula = $M_2X_4 = MX_2$

EXERCISE # 3

PART - I

1. A atoms are present at the corners of a cube. So, the number of A stoms per unit cell = $8 \times \frac{1}{8} = 1$.

Similarly, B atoms are present at face centres of a cube.

So, the number of B atoms per unit cell = $6 \times \frac{1}{2} = 3$.

2. HCP is a closed packed arrangement, in which the unit cell is hexagonal and coordination number is 12.

3. In unit cell, X-atoms at the corners = $\frac{1}{8} \times 8 = 1$

Y-atoms at the face centres = $\frac{1}{2} \times 6 = 3$

Ratio of X and Y = 1 : 3

Hence, formula is XY_3.

4. In a face centred cubic lattice, a unit cell is shared equally by six unit cells.

5. Density of CsBr = $\frac{Z \times M}{a^3 \times N_0}$

Z = 1(because 1 formula unit is presence)

M = molar mass of CsBr = 133 + 80 = 213

a = edge length of unit cell = 436.6 pm = 436.6×10^{-10} cm

$\therefore$ Density = $\frac{1 \times 213}{(436.6 \times 10^{-10})^3 \times 6.02 \times 10^{23}} = 4.25\ g/cm^3$

6. The appearance of colour in solid alkali metal halides is generally due to F-centres.

7. For simple cubic Radius (r) = $\frac{a}{2}$

Volume of the atom $\frac{4}{3} = \pi\left(\frac{a}{2}\right)^3$

Packing fraction = $\frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6}$

8. In NaCl (Na^+) is doped with 10^{-4} mol % of $SrCl_2$ (Sr^{2+}), 2 Na^+ ion doped by Sr^{2+}, $N_A = 6.02 \times 10^{23}$

The concentration of cation vacancies = $6.02 \times 10^{23} \times 10^{-8} = 6.02 \times 10^{15}$ mol^{-1}

9. Volume of atoms in a unit cell (ν) = $\frac{4}{3}\pi r^3$

For primitive cell, r = $\frac{a}{2}$

$$\nu = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$$

Volume of the unit cell (V) = a^3

Thus, total volume occupied by the atom = $\frac{\text{Volume of the atoms in unit cell}}{\text{Volume of unit cell}}$

$= \frac{\pi a^3}{6} \times \frac{1}{a^3} = \frac{\pi}{6} = 0.52$ Hence. Statement (1) is incorrect.

10. If a = edge length of cubic systems then, for simple cubic structure, radius = $\frac{a}{2}$

For body centred cubic structure, radius = $\frac{\sqrt{3}}{4}$ a

For face centred cubic structure, radius = $\frac{a}{2\sqrt{2}}$

Hence, the ratio of radii = $\frac{1}{2}$ a : $\frac{\sqrt{3}}{4}$ a : $\frac{1}{2\sqrt{2}}$ a.

11. In bcc unit cell, the number of atoms = 2

Thus, volume of atoms in unit cell (ν) = $2 \times \frac{4}{3}\pi r^3$

For bcc structure (r) = $\frac{\sqrt{3}}{4}a$

$$(\nu) = 2 \times \frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3 = \frac{\sqrt{3}}{8}\pi r^3$$

Volume of unit cell (V) = a^3

Percentage of volume occupied by unit cell = $\frac{\frac{\sqrt{3}}{8}\pi a^3}{a^3} \times 100 = \frac{\sqrt{3}}{8}\pi \times 100 = 68\%$

Hence, the free space in bcc unit cell = 100 – 68 = 32%

12. In case of face-centre cubic lattice, radius = $\frac{\sqrt{2}a}{4}$

∴ Radius of copper atom (fcc lattice) = $\frac{\sqrt{2}\times 361}{4}$ = 128 pm.

13. In case of body centred cubic (bcc) crystal, a $\sqrt{3}$ = 4r

Hence, atomic radius of lithium, r = $\frac{a\sqrt{3}}{4}$ = $\frac{351\times 1.732}{4}$ = 151.98 pm

14. For body centred cubic (bcc) lattice, distance between two oppositely charged ions,

$d = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3}\times 387}{2}$ pm = 335.15 pm

15. Radius ratio of NaCl like crystal = $\frac{r^+}{r^-}$ = 0.414

r^- = $\frac{100}{0.414}$ = 241.5 pm

16. For CCP $\sqrt{2}\ a = 4R$

$\frac{\sqrt{2}\times 408}{2}$ = 2R (2R = Diameter)

Diameter = 288.5

17. Number of octahedral voids in ccp, is equal to effective number of atoms in ccp, effective number of atoms are 4 so, 4 octahedral voids. So, 1 octahedral voids per atom.

18. $A^{2+} = \frac{1}{4} \times 8 = 2$

$B^+ = 4 \times 1 = 4$

$O^{2-} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

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

$2.72 = \frac{4\times M}{6.02\times 10^{23}\times (404\times 10^{-10})^3}$

$M = \frac{2.72\times 6.02\times (404)^3}{4\times 10^7}$ = 26.99 = 27 gm $mole^{-1}$

20. Diamond is like ZnS (Zinc blende)

Carbon forming CCP(FCC) and also occupying half of tetrahedral voids.

Total no. of carbon atoms per unit cell = $8\times\frac{1}{8}$ (Corners) + $6\times\frac{1}{2}$ (FC) + 4 (TV) = 8

21. In FCC unit cell (Z = 4)

4 r = $\sqrt{2}a$

r = $\frac{\sqrt{2}\,a}{4} = \frac{1.414\times 361}{4}$ = 127.25 Pm

22. d = $\frac{ZA}{N_A - a^3}$ for BCC Z = 2

530 kg/m³ $= \dfrac{2 \times 6.94 \times 10^{-3}}{6.02 \times 10^{23} \times a^3}$

$a^3 = 43.50 \times 10^{-30}$

$a = 3.52 \times 10^{-10}$ m = 352 pm.

23. $\dfrac{rA^+}{rB^-} = \dfrac{0.98 \times 10^{-10}}{1.81 \times 10^{-10}} = 0.54$

Octahedral range $0.414 \le \dfrac{r+}{r-} < 0.732$

Co-ordination no. of each ion is 6 like NaCl structure.

24. Ca^{2+} is surrounded by $8F^-$

F^- is surrounded by $4Ca^{+2}$

25. (1) $FeO_{0.98}$ has a non-stoichiometric metal excess defect (Compare this molecule with FeO)

(4) Frenkel defect is favoured in those ionic compounds if there is a large diffrence between sizes of cation and anions.

26. d = $\dfrac{Z \times M}{N_A \times \text{Volume of unit cell}}$ so $\dfrac{d_{bcc}}{d_{fcc}} = \left[\dfrac{Z_{bcc}}{Z_{fcc}} \times \left[\dfrac{a_{fcc}}{a_{bcc}}\right]^3\right]$

$\dfrac{d_{bcc}}{d_{fcc}} = \left[\dfrac{2}{4} \times \left[\dfrac{4R}{\sqrt{2}}\right]^3 \times \left[\dfrac{\sqrt{3}}{4R}\right]^3\right]$ $= \dfrac{d_{bcc}}{d_{fcc}} = \dfrac{3\sqrt{3}}{4\sqrt{2}}$

27. Number of atom per unit cell in hcp = 6
Number of octahedral void in hcp = 6
Number of anions per unit cell = 6

cation occupy 75% of octahedral void = $6 \times \dfrac{75}{100} = \dfrac{9}{2}$

C : A
9/2 : 6
9 : 12
3 : 4

Fomula of compound = C_3A_4

28. $Ni_{0.98}O$ → Ni^{+2}, Ni^{3+} Let Ni^{2+} = x

x (0.98 – x)

from charge Balencing

2x + (0.98 – x)3 – 2 = 0

2x + 2.94 – 3x – 2 = 0

x = 0.94 the fraction of nickel (N_1^{2+}) = $\dfrac{0.94}{0.98}$ = 96

PART - II

1. CaF_2 is an example of AB_2 type solid

$$AB_2 \rightleftharpoons A^{2+} + 2B^-$$

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

Atoms 'A' are arranged in cubic closed packing (ccp). Atom B occupy all the octahedral voids and half tetrahedral voids.

2. Schottky defect defines imperfection in the lattice structure of ionic solids. This defect is created when one positive ion and one negative ions are missing from their respective positions to creat a pair of holes.

Other defects of solids are **Interstitial defect** (due to presence of ions in interstitial spaces) and Frankels defects when only one ion leaves its correct lattice and occupy interstitial space.

4. ABC ABC... arrangment of layers is found in cubic closed pack system (CCP system). In this there are at the corner as well as centre of the unit cell.

$\therefore$ number of atoms per unit cell = $8 \times \frac{1}{8} + 1 = 2$ $\Rightarrow$ number of tetrahedral voids in a unit cell = 2Z.

6. In AgI crystal number of Ag^+ ions is equal to I^- ions. However, the number of tetrahedral voids are twice the number of atoms forming the cubic lattice.

$\therefore$ Number of tetrahedral voids occupied by Ag^+ ion = 50 %

7. Certain ionic solids (for example, AgBr) have both Schottky and Frenkel defects. Only Schottky defects change the density of solids because anions or cations are missing and Frenkel defects have no change in density because they have same number of cations or anions, only change the position of ions.

8. Given, a - 2 r = 53pm .... (i)

For bcc structure,

$4r = \sqrt{3}\,a$ or $2r = \frac{\sqrt{3}}{2}a$ $\Rightarrow a - \frac{\sqrt{3}}{2}a = 53$ $\therefore$ a = 395.6 pm

Density (4) = $\frac{Z\ \ M}{N_a\ \ a}$ $\Rightarrow$ $d = \frac{2 \times 23}{6.023 \times 10^{23} \times (3.956)^3 \times 10^{-24}}$ = 1.23 g/cc.

14. Barium titanate is both piezoelectric as well as ferroelectric.

16. F-center is unpaired e^-

17. **i**t is diamagnetic substance so weakly repel.

PART - III

1. BCC - points are at corners and one in the center of the unit cell.

Number of atoms per unit cell = $8 \times \frac{1}{8} + 1 = 2$.

FCC - Points are at the corners and also center of the six faces of each cell.

Number of atoms per unit cell = $8 \times \frac{1}{8} + 6 \times \frac{1}{2}$ = 4.

2. mass (m) = density × volume = 1.00 g

Mol. wt. (M) of NaCl = 23 + 15.5 = 58.5

Number of unit cells present in a cube shaped crystal of NaCl of

mass 1.00 g = $\frac{\rho \times a^3 \times N_A}{M \times Z} = \frac{m \times N_A}{M \times Z} = \frac{1 \times 6.023 \times 10^{23}}{58.5 \times 4}$

(In NaCl each unit cells has 4 NaCl units. Hence Z = 4)

$\therefore$ Number of unit cells = 0.02573×10^{23} = 2.57×10^{21} unit cells.

3. When an atom or ion is missing from its normal lattice site, a lattice vacancy is created. This defect is known as Schottky defect. Here equal number of Na^+ and Cl^- ions are missing from their regular lattice position in the crystal. So it is Schottky defect.

4. Number of A ions per unit cell = $\frac{1}{8} \times 8 = 1$

Number of B ions per unit cell = $\frac{1}{2} \times 6 = 3$ Empirical formula = AB_3.

5. In case of a face-centerd cubic structure, since four atoms are present in a unit cell, hence volume.

$V = 4\left(\frac{4}{3}\pi r^3\right) = \frac{16}{3}\pi r^3$

6. According to question : Number of Y atom in ccp unit cell = 4

Number of X atom in ccp unit cell = $8 \times \frac{2}{3} = \frac{16}{13}$

Formula of compound = $X_{16/3}Y_4 = X_{16}Y_{12} = X_4Y_3$

7. In fcc unit cell $4r = \sqrt{2}a$ [r = radius of Cu atom, a = edge length]

So $r = \frac{\sqrt{2}a}{4}$ $\Rightarrow$ $r = \frac{\sqrt{2} \times 361}{4}$ = 127 pm.

8. Packing fraction of CCP = $\frac{\pi}{3\sqrt{2}} = 0.74 \Rightarrow 74\%$

$\therefore$ Percentage of free space in CCP = 100 – 74 = 26%

Packing fraction of BCC = $\frac{\pi\sqrt{3}}{8} = 0.68 \Rightarrow 68\%$

$\therefore$ Percentage of free space in BCC = 100 – 68 = 32%

9. $A_{8\times\frac{1}{8}} \quad B_{5\times\frac{1}{2}}$

Formula of compound A_2B_5.

10. For BCC structure $\sqrt{3}\,a = 4r$ $r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 351$ = 152 pm.

11. $M_{0.98}O$

consider one mole of the oxide.

Moles of M = 0.98, Moles of O^{2-} = 1

Let moles of M^{3+} = x $\Rightarrow$ Moles of M^{2+} = 0.98 – x

$\Rightarrow$ Doing charge balance

(0.98 – x) × 2 + 3x – 2 = 0

$\Rightarrow$ 1.96 – 2x + 3x – 2 = 0 $\Rightarrow$ x = 0.04 $\Rightarrow$ % of M^{3+} = $\frac{0.04}{0.98}\times 100$ = 4.08%

12. In CsCl, Cl^- lie at corners of simple cube and Cs^+ at the body centre.

Hence. Along the body diagonal, Cs^+ & Cl^- touch each other so.

$$\frac{\sqrt{3}a}{2} = r_{Cs^+} + r_{Cl^-}$$

13. R = $\frac{\sqrt{3}}{4}$ a = 1.86 Å

14. NCERT based (Solid state).

15. For FCC, $\sqrt{2}a = 4R$

So, 2R = $\frac{a}{\sqrt{2}}$

16. Frenkel Defect.

17. Piezoelectric material are those that produce an electric current when they are placed under mechanical stress

18. d = $\frac{Z\times M}{N_A \times a^3}$ or, d = $\frac{4\times 63.55}{6\times 10^{23}\times (x\times 10^{-8})^3}$ or, d = $\frac{422}{x^3}$ g/ml.

19. Factual

20. B forms HCP $\therefore$ No. of B = 6

A occupies $\frac{1}{3}$ TV $\therefore$ No. of A = $\frac{1}{3}$ ×12 = 4 $\therefore$ Formula = $A_4B_6 = A_2B_3$

21. $\frac{a}{2}$ = R + r

$\sqrt{3}a = 4R$

0.5 a = 0.433 a + r

r = 0.067 a

22. d = $\frac{Z\times M}{N_A \times a^3}$

$$9 \times 10^3 = \frac{4\times \frac{M_0}{6\times 10^{23}}}{(200\times \sqrt{2}\times 10^{-12})^3} \Rightarrow 9 \times 10^3 = \frac{4\times \frac{M_0}{6\times 10^{23}}}{2^3\times 2\times \sqrt{2}\times 10^{-30}}$$

$$M_0 = \frac{9\times 10^3\times 6\times 10^{23}\times 2^4\times \sqrt{2}\times 10^{-30}}{4} = 9 \times 6 \times 10^{-4} \times 4 \times \sqrt{2} = 0.03 \text{ kg}$$