HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

1. **Unit cell :** Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

4. In Bravais lattices, each point has identical surroundings.

5. For rhombohedral system, axial distance and axial angles are $a = b = c,\ \alpha = \beta = \gamma \neq 90^0$

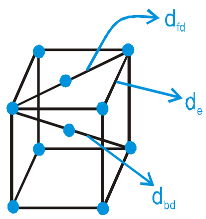
6. Distance between two nearest neighbours in bcc $= \dfrac{\sqrt{3}a}{2}$

$$= \frac{\sqrt{3}\times\sqrt{2}}{2} = \frac{1.732\times\sqrt{2}}{2} = 4.503\ \text{Å}.$$

8. $de = a$

$d_{fd} = \sqrt{2}a$

$d_{bd} = \dfrac{\sqrt{3}a}{2}$ $\quad \therefore\ d_{fd} > d_e > d_{bd}$



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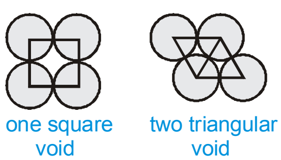
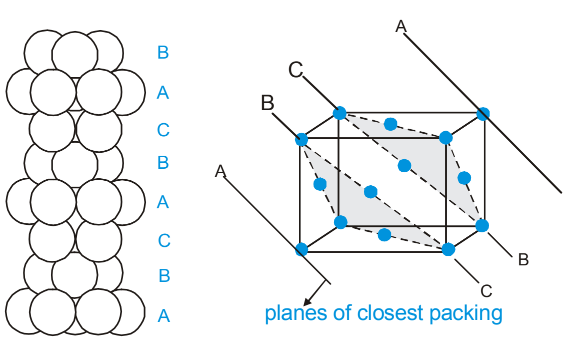


12. In ABB AABB A, there is no close packing as there are repeated planes adjacent to each other.

13. $4r = a\sqrt{2}$

$$a = \frac{4r}{\sqrt{2}} = \frac{4\times 1.28}{\sqrt{2}}\ \text{Å} = 3.62\ \text{Å}$$

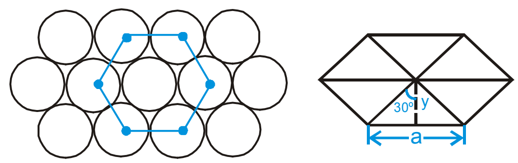
16.



19. No. of tetrahedral voids $= 8 \times \dfrac{1}{8} = 1$

No. of Octahedral voids $= 1\times 1 = 1$ (at body center).

20. **Volume of hexagon :**



$\tan 30^o = \dfrac{a}{2\times y}$ So $y = \dfrac{a\times\sqrt{3}}{2\times 1} = \dfrac{\sqrt{3}}{2}a$ and Area of hexagonal surface $= 6\left[\dfrac{1a}{2}\times\dfrac{\sqrt{3}\,a}{2}\right] = \dfrac{6\sqrt{3}a^2}{4}$

volume of hexagon = area of base × height

$$= \frac{6.\sqrt{3}}{4}\times a^2\times 2\sqrt{\frac{2}{3}}\,a = \frac{6.\sqrt{3}}{4}\times(2r)^2 + 2\sqrt{\frac{2}{3}}\times(2r) = 24\sqrt{2}\,r^3$$

22. No. of A atoms = 6.

No. of C atoms $= 6\times\dfrac{2}{3} = 4$.

$\therefore$ Formula $= C_4A_6$ or C_2A_3.

25. 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.

27. $A \to \dfrac{1}{8}\times 8 = 1,\ B \to 4\times\dfrac{1}{2} = 2$ and $O^{2-} = 4$ so formula of spinal $= AB_2O_4$

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

32. On increasing temp^r C.N. decreases.

$\therefore$ CsCl (8 : 8) structure changes into (6 : 6) NaCl type structure.

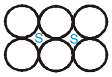
33. Since Ag^+ (cation) is smaller than Cl^- (anion) & hence cation is present in voids.

In CaF_2, F^-_{anion} is smaller.

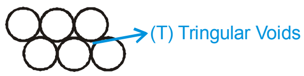
35. p-type semiconductors acquired positive charge because p-type semiconductor have holes due to presence of 13 group elements in 14 group elements.

37. $X = 7x\frac{1}{8} = \frac{7}{8}$; $Y = \frac{1}{2}$ x $6 = 3.$; $Z = \frac{1}{8}.$

$\Rightarrow X_{7/8}Y_3Z_{1/8} = X_7Y_{24}Z$

41. 

2 Square Voids



(4)

43. For (bcc) $= r^+/r^- = 0.732$ and $a = \frac{2(r^+ + r^-)}{\sqrt{3}}$

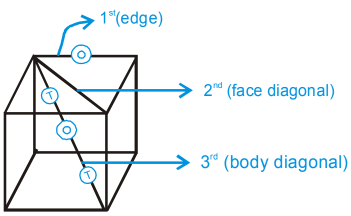
and diameter of cubical void $(2r^+) = a(\sqrt{3} - 1)$
$= 2.888 \times 0.732 = 2.108$ Å.

44. no. of oxide ions = 4

no. of A particles $= \frac{1}{6} \times 8 = \frac{4}{3}$

no. of B particles $= \frac{1}{3} \times 4 = \frac{4}{3}$

so formula is $A_{4/3}B_{4/3}O_4$ or ABO_3.

45. 

47. Cu_4 ↓ Froms c.c.p., z = 4

Ag_3 ↓ $\frac{3}{8}$ th of tetrahedral voids,

Au ↓ $\frac{1}{4}$ of Octahedral voids [∴ No. of O- voids = 4]

[∴ No. of T- voids = 8].

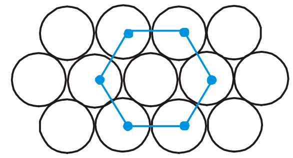
50. Distance between nearest neighbours is along the face diagonal $= \frac{a\sqrt{2}}{2}$.

51. Density $= \frac{Z \times M}{N_A \times a^3} = \frac{4 \times 195}{6.02 \times 10^{23} \times (3.9231 \times 10^{-8})^3}$
$= 21.86\ g/cm^3$

for fcc lattice, $4r = a\sqrt{2}$

so, $r = \frac{a\sqrt{2}}{4} = \frac{3.9231\sqrt{2}}{4}$ Å $= 1.387$ Å.

53. Number of nearest neighbours in hcp pattern in its own layer = 6.



56. It is fluorite (CaF_2) structure. Since formula is AB_2

$\Rightarrow$ No. of B atoms is twice the no. of A atoms. Hence B occupies all the tetrahedral voids (100%).

AB_2 is (8 : 4) compound (Fluorite Structure Compound)
↓ ↓
C.N. of A C.N. of B.

60. $(r_{Rb^+} + r_{Cl^-}) + (r_{K^+} + r_{Br^-}) - (r_{K^+} + r_{Cl^-}) = (r_{Rb^+} + r_{Br^-})$

$3.285 + 3.293 - 3.139 = 3.439.$

63. Some of O^{2-} combine with each other forming O_2 gas which is liberated learning behind electrons at the site vacated by oxide ions.

65. $Na = 1 \times 1 = 1$

$W = 8 \times \frac{1}{8} = 1$ $\Rightarrow NaWO_3$

$O = 12 \times \frac{1}{4} = 3.$

66. Number of F atom in metal fluoride $= \frac{1}{8} \times 8 = 1.$

Number of M atom in metal fluoride $= 1 \times 1 = 1.$

So formula of metal fluoride = MF.

67. $r_+ + r_- = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3} \times 4.3}{2} = 3.72$ Å

68. Coordination number of square packing pattern is 4.

69. for X, $8 \times \frac{1}{8} = 1$; for Y, $6 \times \frac{1}{2} = 3$

so, XY_3

70. No. of X atom per unit cell $= 7 \times \frac{1}{8} = \frac{7}{8}$

No. of Y atom per unit cell $= 6 \times \frac{1}{2} = 3$

∴ Formula $= X_{7/8}Y_3$ or X_7Y_{24}.

71. CsCl compound has bcc arrangement. Cl^- ion forms cubic lattice and Cs^+ ion occupied at body center of unit cell.

72. Density of crystalline CsCl = 3.988 g/cc then,

$d = \frac{d \times M_{CsCl}}{N_A \times (a)^3}$

Volume of unit cell $(a)^3 = \frac{Z \times M_{CsCl}}{N_A \times d}$

$= \frac{1 \times (132.9 + 35.5)}{6.023 \times 10^{23} \times 3.988} = 7.01 \times 10^{-23}\ cm^3$.

73.

Radius ratio	Types of structure	Coordination No.
$r_+/r_- < 0.155$	linear void	2
$0.155 \le r_+/r_- < 0.225$	triangular void	3
$0.225 \le r_+/r_- < 0.414$	tetrahedral void	4
$0.414 \le r_+/r_- < 0.732$	octahedral void	6
$0.732 \le r_+/r_- < 1$	cubical void	8

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

$\therefore\ v = a^3 = 16\sqrt{2}\ r^3 = 16 \times \sqrt{2} \times (2 \times 10^{-8})^3 = 1.8 \times 10^{-22}\ cm^3$

75. When all particle along one body diagonal are removed, these 2 X particles from corner are removed, one Y particle removed & 2 Z particle removed.

Hence new arrangement, X particle $= \frac{1}{8} \times 6 + \frac{1}{2} \times 6 = \frac{15}{4}$

Y particle = 3 ; Z particle = 6

Hence formula $= X_{15/4}Y_3Z_6 = X_{5/4}YZ_2 = X_5Y_4Z_8$

76. In new arrangement, A particles

$= \left(\frac{1}{8} \times 8 + \frac{1}{2} \times 6\right) - \left(\frac{1}{8} \times 4 + \frac{1}{2} \times 2\right) = \frac{5}{2}$

& B particles $= \left(\frac{1}{4} \times 12 + 1\right) - \left(1 + \frac{1}{4} \times 2\right) = \frac{5}{2}$

So, formula is AB.

77. for tetrahedral voids $\frac{r}{R} = 0.225$

$\Rightarrow$ for octahedral voids $\frac{r}{R} = 0.414$

78. $d_{1-2} = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}$; $d_{2-3} = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2} = \frac{a}{\sqrt{2}}$

Hence $d_{1-2} = d_{2-3}$.

79. According to figure, it shows a simple cubic lattice. Now observe the center atom , its has 6 nearest neighbours.

80. Perimeter of plane is $= 2C + 8R = \frac{2 \times 4\sqrt{2}R}{3} + 8R = 6.437\ R$

81. Ionic solid having C.N. = 6 cation in octahedral holes.

Hence, $0.414 < \left(\frac{r+}{r-}\right) < 0.732$.

82. For ZnS $\Rightarrow 4(r_{Zn^{2+}} + r_{S^{2-}}) = \sqrt{3}\ a$.

$a = \frac{4(r_{Zn^{2+}} + r_{S^{2-}})}{\sqrt{3}} \Rightarrow a = 4\frac{(0.83 + 1.74)}{1.732} = 5.93\ Å$.

83. Ferromagnetic substances can be magnetised permanently.

84. Refer NaCl (Rock salt structure).

85. Z = 4, M = 60

60 × 4 gram ———— 6.023×10^{23} unit cells

1 gram ———— $\frac{6.02 \times 10^{23}}{60 \times 4} = 2.5 \times 10^{21}$

86. Total positive charge = Charge on Mg^{2+} + Charge on $Al^{3+} = \frac{1}{8} \times 8 \times 2 + \frac{1}{2} \times 4 \times 3 = 8$ electronic charge.

EXERCISE - 2

Part # I : Multiple Choice

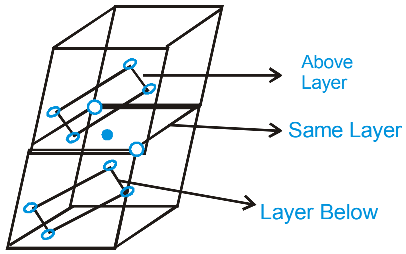
1. Randomness (entropy) in amorphous solids is more than that in crystalline solids.

3. Fcc can be viewed in two following ways -

(i) Planes along the faces (and parallel to it) of the unit cell.

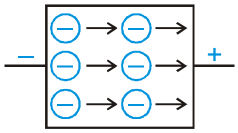
$\Rightarrow$ Each atom touches 4 in same layer, 4 in layer above and 4 in layer bellow it.

(ii) Planes along closest packed spheres $\rightarrow$ each atom touches 6 atom in same layer, 3 in layer above and 3 in layer below it.



5. When silicon is doped with some group-15 element, the some of the positions in the lattice are substituted by atoms of groups -15 elements have five valence electrons. After forming the four covalent bonds with silicon

(or anyother group-14 element such as germanium). One excess electron is left on them.
Since this electron is not involved in bonding it becomes delocalized and contribute to electrical conduction. Silicon doped with group 15 element behaves as a n-type semiconductor.



n-type semiconductor

6. Density = $\dfrac{Z \times M}{N_A \times \text{volume}}$

so, Volume = $\dfrac{4 \times 207}{6.02 \times 10^{23} \times 11.34} = 1.213 \times 10^{-22}\ \text{cm}^3$

$4r = a\sqrt{2}$

$r = \dfrac{4.95 \times 10^{-8} \times \sqrt{2}}{4} = 175\ \text{pm}$

Volume = $a^3 = 1.213 \times 10^{-22}$
so, $a = (1.213 \times 10^{-24})^{1/3}$
$a = 4.95 \times 10^{-8}$ cm.

7. Na^+ & F^- are isoelectronic hence they will have same screening const (s) but not the effective nuclear charge.

and $r_{Na^+} + r_{F^-} = 2.31$ Å and $r_{F^-} = 1.36$Å

$\therefore\ r_{Na^+}/r_{F^-} \approx 0.7$
(coordination = 6, rock salt structure)

8. Schottky defect is only observed in ionic compound.

9. Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic. In ferromagnetic substances all the domains get oriented in the direction of magnetic field and remain as such even after removing magnetic field.

Part # II : Assertion & Reason

1. In HCP structure corner atom contribution is $\left(\dfrac{1}{6}\right)$.

3. Zinc oxide losses oxygen reversible at high temperature and turn yellow.
6. Based on radius ratio.
7. There is both a vacancy and an interstitial ion.
8. In these defects stoichiometry of compound maintained.
9. In schottky defect density decreases while interstitial defect density increases.

EXERCISE - 3

Part # I : Matrix Match Type

1. **(A)** ZnS crystal → Zinc blende → fcc; → Wurtzite → hcp

S^{2-} ion are present in fcc lattice & Zn^{2+} ion occupy all the tetrahedral voids distance of tetrahedral voids

from corner = $\dfrac{\sqrt{3}a}{4}$

(B) CaF_2 → Fluorite structure
Ca^{2+} ion are present in ccp lattice & F^- ion are present in all tetrahedral voids.

(C) NaCl → Rock salt Type structure
Cl^- ion are present in ccp lattice & Na^+ ion occupy all the octahedral voids.

(D) Diamond crystal → C atom present in fcc lattice in which alternate tetrahedral voids are occupied by C atom.

Part # II : Comprehension

Comprehension # 1 :

1. On heating, $ZnO_{(s)}$ dissociates reversibly as

$ZnO \rightleftharpoons Zn^{2+} + \frac{1}{2} O_2 + 2e^-$

Zn^{2+} ions occupy certain interstitial sites whereas the electrons released are present at the neighbouring sites, which act as F-centers.

2. In the crystallization, some Ag^+ ions will get replaced by as many half of Cd^{2+} ions. Thus the cation vacancies will be the same as the number of Cd^{2+} is ions incorporated.

Comprehension # 2 :

2. No. of $X = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$ $\Rightarrow$ 4 XY unit per cell.

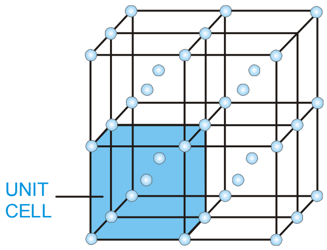
No. of $Y = 1 + 12 \times \frac{1}{4} = 4$

3. At edge center , there is octahedral void in f.c.c. lattice.
$\Rightarrow$ C.N. of Y = 6
(6 : 6) C.N. $\Rightarrow$ NaCl Structure.

EXERCISE - 4
Subjective Type

1. Number of atom effectively present in a cubic unit formed by arrangement of eight B.C.C unit cell

$= 8\times\frac{1}{8}+12\times\frac{1}{4}+6\times\frac{1}{2}+1+8=16.$



2. $n=8\ ,\ p=\frac{11}{21}$

3. Density **(d)** $=2=\frac{2\times M}{(3)^3}$ M = 27 amu

Then No. of atoms present in 243×10^{24} amu is

$\Rightarrow \frac{243\times10^{24}}{27}=\mathbf{9\times10^{24}}$

4. Ionic – NaCl, $ZnSO_4$ Metallic – Bronze, Fe
Molecular – S_8, I_2
Network – SiO_2, Diamond, Si Amorphous – Rubber, Glass

5. **(a)** Number of atoms in 2D unit cells $=\frac{1}{3}\times6+1\times1=3.$

(b) Packing efficiency (of 2 layers)

$=\frac{\text{Number of atoms}\times\text{Volume of 1 atom}}{\text{Total volume of 2 layers of unit cells}}\times100$

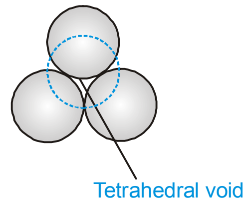
$$\text{Packing efficiency}=\frac{3\times\frac{4}{3}\pi r^3}{\text{area of hexagon}\times\text{height}}\times100$$

$$=\frac{3\times\frac{4}{3}\pi r^3}{6\times\frac{\sqrt3}{4}\times(2r)^2\times(2r)}\times100=60.43\%.$$

6. **(i)** $r^2\sqrt3$; **(ii)** $2r\sqrt{2/3}$; **(iii)** Yes, of course

7. **(a)** 4.50 Å, **(b)** 5.20 Å, **(c)** 12, **(d)** 6, **(e)** 0.925 g/cm³

8. It is formed by four spheres the centres of which form a regular tetrahedron.

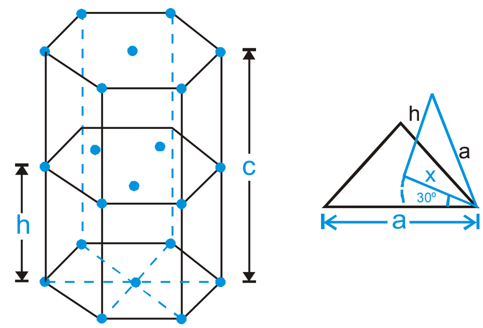


9. **(i)**

	Octahedral void	Tetrahedral void
HCP	6	12
FCC	4	8

(ii) False

10. **Calculation of c.**



$\cos30^\circ=\frac{a}{2\times x}$ so $x=\frac{2a}{2\times\sqrt3}=\frac{a}{\sqrt3}$

Applying pythogoras theorem : $x^2+h^2=a^2$

so $h^2=a^2-x^2=a^2-\frac{a^2}{3}=\frac{2}{3}a^2$ and

$h=\sqrt{\frac{2}{3}}a=2\sqrt{\frac{2}{3}}r.$

so height of hexagon $c=2h=2\sqrt{\frac{2}{3}}a.$

11. Density of hcp $=\frac{Z\times M}{N_A\times(\text{Volume of unit cell})}$

Volume of unit cell $=6\times\frac{\sqrt3}{4}a^2\times C$

$=\frac{6\times1.732}{4}\times295.5\times295.5\times472.9\times10^{-30}$

$=107.281\times10^{-24}\ cm^3.$

$\text{density}=\frac{6\times47.8}{6.023\times10^{-23}\times107.281\times10^{-24}}=4.438\ g/cm^3.$

12. **(a)** Fe_2O_3, **(b)** CdI_2

13. **(a)** 2.878 Å, **(b)** 12, **(c)** 19.4 g/cm^3, **(d)** 0.7405

14. Edge length a = 500 pm = 500 × 10^{-10} cm
Volume, $a^3 = (500\text{ pm} = 500 \times 10^{-10}\text{ cm})^3 = 12.5 \times 10^{-23}\text{ cm}^3$.
For fcc structure, number of atoms per unit cell, Z = 4
Atomic mass, M = 98.5 g
density, r = 5.22 g cm^{-3}
We know that :

$$\text{Avogadro constant, } N_0 = \frac{M \times Z}{a^3 \times p} = \frac{98.5 \times 4}{12.5 \times 10^{-23} \times 5.22}$$
$$= 6.038 \times 10^{23} \text{ atoms mol}^{-1}.$$

15. **(a)** XY_3 **(b)** **(i)** X_7Y_{24} **(ii)** XY_4 **(iii)** $X_7Y_{24}Z$

16. $N_A = 6.04 \times 10^{23}$

17. Number of octahedral void in ccp = Z ;
Number of tetrahedral void in ccp = 2Z.
For A_2B, Number of anion B = 4.
Cation **(A)** present in all octahedral void (100% occupied) and half tetrahedral void (50% occupied), then number

of cation **(A)** in unit cell = $4 + 8 \times \frac{1}{2} = 8.$

So, formula of compound = A_2B.

18. 4 Fe^{2+} & 4 O^{2-}

19. In ferromagnetic substance the magnetic moment is aligned spontaneously in one direction under the influence of external magnetic field and they become permanently magnetised. When magnetic moments are aligned in parallel and antiparallel directions in unequal numbers resulting net magnetic moment it is called ferrimagnetism.

20. In Silicon, electrons are fixed in covalent bonds and are not free for conduction, hence it is an insulator. On heating some of covalent bonds break and released excited electrons which can move under the electric field, and thus make the silicon, semiconductor.

21. No. of Mg^{2+} per unit cell = 8 [At corners] × $\frac{1}{8}$ = 1

No. of Ti per unit cell = 1 [body center] × $\frac{1}{1}$ = 1

No of O per unit cell = 6 [Face center] × $\frac{1}{2}$ = 3

so formula = $MgTiO_3$
atom are removed along face diagonal

No. of Mg^{2+} = 6[At corner] × $\frac{1}{8} = \frac{6}{8} = \frac{3}{4}$

No. of Ti per unit cell = 1 [Body center] × $\frac{1}{1}$ = 1

No. of O per unit cell = 5 [Face center] × $\frac{1}{2} = \frac{5}{2}$

So formula of compound = $Mg_{\frac{3}{4}}TiO_{\frac{5}{2}}$

Formula mass = $24 \times \frac{3}{4} + 48 + 16 \times \frac{5}{2} = 18 + 48 + 40$
= 106 amu

As corner ion are touching so = a = 2 $r_{Mg^{2+}}$ = 2 × 0.7 = 1.4 Å

$$d = \frac{\text{mass}}{\text{Volume}} = \frac{106 \times 1.67 \times 10^{-24}}{(1.4)^3 \times 10^{-24}} \text{ g/cm}^3 = 64.5 \text{ g/cm}^3$$

22. When the atoms or ions are missed or misplaced in the crystal, the defects are called point defects.

23. **(i)**
$Fe_{0.93}O$
Fe^{2+} : x Fe^{3+} : 0.93 – x

by charge balancing
2x + 3 [0.93 - x] = x
x = 2.79 so Fe^{3+} = 0.14
In 0.1 mole compound Fe^{2+} = 0.279 & Fe^{3+} 0.014
No. of vacancies = 0.007 mole
= 0.007 × 6.02 × 10^{23} vacancies.
(ii) No. of Fe^{2+} ion = 0.079 mole which are replaced by Sn^{4+} with each replacement one vacancies is created.
So no. of vacancies due to replacement of Fe^{2+} by Sn^{4+}

$= \frac{0.079}{2}$ mole $= \frac{0.079}{2}$ = 0.0395 mole

Total vacancies = [0.007 + 0.0395] mole
= 0.0465 × 6.02 × 10^{23} vacancies

24. **(a)** volume occupied by N_A unit cells

$$= \frac{\text{mass of } N_A \text{ unit cells}}{\text{density}} = \frac{168.5}{3.988} = 42.25 \text{ cm}^3$$

so volume of one unit cell $= \frac{42.25}{6.02 \times 10^{23}}$
$= 7.014 \times 10^{-23}$ cm^3

(b) smallest Cs – Cs distance = a = (volume)$^{1/3}$
= $(7.014 \times 10^{-23})^{1/3}$ = 4.125 Å

(c) smallest Cs – Cl distance = $\frac{a\sqrt{3}}{2} = \frac{4.125\sqrt{3}}{2}$ 3.572 Å.

25. For simple cubic lattice

$2(R+r) = a\sqrt{3} = 2R\sqrt{3}$ [for simple cubic lattice a= 2R]

$R = \frac{r}{(\sqrt{3}-1)} = \frac{10}{(\sqrt{3}-1)}$ Å

Then volume $= a^3 = (2R)^3 = \left(\frac{2\times10}{(\sqrt{3}-1)}\right)^3 = 1000(\sqrt{3}+1)$ Å^3

26. Volume of one unit cell $= a^3 = (288\times10^{-10})^3\ cm^3$

Volume of 208 g of element $= \frac{mass}{density} = \frac{208}{7.2} = 28.88\ cm^3$

so no. of unit cells in this volume $= \frac{28.88}{[2.88\times10^{-8}]^3}$

$= 12.09\times10^{23}$ unit cells

Since Z = 2

so Total no. of atoms $= 2\times12.09\times10^{23} = 24.18\times10^{23}$.

27. $d = \frac{mass}{volume}$

For orthorhombic volume = (a × b × c)

$= \frac{128\times32\times1.67\times10^{-24}}{[10.46\times12.87\times24.49]\times10^{-24}}\ gram/cm^3$

$= 2.075\ gram/cm^3$

28. $A\ell_2O_3$ – ionic

Br_2 – vanderwaal

F_2 – vanderwaal

$IC\ell$ – dipole dipole

H_2O – dipole - dipole (H–bonding)

NaCl – ionic,

$F_2 < Br_2 < IC\ell < H_2O < NaCl < Al_2O_3$

29. $d = \frac{Z\times M}{6.02\times10^{23}\times[a\times b\times c]}$

$1.419 = \frac{2\times M}{6.02\times10^{23}\times[12.05\times15.05\times2.69]\times10^{-24}}\ gram/cm^3$

$\Rightarrow M = 208.4$ gram/mol.

30. $a^3 = \frac{Z\times M}{N_A\times d} = \frac{2\times183.9}{6.02\times10^{23}\times19.3}$

so a = 3.16 Å

now length of the body diagonal = $a\sqrt{3}$ = 5.48 Å.

31. Actual given density $= \frac{2}{3}$ amu / Å^3

Density when 100% solid Ar filled $= \frac{40}{\frac{4}{3}\pi\times\left(\frac{3}{\pi^{1/3}}\right)^3}$

$= \frac{40}{36}$ amu / Å^3

then % of solid Ar without anything $= \left(\frac{\frac{40}{36}-\frac{2}{3}}{\left(\frac{40}{36}\right)}\right)\times100$

= 40% Ans.

32. $\frac{72.36}{56}$ 'Fe', $\frac{27.64}{16}$ 'O' $\Rightarrow$ 1.292 'Fe', 1.7275 'O'

Hence proportion is 1 : 1.33 ;

So Empirical formula is Fe_3O_4,

Empirical formula mass = 232 amu

Now if there are x formula units in the unit cell

$5.2 = \frac{\frac{x(232)}{6.02\times10^{23}}}{(8.39\times10^{-8})^3}$ $\Rightarrow$ $x = 7.968 \approx 8$

Hence number of ions in the unit cell = 56

33. Perimeter $= 2a + \sqrt{2}\,a$

$= 2[2(R+r)] + 4R = 4[r+2R]$

34. Number of Au atoms in unit cell $= \frac{1}{8}\times8 = 1$

Number of Cd atoms in unit cell $= \frac{1}{2}\times6 = 3$

The formula the alloy will be $AuCd_3$.

35. $d_{fcc} = \frac{Z_{fcc}\times M}{N_0\times(a_{fcc})^3} = \frac{4\times M}{N_0\times(a_{fcc})^3}$

$\Rightarrow$ $d_{BCC} = \frac{Z_{BCC}\times M}{N_0\times(a_{bcc})^3} = \frac{2\times M}{N_0\times(a_{bcc})^3}$

$\frac{d_{fcc}}{d_{BCC}} = 2\left[\frac{a_{bcc}}{a_{fcc}}\right]^3$

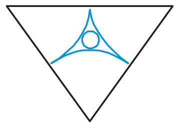
According to question $\sqrt{2}\,a_{fcc} = \sqrt{3}\,a_{bcc}$

$= \left(\frac{a_{bcc}}{a_{fcc}}\right) = \left(\frac{\sqrt{2}}{\sqrt{3}}\right)$

$\Rightarrow$ $\frac{d_{fcc}}{d_{BCC}} = 2\left[\frac{\sqrt{2}}{\sqrt{3}}\right]^3 = 1.09.$

36. Octahedral void is present at the body center, which is formed by six face centered atoms.

37. Packing fraction $= \dfrac{\frac{1}{2}\pi R^2 + \pi(0.155R)^2}{\frac{1}{2}(2R)^2\frac{\sqrt{3}}{2}} \times 100 = 95\%$



38. **(a)** For titanium hydride

No. of Ti atom per unit cell = 4

No. of H atom = 8 [in tetrahedral voids] × 1 = 8.

So formula of compound = Ti_4H_8 or TiH_2

For titanium carbide

No. of Ti atom per unit cell = 4

No. of C atom per unit cell = 4 [in octahedral voids] × 1 = 4.

So formula of compound = $Ti_4C_4 = TiC_4$

(b) For tetrahedral void. $\dfrac{r_H}{r_{Ti}} = 0.225$

(c) For octahedral void $\dfrac{r_C}{r_{Ti}} = 0.414$

(d) The void occupied by small size particle is depends on radius ratio. As per radius ratio H atom occupy tetrahedral void not octahedral void.

39. $P_{CO_2} \times 9.56 = \left[\dfrac{39.6}{44}\right] \times 0.082 \times 373$

$P_{CO_2} = 2.88$

$(P_A)_{gas} = 0.32$

For A- gas $\rightarrow P_A \times V = nRT$

$= 0.32 \times 9.56 = n_A \times 0.082 \times 373$

$n_{gas} = 0.1$ mole.

so molar mass of A = 254.5

Again $d_A = \dfrac{Z \times M}{N_0 \times a^3}$

$a^3 = \dfrac{4 \times 254.5}{6.02 \times 10^{23} \times 2.3}$

$a^3 = 735.2 \times 10^{-24}$

$a = 9 \times 10^{-8}$

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

For FCC lattice

$r = \dfrac{\sqrt{2}}{4}a = 3.19 \times 10^{-8}$ cm.

$b = 4\left[\dfrac{4}{3}\pi r^3\right] \times N_A = 4 \times \dfrac{4}{3} \times 3.14\,[3.19]^3 \times 10^{-24} \times 6.02 \times 10^{23}$

$= 327.26\ cm^3/mole.$

40. $a = 2R,\ c = \sqrt{\dfrac{2}{3}}\,2a = \sqrt{\dfrac{2}{3}}\,4r$

41. $d = \dfrac{Z \times M}{N_0 \times \text{Volume}} \Rightarrow 0.92 = \dfrac{Z \times 18}{6.02 \times 10^{23}\left[\dfrac{6\sqrt{3}a^2}{4} \times c\right]}$

$\Rightarrow 0.92 = \dfrac{Z \times 18}{6.02 \times 10^{23}\left[\dfrac{6\sqrt{3}}{4} \times (4.53)^2 \times 7.41 \times 10^{-24}\right]}$

$\Rightarrow Z = 4.$

42. **(a)** Distance $= \dfrac{a\sqrt{3}}{2} = \dfrac{387 \times \sqrt{3}}{2} = 335.15$ pm

(b) $r_{NH_4^+} = 335.15 - 181 = 154.15$ pm.

43. **(a)** $d_{c-c} = \dfrac{1}{2} \times \sqrt{3}\,.\,\dfrac{a_{fcc}}{2} = 154.4$ pm

(b) fraction $= \dfrac{8 \times \frac{4}{3}\pi\left(\frac{d_{c-c}}{2}\right)^3}{a^3} = 0.34$

44. $O_4\,Zn_{\frac{1}{8}\times 8}\,Al_{\frac{1}{2}\times 4}$

So, formula is $ZnAl_2O_4$.

45. **(a)** As each Zn^{2+} ion is present in tetrahedral void. So it is coordination number is = 4.

(b) Similarly S^{2-} ion have coordination number = 4.

(c) As Zn^{2+} ion is present in tetrahedral void that's why line's connecting any two nearest neighbour and Zn^{2+} have angle = 109°28'.

(d) For tetrahedral voids radius ratio is $\dfrac{r_{Zn^{2+}}}{r_{S^{2-}}} = 0.225.$

46. $r_+ + r_- = \dfrac{a}{2} \Rightarrow \dfrac{3r_-}{2} = \dfrac{a}{2};\quad r_- = \dfrac{a}{3}$ and $r_+ = \dfrac{a}{6}$

Packing fraction $= \dfrac{4 \times \frac{4}{3}\pi(r_+^3 + r_-^3)}{a^3}$

$= \dfrac{4 \times \frac{4}{3}\pi\left[\left(\frac{a}{6}\right)^3 + \left(\frac{a}{3}\right)^3\right]}{a^3} = 0.7.$

Percentage void = 30%.

47. $\frac{r_+}{r_-} = \frac{1.6}{1.864} = 0.858$

So, it is CsCl type unit cell

So $\sqrt{3}\ a = 2(r_+ + r_-)$

So $a = \frac{2(1.864 + 1.6)}{\sqrt{3}}$ Å = 2 x 2Å = 4Å

48. No. of Sr atom per unit cell = 8 [corner] × $\frac{1}{8} = 1$

No. of Ti atom per unit cell = 1 [center] × 1 = 1

No. of O atom per unit cell = 6 [face center] × $\frac{1}{2} = 3$

So formula of compound $SrTiO_3$

Edge length = 391 pm.

(a) Ti atom is present at body center of fcc lattice which act as octahedral voids. Which has coordination number = 6.

(b) Sr atom is present at corner of fcc lattice with has coordination number = 12.

(c) density = $d = \frac{Z \times M}{N_0 \times a^3} = \frac{184}{6.02 \times 10^{23} \times (3.91 \times 10^{-8})^3}$

= 5.1 gram/cc.

(d) In fcc lattice distance of nearest neighbour of Sr atom

$= \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}} = 276.5$ pm.

49. **(i)** In schottky defects density decreases.

(ii) In interstitial defects density increases.

(iii) In frenkel defects density remain same.

50. **2 (1 – x) / (3x – 2)**

M_x → M^{2+} (Let y) ; M^{3+} = x–y

⇒ Applying charge balance , $2y + 3(x - y) - 2 = 0$

⇒ $y = 3x - 2$

$\therefore \frac{M^{3+}}{M^{2+}} = \frac{x-y}{y} = \frac{x-(3x-2)}{3x-2} = \frac{(-2x+2)}{3x-2}$

$= \frac{2(1-x)}{(3x-2)}$

EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

1. 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.

2. 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.

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

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

4. According to question :

Number of Y atom in ccp unit cell = 4

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

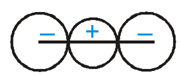
Formula of compound = $X_{16/3}Y_4 = X_{16}Y_{12} = X_4Y_3$

5. In fcc unit cell $4r = \sqrt{2}a$

[r = radius of Cu atom, a = edge length]

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

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

6. 

$2 \times 110 + 2 \times r_- = 508$

$2r_- = 288$

$r_- = 144$ pm

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

∴ Percentage of free space in CCP = 100 – 74 = 26%

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

∴ Percentage of free space in BCC = 100 – 68 = 32%

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

Formula of compound A_2B_5.

9. FCC lattice

$a = 361$ pm

$a\sqrt{2} = 4r$

$$r = \frac{361 \times \sqrt{2}}{4} = 127.6 \approx 128 \text{ pm.}$$

10. For BCC structure $\sqrt{3}\ a = 4r$

$$r = \frac{\sqrt{3}}{4} a = \frac{\sqrt{3}}{4} \times 351 = 152 \text{ pm.}$$

11. In FCC unit cell atoms are in constant along face diagonal.

So, $\sqrt{2}\ a = 4R$

$$\therefore \text{ closest distance } (2R) = \frac{\sqrt{2}\ a}{2} = \frac{a}{\sqrt{2}}$$

12. In Frenkel defect, some of iron (usually cation due to their small size) missing from their correct position and occupies position in interstitial.

Part # II : IIT-JEE ADVANCED

1. **(a)** $\frac{a}{2} = Y^{\frac{1}{3}}$

$a = 2Y^{\frac{1}{3}}$

$$\text{density } (d) = \frac{4 \times 6.023 \times Y \times 10^{-3}}{6.023 \times 10^{23} \left(2Y^{1/3} \times 10^{-9}\right)^3} = 5.0 \text{ Kg/M}^3$$

(b) Observed density of AB is 20 Kg/M^3

Which is Higher then calculate density 5kg/m^3 thus AB has either interstitial impurity defect or substitutional impurity defect.

2. 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 $(0.225 < \frac{r^+}{r^-} < 0.414)$.

3. For f.c.c. $\left(\frac{r_1}{r_2} = 0.414\right)$ octahedral void

$\frac{r_1}{r_2} = 0.225$ Tetrahedral void

We know along face diagonal for f.c.c. $4r_2 = a\sqrt{2}$

$$\Rightarrow r_2 = \frac{a\sqrt{2}}{4}$$

required diameter of interstitial sites $= 2r_1 = 2 \times 0.414 r_2$

$$\text{Diameter} = \frac{2 \times .414 \times \sqrt{2} \times a}{4} = \frac{2 \times .414 \times \sqrt{2} \times 400}{4}$$

$= 117.1$ pm.

4. $d = \frac{ZM}{N_A a^3} \Rightarrow Z = 20 \times 10^{-1} = 2$

So its is a bcc unit cell. Hence $\sqrt{3}\ a = 4R$

so $R = \frac{\sqrt{3}}{4} \times 5\text{Å} = 216.5$ pm.

5. **(A)** Simple cubic and fcc **(i)** have the cell parameters $a = b = c$ & $\alpha = \beta = \gamma$ (choice P) and belong to the same crystal system (choice (s)).

(B) Cubic & rhombohedral **(i)** have the cell parameters $a = b = c$ and $\alpha = \beta = \gamma$ (choice P) and **(ii)** are two crystal systems (choice (q)).

(C) Cubic and tetragonal are two crystal system (q).

(D) Hexagonal & monocubic **(i)** two crystal system choice (q) p **(ii)** have only two crystallographic angles of 90º choices.

6. $$\text{Total no. of atoms in 1 unit cell} = \left(12 \text{x} \frac{1}{6}\right) + 3 + \left(2 \text{x} \frac{1}{2}\right)$$

$= 6$

7. $C = \sqrt{\frac{2}{3}}\ 4r$ = Height of the unit cell.

Base area $= 6 \times \frac{\sqrt{3}}{4} (2r)^2$.

Volume of the hexagon = Area of base x Height = 6 .

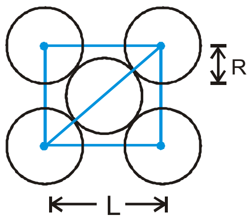
$$\frac{\sqrt{2}}{3} a^2 \times c = 4r^2 \times \frac{\sqrt{2}}{3} 4r = 24\sqrt{2} \cdot r^3$$

8. $$\text{Packing fraction} = \frac{\text{volume of the atoms in one unit cell}}{\text{volume of one unit cell}}$$

$$= \frac{6 \times \frac{4}{3} \pi r^3}{24\sqrt{2}\ r^2} = \frac{\pi}{3\sqrt{2}} = 0.74 = 74\%$$

$\Rightarrow$ empty space $= 100 - 74 = 26\%$.

9. Frenkel defect is a dislocation defect.
Trapping of an electron in the lattice leads to the formation of F-center.

10. 

$4R = L\sqrt{2}$

so, $L = 2\sqrt{2}R$

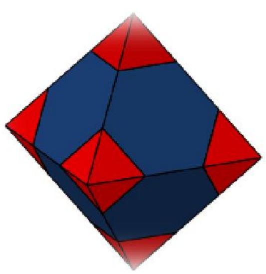
Area of square unit cell $= (2\sqrt{2}R)^2 = 8R^2$

Area of atoms present in one unit cell

$= \pi R^2 + 4\left(\frac{\pi R^2}{4}\right) = 2\pi R^2$

so, packing efficiency $= \frac{2\pi R^2}{8R^2} \times 100$

$= \frac{\pi}{4} \times 100 = 78.54\%$

11. 

12. 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 $= M_2X_4 = MX_2$

13. **2**

FCC $a = 400$ pm

$$df_{FCC} = \frac{Z_{FCC} \times GMM}{N_A \times a^3}$$

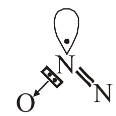
$$8g/ml = \frac{4 \times GMM}{N_A \times 64 \times 10^{-24}}$$

$$GMM = 128 \times N_A \times 10^{-24}$$

$$= \frac{N_A}{128 \times N_A \times 10^{-24}} \times 256$$

$N = 2$ Ans.

14. H atom : $\boxed{1}_1$ - Paramagnetic

NO_2 monomer -  Paramagnetic

O_2^- (Superoxide) :- $\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_z^2$

$\begin{vmatrix}\pi 2p_x^2 \\ \pi 2p_y^2\end{vmatrix}\begin{vmatrix}\pi^* 2p_x^2 \\ \pi^* 2p_y^1\end{vmatrix}$

One unpaired electron is present in either π^*2p_x or π^*2p_y.
So it is paramagnetic in nature.
Dimetric sulphur in vapour phase :- It is similar as O_2 in vapour state, paramagnetic in nature.
Mn_3O_4 :- It is combined form of MnO and Mn_2O_3
Mn^{+2} has 5 unpaired electrons (d^5 electronic configuration)
Mn^{+3} has 4 unpaired electrons (d^4 electronic configuration)
So it is paramagnetic in nature.
$(NH_4)_2[FeCl_4]$:- Consist $[Fe^{+2}Cl_4]^{-2}$ ion.
$[FeCl_4]^{-2}$ tetrahedral, sp^3 Hybridized, has configuration eg^3, t^2g^3.(Paramagnetic in nature)
$(NH_4)_2[NiCl_4]$:- Consist $[Ni^{+2}Cl_4]^{-2}$ ion.
$[NiCl_4]^{-2}$ tetrahedral, sp^3 Hybridized, has configuration eg^4, t_2g^3. (Paramagnetic in nature)
K_2MnO_4 :- Mn^{+6} is present in compound which has one unpaired electron in 3rd subshell. Mn^{+6} -[Ar]$3d^1$ Paramagnetic in nature.
K_2CrO_4 : Cr^{+6} is present in compound which has zero unpaired electron, diamagnetic in nature.

15. As per given information cation form FCC lattice and anion occpy all the octahedral void.

So	M^+	X^- &	Formula MX
	4 ion	4 ion	
After step I	4 ion	1 ion	
After step II	1 ion	4 ion	
After step III	0 ion	4 ion	
After step IV	1 ion	3 ion	

So ratio of $\frac{\text{No. of anion}}{\text{No. of cation}} = \frac{3}{1}$

MOCK TEST

1. (A)

2. (D)

When all particle along body diagonal one removed, these 2 X atoms from corner are removed, one Y particle removed & 2 Z particle removed.

Hence new arrangement, X particle $= \frac{1}{8}\times 6 + \frac{1}{2}\times 6 = \frac{15}{4}$

; Y particle = 6; Z particle = 3

Hence formula $= X_{\frac{15}{4}}Y_3Z_6 = X_{\frac{5}{4}}YZ_6 = X_6Y_4Z_8$

3. (B)

From the sizes of octahedral and tetrahedral voids, it is clear that the atoms occupying these voids will not touch each other as we have along body diagonal of FCC.

4. (A)

$$d_{c-c} = \sqrt{\frac{1}{16}+\frac{1}{16}+\frac{1}{16}} = \sqrt{\frac{3}{16}} \quad \text{and } a_{FCC} = 1$$

5. (A)

6. (B)

7. (A)

Formula $ZnAl_2O_4$

Packing fraction

$$= \frac{\text{Total volume of particles present in one unit cell}}{\text{volume of one unit cell}}$$

$$= \frac{\left(\frac{4}{3}\pi r^3_{Zn^{2+}}\right) + \left(\frac{2\times 4}{3}\pi r^3_{Al^{3+}}\right) + \left(\frac{4x4}{3}\pi r^3_{O^{2-}}\right)}{a^3}$$

$$= \frac{\left(\frac{4}{3}\pi\frac{a^3(0.225)^3}{(2\sqrt{2})^3}\right) + \left(2\times\frac{4}{3}\pi\frac{a^3(0.414)^3}{(2\sqrt{2})^3}\right) + \left(4\times\frac{4}{3}\pi\frac{a^3}{(2\sqrt{2})^3}\right)}{a^3}$$

$= 0.77$

8. (D)

In 1 mole of M_xO,

mole of M^{2+} ion = y

$\therefore$ mole of M^{3+} x – y.

Applying charge balance, $2y + 3(x-y) - 2 = 0$

$$\therefore \frac{M^{3+}}{M^{2+}} = \frac{x-y}{y} = \frac{x-(3x-2)}{3x-2} = \frac{(2x-2)}{3x-2} = \frac{2(x-1)}{3x-2}$$

9. (B, C)

From FCC unit cell

10. (C)

Atoms along one ed ge or at corners do not touch each other in FCC cell.

11. (ABCD)

12. (A)

13. (B)

Zinc oxide losses oxygen reversible at high temperature and turn yellow.

14. (A)

15. (C)

16. (A)

$3x + (0.93 - x)\times 2 = 2$

$x = 0.14$

% of Fe as Fe (III) $= \frac{0.14}{0.93}\times 100 = 15\%$

17. (A)

$4\,d_{c-c}\sin(54°44') = \sqrt{2}\,a \Rightarrow \quad r = \frac{d_{c-c}}{2} = 0.78$

18. (C)

$$d = \frac{8\times 12}{N_A\times a^3} = 3.37 \text{ gm/cc.}$$

19. (C)

Total number of unit cells $= \frac{1.2\times N_A}{12\times 8} = 7.5\times 10^{21}$.

20. [A → p, q, s] ; [B → p, q, r] ; [C → s] ; [D → p, q, s].

21. [A → p, q, r, s] ; [B → p, r, s] ; [C → p, s] ; [D → p, r, s]

22. $d = \frac{81 \times 2 \times 1000}{6 \times 10^{23}[4 \times 4 \times 5] \times 10^{-24}}$ mg/cc = 375 mg/cc.

23. Mass of 1 units cell = 4 × mass of 1 NaCl unit

$= 4 \times \frac{58.5}{6.022 \times 10^{-22}}$ g = 3.885×10^{-22} g.

∴ Number of unit cells per 1.0 g of NaCl = $\frac{1.0}{3.885 \times 10^{-22}}$

= 2.57×10^{21}

No. of unit cels per edge = $\sqrt[3]{2.57 \times 10^{21}}$ = 1.37×10^{7}.

24. (a) Moles of H_2 gas = $\frac{701.1 \times 4}{760 \times 0.082 \times 300}$ = 0.15.

$$M + 3H^{+} \longrightarrow M^{3+} + \frac{3}{2}H_2$$

∴ moles of M used = 0.1 = $\frac{2.7 \times 1}{\text{atomic weight}}$

⇒ Atomic weight of metal = 27 gm/mol.

∴ metal is Al.

(b) Density = $\frac{Z}{N_A}\left(\frac{M}{a^3}\right)$

⇒ $2.7 = \frac{Z}{6 \times 10^{23}}\left(\frac{27}{(405.5 \times 10^{-10})^3}\right)$

⇒ Z = 4.

(c) For FCC unit cell, $4r = \sqrt{2}\,a$

⇒ r = 143.4 pm.

25. (a) n = no. of moles = $\frac{PV}{RT} = \frac{12.5}{760} \times \frac{1}{2} \times \frac{1}{0.082 \times 1075}$

= 9.318×10^{-5}

Number of atoms = nN_A = 5.612×10^{19}

So number of unit cells = $\left(\frac{nN_A}{2}\right)$ = 2.806×10^{19}

So, if there are x unit cells along one edge of given cube then

Then total number of unit cells in the cubic crystal

$= x^3 = \frac{nN_A}{2} = 2.806 \times 10^{19}$ ⇒ $x = 3.04 \times 10^{6}$

Now if edge length of unit cell = a ⇒ ax = 1.62 mm.

⇒ $a = 5.33 \times 10^{-9}$ mm ⇒ a = 533 pm

∴ $r = \frac{\sqrt{3}a}{4}$ = 230.8 pm

(b) So metal must be potassium

(c) $\rho_{solid} = \frac{2 \times 39}{6.022 \times 10^{23} \times a^3}$ = 0.86 gm/cm³

$\rho_{gas} = \frac{PM}{RT} = \frac{12.5 \times 39}{760 \times 0.0821 \times 1075}$ = 7.27×10^{-3} gm/cm³

Ans. (a) 231 pm, (b) K, (c) density of solid = 0.857 g/cc, density of vapour = 7.29 × 10–6 g/cc

26. $pH = \frac{1}{2}\{pK_w - pK_b - \log C\}$

⇒ $6 = 7.0 - \frac{5}{2} - \frac{1}{2}\log C$ ⇒ C = 0.01 M

∴ $C = \frac{1.296}{\text{Molar mass}} = \frac{1}{100}$

⇒ molar mass of salt = 129.6

For rock salt, $600\sqrt{2} = \sqrt{2}\,a$

∴ a = 600 pm = 600×10^{-10} cm.

Now density

$= \frac{Z}{N_A}\left(\frac{M}{a^3}\right) = \frac{4}{6.0 \times 10^{23}}\left[\frac{129.6}{(600)^3 \times 10^{-30}}\right]$ = 4 gm/cc.

Ans. 4g/cc