Study Material for JEE (Main + Advanced)
(Distance Learning Programme)
SOLUTIONS
UNIT # 09 to 12

UNIT # 09

METALLURGY — EXERCISE # 1

3. Magnesite $\longrightarrow$ $MgCO_3$
   Calamine $\longrightarrow$ $ZnCO_3$
   Carnalite $\longrightarrow$ $KCl\ MgCl_2\ 6H_2O$
   Dolomite $\longrightarrow$ $CaCO_3\ MgCO_3$
4. Haematite $\longrightarrow$ Fe_2O_3
   Limonite $\longrightarrow$ $Fe_2O_3\ 3H_2O$
   Cassiterite $\longrightarrow$ SnO_2
   Magnetite $\longrightarrow$ Fe_3O_4
5. Litharge $\longrightarrow$ PbO
6. Magnesite $\longrightarrow$ $MgCO_3$
   Malachite $\longrightarrow$ $Cu(OH)_2\ CuCO_3$
   Magnetite $\longrightarrow$ Fe_3O_4
   Pyrolusite $\longrightarrow$ MnO_2
23. Magnesite $\longrightarrow$ $MgCO_3$
   Siderite $\longrightarrow$ $FeCO_3$
   Zincite $\longrightarrow$ ZnO (Philosophers wool)
   Argentite $\longrightarrow$ Ag_2S (Silver glance)

32. FeS_2 $\longrightarrow$ Iron pyrites or Fool's gold
33. In calcination, carbonates are decomposed to CO_2
40. Ag_2S $\longrightarrow$ Argentite
   Cu_2O $\longrightarrow$ Cuprite (Ruby copper)
41. Self reduction for Pb

(i) $\underset{\text{(galena)}}{2PbS} + \underset{\text{(air)}}{3O_2} \xrightarrow{\text{Roasting}} 2PbO + 2SO_2\uparrow$

(ii) $\underset{\text{(un roasted or)}}{PbS} + \underset{\text{(roasted ore)}}{2PbO} \xrightarrow[\text{Absence of air}]{\text{High temperature}} \underset{\text{(Self reduction)}}{3Pb + SO_2\uparrow}$

carbon reduction for Sn

$SnO_2 + 2C \longrightarrow Sn + 2CO$

METALLURGY — EXERCISE # 2

1. $Ag_2S + 4KCN \rightleftharpoons 2K[Ag(CN)_2] + K_2S$

3. $\left.\begin{array}{ll} KCl\ MgCl_2\ 6H_2O & \text{– Carnalite} \\ K_2SO_4\ Al_2(SO_4)_3\ 24H_2O & \text{– Alum} \\ CaCO_3\ MgCO_3 & \text{– Dolomite} \end{array}\right]\text{— Double salt}$
   $PbCO_3$ – Cerrusite

4. PbS $\longrightarrow$ Galena
   $FeCO_3$ $\longrightarrow$ Siderite
   $Al_2O_3\ 24H_2O$ $\longrightarrow$ Bauxite
   $MgCO_3$ $\longrightarrow$ Magnesite

7. $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$

14.(i) $P_2O_5 + 3Ca(OH)_2 \longrightarrow \underset{(X)}{Ca_3(PO_4)_2}$

(ii) $2Cu_2O + Cu_2S \longrightarrow \underset{(Y)}{6Cu + SO_2\uparrow}$

(iii) $Fe_2O_3 + 3CO \longrightarrow \underset{(Z)}{FeO + 3CO_2\uparrow}$

18. $Cu(OH)_2\ CuCO_3 \longrightarrow \underset{(A)}{CuO} + CO_2 + H_2O$
   $CuO + C \longrightarrow CO + \underset{(B)}{Cu}$

28. $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + SO_2\uparrow$
   $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2\uparrow$

30. $Ag_2S + 4NaCN \longrightarrow \underset{(A)}{2Na[Ag(CN)_4]} + Na_2S$

   $\underset{(A)}{2Na[Ag(CN)_4]} \xrightarrow{Zn} \underset{\underset{(B)}{(Impure)}}{Ag\downarrow} + Na_2[Zn(CN)_4]$

38.(i) $2PbS + 3O_2 \xrightarrow{\text{Roasting}} 2Pb + 2SO_2\uparrow$

$\underset{\text{(un roasted or)}}{PbS} + \underset{\text{(roasted ore)}}{2PbO} \xrightarrow[\text{Absence of air}]{\text{High temperature}} \underset{\text{(Self reduction)}}{3Pb + SO_2\uparrow}$

(ii) $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$

(iii) $HgS + 2HgO \longrightarrow 3Hg + SO_2$

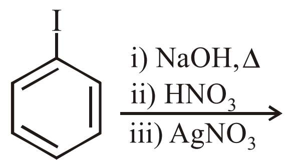
UNIT # 11

EXERCISE # JEE MAIN

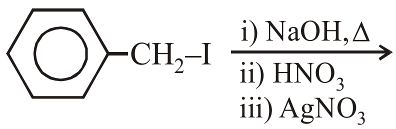
ALL QUESTIONS BASED ON

HALOGEN & OXYGEN CONTAINING ORGANIC COMPOUND

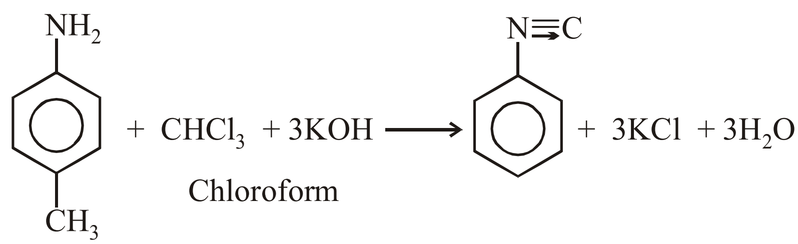
2. Formation of stable carbocation favours S_N1 reaction.

3. 

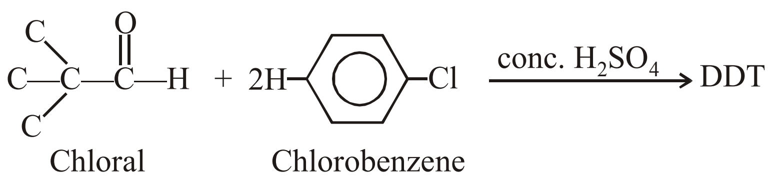
No ppt [Because C–I bond is stable]

Where as 

, Yellow ppt (AgI) [As C–I bond is reactive (Benzylic)]

4. 

p-Tolvidine

5. 

6. To give positive iodoform test presence of $CH_3-\overset{\overset{\displaystyle O}{||}}{C}-$ group or any group which can convert to $CH_3-\overset{\overset{\displaystyle O}{||}}{C}-$ group upon reaction with I_2 & NaOH should be present.

7. (4)

8. $$CH_3-CH_2{<}^{Cl}_{Cl} \xrightarrow{\text{as KOH}/\Delta} CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H$$

9. Maximum dehydration depend on stability of Carbocation as it follows E_1 mechanism

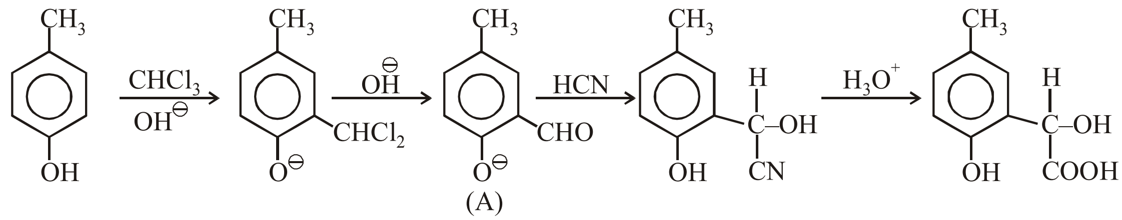
12. $LiAlH_4$ can reduce COOH group & not the double bond

$$CH_2=CH-\overset{\overset{\displaystyle O}{||}}{C}-OH \xrightarrow{\text{LAH}} CH_2=CH-CH_2-OH$$

14. Benzaldehyde $\xrightarrow{50\%\ \text{NaOH}}$ $\underset{\text{Alcohol}}{Ph-CH_2-OH} + \underset{\text{Acid}}{Ph-\overset{\overset{\displaystyle O}{||}}{C}-\overset{\ominus}{O}-\overset{\oplus}{Na}}$ [Cannizzaro's Reaction]

15. Dehydration rate $\propto$ Stability of $C^{\oplus}$ formed.

3° carbocation is most stable among all.

16. 

17. Electrophilic addition reaction more favourable

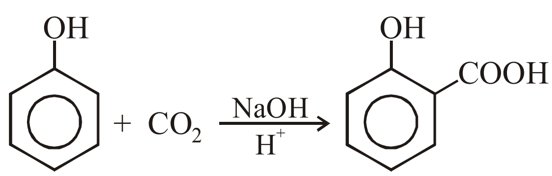
$$CH_2=CH-OCH_3 \xrightarrow{HBr} \underset{\substack{| \\ H}}{CH_2}-\overset{\oplus}{C}H-OCH_3 \xrightarrow{Br^{\ominus}} CH_3-\overset{\substack{Br \\ |}}{C}H-OCH_3$$

18. (4)

23. $$CH_3-CH_2-OH \xrightarrow{P+I_2} \underset{(A)}{CH_3-CH_2I} \xrightarrow[Ether]{Mg} \underset{(B)}{CH_3-CH_2-Mg-I}$$

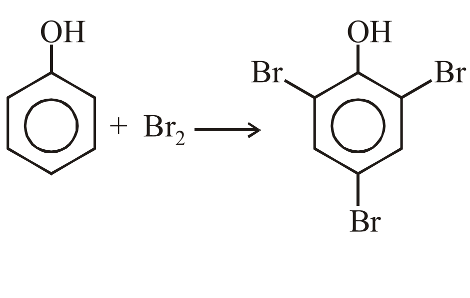
$$\xrightarrow{HCHO} CH_3-CH_2-\overset{\substack{OMgI \\ |}}{\underset{\substack{| \\ H}}{C}}-H \xrightarrow{H_2O} \underset{\text{Propyl alcohol}}{CH_3-CH_2-\overset{\substack{OH \\ |}}{C}H_2}$$

24. $$CH_3-CH_2-COOH \xrightarrow[\substack{\text{Red P} \\ \text{(hvz)}}]{Cl_2} CH_3-\underset{\substack{| \\ Cl}}{C}H-\overset{\substack{O \\ ||}}{C}-OH \xrightarrow{\text{Alc KOH}} CH_2=CH-\overset{\substack{O \\ ||}}{C}-OH$$

26.  Kolbe's Schemidt reaction

30. $$\underset{\text{Ethanoyl chloride}}{CH_3-\overset{\substack{O \\ ||}}{C}-Cl} + C_2H_5O^{\ominus}\,Na^{+} \longrightarrow CH_3-\overset{\substack{O \\ ||}}{C}-O-C_2H_5 + NaCl$$

31. $3\,KBr + KBrO_3 + 3H_2O \rightarrow 3Br_2 + 6KOH$

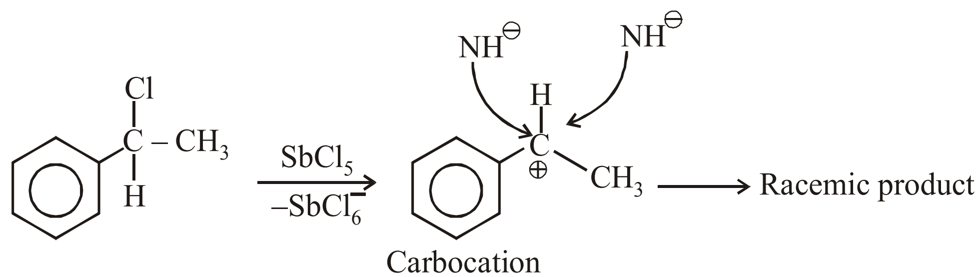


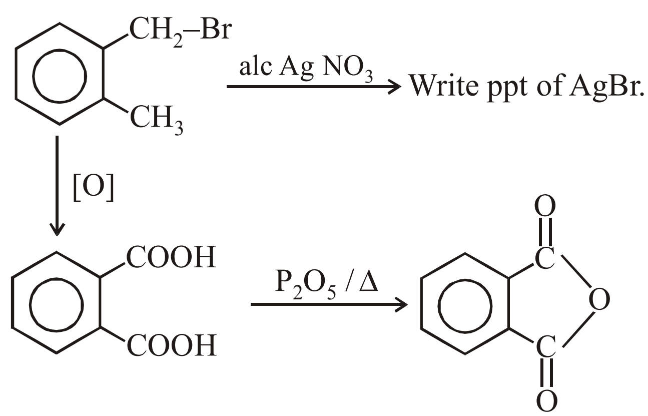
32. $$\mathrm{Cl_3C-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\overset{\ominus}{O}H} Cl_3C-\underset{OH}{\underset{|}{\overset{O^{\ominus}}{\overset{|}{C}}}}-H \xrightarrow{H-\overset{O}{\overset{\|}{C}}-CCl_3} Cl_3C-\overset{O}{\overset{\|}{C}}-OH + Cl_3C-\underset{H}{\underset{|}{\overset{O^{\ominus}}{\overset{|}{C}}}}-H}$$

$$\xrightarrow{\text{Proton transfer}} \mathrm{CCl_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} + Cl_3C-CH_2OH}$$

33. $$\mathrm{R-\overset{O}{\overset{\|}{C}}-H + Ag(NH_3)_2^+ + \overset{\ominus}{O}H \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + Ag + NH_4^{\oplus}}$$

Both formaldehyde & $\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-H}$

39. 

41. 

42. $$\mathrm{CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow CH_3CH_2-\overset{O}{\overset{\|}{C}}-ONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CH_2-\overset{O}{\overset{\|}{C}}-NH_2}$$

$$\xrightarrow{KOH\ |\ Br_2} \mathrm{CH_3-CH_2-NH_2}$$

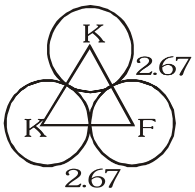
UNIT # 12 (PART-I)

SOLID STATE — EXERCISE # 1

11. B = 8 $\frac{1}{8}=1$ A = 1 AB

12. Au = 8 $\frac{1}{8}=1$

Cu = 6 $\frac{1}{2}=3$ $AuCl_3$

13. 

K – K $\Rightarrow$ $a\sqrt{2}$

(distance) $\Rightarrow 267\sqrt{2}$ $\Rightarrow$ 377.6 pm

14. Density (घनत्व) $=\frac{\cancel{Z}\times M}{N_0\times V}$

V = $\frac{4\times 143.5}{6.023\times 10^{23}\times 5.561}$

V = 17.137 10^{-23}

% occupied = $\frac{(5.55\times 10^{-8})^3}{\text{Volume}}\times 100$ = 99.75

% unoccupied $\Rightarrow$ 0.245

16. for FCC

$$Z=8\times\frac{1}{8}+6\times\frac{1}{2}=4$$

density = $\frac{Z\times M}{N_0\times V}$ = $\frac{4\times 56}{6.023\times 10^{23}\times(1.42\times 10^{-8})^3}$

SOLID STATE — EXERCISE # 2

1. d = 3.18 = $\frac{4\times\left[\frac{40+2\times 38}{6.023\times 10^{23}}\right]}{(a\times 10^{-10})^3}$ $\Rightarrow$ a = 344 pm

2. A = 6 C = 6 $\frac{2}{3}=4$

$A_6C_4\Rightarrow A_3C_2$ or C_2A_3

3. X = 4

Y = 8 or $X_4Y_8Z_2$

Z = 4 $\frac{1}{2}$ $\Rightarrow$ X_2Y_4Z

4. a = 480 pm

$a\sqrt{3}=2r_{x^+}+2r_{y^-}$

$480\sqrt{3}=2r_{x^+}+2\times 225$ $\Rightarrow$ r_{x^+} = 190.68 pm

6. $\frac{r_{A^{+1}}}{r_{B^{-1}}}=0.225=\frac{22.5}{r_{B^-}}$

$r_{B^{-1}}=100\text{pm}$

7. a = 387 pm

$d_{NH_4^+-Cl^-}=\frac{a\sqrt{3}}{2}=335.1\,\text{pm}$

11. A = 4 B = 8 $\frac{1}{4}$

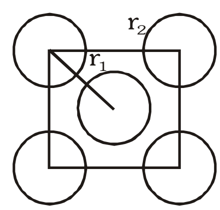
C = 8 $\frac{1}{2}$ $A_4B_2C_4\Rightarrow A_2BC_2$

15. Z = 8 $\frac{1}{8}+2=3$

$7.2=\frac{[3\times M/6.023\times 10^{23}]}{24\times 10^{24}}$

$\Rightarrow$ No. of atom in 200 gm = $\left(\frac{200}{M}\times N_A\right)$

= 3.472 10^{24} atoms

17. 

a = 620 pm

r_1 = nearest neighbour (निकटतम पडौसी)

r_2 = next nearest neighbours (अगला निकटतम पडौसी)

= 620

19. $\frac{200}{M}\times N_A=5\times 10^{24}$ $\frac{M}{N_A}=\left(\frac{200}{5\times 10^{24}}\right)$

d = $\frac{4\times\frac{M}{N_A}}{(200\times 10^{-10})^3}$ = 20 gm cm^3

20. $a\sqrt{3}=2r_{Cs^+}+2r_{Cl^-}$ $r_{Cl^-}=1.81\,\text{Å}$

4. $r_{Pb^{+2}} + r_{S^{-2}} + 297$ pm

$a = 2 \quad 297 \text{ pm} = 5.94 \quad 10^{-8}$ cm

$V = a^3 = 2.096 \quad 10^{-22}$ cm^3

6. $a\sqrt{3} = 2r_{Cl^-} + 2r_{CS^+}$

$412\sqrt{3} = 2\times181 + 2r_{CS^+}$

$r_{CS^+} = 175.8\,\text{pm}$

10. MgS $\Rightarrow \dfrac{r_{Mg^{+2}}}{r_{S^{-2}}} = \dfrac{0.65}{1.84} = 0.35$

CN = 4

MgO $\Rightarrow \dfrac{r_{Mg^{+2}}}{r_{O^{-2}}} = \dfrac{0.65}{1.40} = 0.464$

CN = 6

CsCl $\Rightarrow \dfrac{r_{Cs^+}}{r_{Cl^-}} = \dfrac{1.69}{1.81} = 0.933$

CN = 8

11. bcc $\Rightarrow a\sqrt{3} = 4\times124$

$a = \dfrac{4\times124}{\sqrt{3}} = 286.36$ pm

fcc = $a\sqrt{2} = 4\times124$

$a = 350.72$ pm

$$\frac{d_{bcc}}{d_{fcc}} = \frac{(2\times M/N_A)/(286.36)^3}{(4\times M/N_A)/(250.72)^3} = \frac{7.887\,\text{gm/mL}}{8.59\,\text{gm/mL}}$$

13. No. of atoms $= \dfrac{10}{100}\times N_A = 0.1\,N_A$

$$d = \frac{\left(2\times\dfrac{10}{N_A}\right)}{(400\times10^{-10})} = 5.188 \text{ gm/cm}^3$$

$$V_{Total} = \left(\frac{10}{5.188}\right) = 19275\,\text{cm}^3$$

$\Rightarrow$ No. of unit cell $= \dfrac{1.9275}{(400\times10^{-10})} = 3.0115 \quad 10^{22}$ unit cell

15. $$d = \frac{4\times\left(\dfrac{58.5}{N_A}\right)}{(0.564\times10^{-7})^3} = 2.16 \text{ gm/cm}^3$$

17. $Fe_{0.93}O$

$\Rightarrow$ $x \quad 3 + y \quad 2 = 2$ ....(i)

$x + y = 0.93$ ....(ii)

% FeO $= \dfrac{y}{0.93}\times100 = 15.053\%$

19. Each doping will create vacancy so total vacancy per mole

(प्रत्येक डोपिंग पर रिक्तियाँ उत्पन्न होगी अतः प्रति मोल कुल रिक्तियाँ)

$= 6.023 \quad 10^{23} \quad \dfrac{10^{-3}}{100} = 6.023 \quad 10^{18}$

24.

x	y
$8 \quad \dfrac{1}{8}$	$6 \quad \dfrac{1}{2} \Rightarrow XY_3$

$$d = \frac{\dfrac{1\times[60+3\times90]}{6.023\times10^{23}}}{(5\times10^{-8}\text{ cm})^3} = 4.38 \text{ gm/cm}^3$$

21. $V = \left[a^2\dfrac{\sqrt{3}}{4}\times2\right]\times b$

$$d = \frac{Z\times\dfrac{M}{N_A}}{V} = \frac{Z\times\dfrac{18}{6.023\times10^{23}}}{\left[\dfrac{\sqrt{3}}{2}\times(4.53)^3\times(10^{-8})^2\times(7.6\times10^{-8})\right]}$$

Z = 4

1. Density $d = \frac{Mz}{N_0a^3}$

M = molar mass

z = number of atoms in unit cell

a = edge length (कोर लम्बाई)

$\therefore$ M (molar mass) $= \frac{dN_0a^3}{z}$

$= \frac{7.2 \times 6.02 \times 10^{23} \times (2.88 \times 10^{-8})^3}{2}$

$= 51.77 \text{ g mol}^{-1}$

$\therefore$ $52.0 \text{ g} = \frac{52.0}{51.77} \text{mol} = \frac{52 N_0}{51.77} = 6.05 \times 10^{23} \text{atoms}$

2. For fcc structure,

edge length $r(K^+) + r(Cl^-) = \frac{a}{2}$

$r(K^+) + r(Cl^-) = \frac{6.28}{2} = 3.14$ A

$r(K^+) = 3.14 - 1.8173 = 1.3227$ Å

3.(a) Number of Mn atoms at corners (कोनों पर Mn परमाणुओं की संख्या) = 8 $\frac{1}{8}$ = 1

Number of F atoms at faces (फलको पर F परमाणुओं की संख्या) $= \frac{6}{2} = 3$

Empirical formula (मूलानुपाती सूत्र)= MnF_3

(b) C.N. = 6 structure being fcc type (संरचना fcc प्रकार की है)

(c) $a = 2(r_+ + r_-) = 2\,(0.65 + 1.36) = 4.02$ Å

(d) Total atoms in the unit cell = 4 [one Mn and three F]

$\therefore$ z = 1

$d = \frac{Mz}{N_0a^3} = 2.86 \text{ g/cm}^3$

4. Density (d) $= \frac{Mz}{N_0a^3}$

$\therefore$ $M = \frac{da^3N_0}{z}$

$= \frac{10.5 \times (4.77 \times 10^{-8})^3 \times 6.02 \times 10^{23}}{4(\text{fcc})}$

$= 107.09 \text{ g mol}^{-1}$

5. $N_0 = \frac{Mz}{a^3d}$

$= \frac{58.45 \times 4(\text{fcc})}{(2 \times 2.184 \times 10^{-8})^3 \times 2.167}$

= 6.05 10^{23} mol^{-1}

6. d (density) $= \frac{Mz}{a^3N_0}$

$z = \frac{da^3N_0}{M}$

$= \frac{9.00 \times (3.85 \times 10^{-8})^3 \times 6.02 \times 10^{23}}{240}$

= 1.3 (=1) being whole number

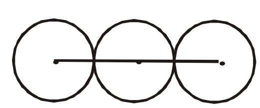
Thus simple cubic lattice. (सरल घनीय जालक)

7. Due to NaCl type structure, z = 4

$\therefore$ $d = \frac{Mz}{a^3N_0}$

$\therefore$ $a^3 = \frac{Mz}{dN_0} = \frac{58 \times 4}{2.48 \times 6.02 \times 10^{23}}$

a = 5.3762 10^{-8} cm



$\therefore$ $2\,(r_+ + r_-) = a$

$\therefore$ $(r_+ + r_-) = \frac{a}{2}$

= 2.688 10^{-8} cm = 269 pm

JEE-[MAINS] : PREVIOUS YEAR QUESTIONS — EXERCISE -5[A]

3. For FCC :

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

$$r = \frac{\sqrt{2}}{4} \times 361 = 127.6$$

6. Suppose Y atoms in CCP lattice = n
Number of tetrahedral voids = 2n
Atoms X occuping tetrahedral voids

$= \frac{2}{3} \quad 2n = \frac{4n}{3}$

Ratio X : Y = $\frac{4n}{3}$ = 4 : 3

formula = $X_4\,Y_3$

7. Total no. of atoms in fcc = 4

assuming atom to be spherical , its volume $= \frac{4}{3}\pi r^3$

Total volume of all atoms present in fcc

$= \frac{16}{3}\pi r^3$

10. As equal number of Na^+ and Cl^- ions are missing from their lattice site so it is Schottky defect.

11. One unit cell of NaCl contains
4 NaCl units which has

mass $= \frac{4 \times 58.5}{6.02 \times 10^{23}}$ g

$\therefore$ Number of unit cells in

$1g = \frac{6.02 \times 10^{23}}{4 \times 58.5} = 2.57 \times 10^{21}$

12. Number of per atom unit cell in BCC and FCC are 2 and 4 respectively.

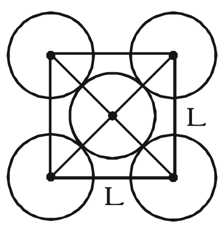
JEE-[ADVANCE] : PREVIOUS YEAR QUESTIONS — EXERCISE -5[B]

1. Number of M = $\frac{1}{4}$ 4 + 1 = 2

Number of X = $\frac{1}{2}$ 6 + $\frac{1}{8}$ 8 = 4

$M_2X_4 = MX_2$

3. Diagonal = 4r = $\sqrt{2}$ L



L = $\frac{4r}{\sqrt{2}}$

Area = $L^2 = 8r^2$

Number of spheres = 1 + 4 $\frac{1}{4}$ = 2

Area of each = πr^2

Packing fraction = $\frac{2 \times \pi r^2}{8r^2} = \frac{\pi}{4} = 0.785$

6. Total atoms = 6

Volume = 6 (area of triangle) height

$= 6 \quad (\sqrt{3}\, r^2) \quad 4r\sqrt{\frac{2}{3}}$

$= 24\sqrt{2}\, r^3$

7. Packing fraction = $\frac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}r^3} = 0.74$

= 74%

Vacant space = 100 – 74 = 26%

9. $d = \frac{n \times M}{a^3 \times N_A}$

$2 = \frac{n \times 75}{(5 \times 10^{-8})^3 \times 6 \times 10^{23}} \Rightarrow n = 2(\text{BCC})$

For BCC : $r = \frac{\sqrt{3}}{4} \times a = \frac{\sqrt{3}}{4} \times 5$

r = 216.5 nm

12. (i) $d = \frac{n \times M}{a^3 \times N_A}$

a = $2Y^{1/3}$ 10^{-9} m

M = 6.023 Y = $\frac{6.023}{1000}$ Y kg.

$$d = \frac{4 \times \frac{6.023}{1000} \times 10^{-3} \times Y}{6.023 \times 10^{23} \times (2Y^{1/3} \times 10^{-9})^3}$$

d = 5 kg / m^3

(ii) Observed density is higher – non-stoichiometric defect.