PHYSICAL CHEMISTRY

SOLID STATE

1. Atoms of metals x, y, and z form face-centred cubic (fcc) unit cell of edge length L_x, body-centred cubic (bcc) unit cell of edge length L_y, and simple cubic unit cell of edge length L_z, respectively.

If $r_z = \frac{\sqrt{3}}{2} r_y ; r_y = \frac{8}{\sqrt{3}} r_x ; M_z = \frac{3}{2} M_y$ and $M_z = 3M_x$, then the correct statement (s) is (are)

[Given : M_x, M_y, and M_z are molar masses of metals x, y, and z, respectively.

r_x, r_y, and r_z are atomic radii of metals x, y, and z, respectively.] **[JEE(Advanced) 2023]**

(A) Packing efficiency of unit cell of x > Packing efficiency of unit cell of y > Packing efficiency of unit cell of z

(B) $L_y > L_z$

(C) $L_x > L_y$

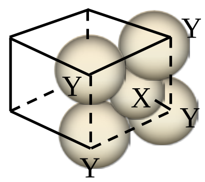
(D) Density of x > Density of y

2. Atom X occupies the fcc lattice sites as well as alternate tetrahedral voids of the same lattice. The packing efficiency (in %) of the resultant solid is closest to **[JEE(Advanced) 2022]**

(A) 25 (B) 35 (C) 55 (D) 75

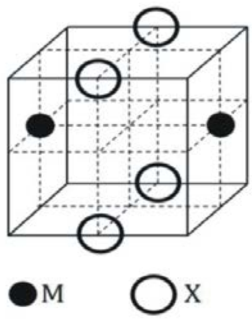
3. For the given close packed structure of a salt made of cation **X** and anion **Y** shown below (ions of only one face are shown for clarity) , the packing fraction is approximately **[JEE(Advanced) 2021]**

(packing fraction = $\frac{\text{Packing efficiency}}{100}$)



(A) 0.74 (B) 0.63 (C) 0.52 (D) 0.48

4. The cubic unit cell structure of a compound containing cation M and anion X is shown below. When compared to the anion, the cation has smaller ionic radius. Choose the correct statement(s). **[JEE(Advanced) 2020]**



(A) The empirical formula of the compound is MX.

(B) The cation M and anion X have different coordination geometries.

(C) The ratio of M-X bond length to the cubic unit cell edge length is 0.866.

(D) The ratio of the ionic radii of cation M to anion X is 0.414.

5. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance. **[JEE(Advanced) 2018]**

(i) Remove all the anions (X) except the central one

(ii) Replace all the face centered cations (M) by anions (X)

(iii) Remove all the corner cations (M)

(iv) Replace the central anion (X) with cation (M)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in Z is____.

6. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8g cm^{-3}, then the number of atoms present in 256g of the crystal is $N \times 10^{24}$. The value of N is : **[JEE(Advanced) 2017]**

7. The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is (are)

[JEE(Advanced) 2016]

(A) The number of the nearest neighbours of an atom present in the topmost layer is 12

(B) The efficiency of atom packing is 74%

(C) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively

(D) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom

8. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions m and n respectively, are - **[JEE(Advanced) 2015]**

(A) $\frac{1}{2},\frac{1}{8}$ (B) $1,\frac{1}{4}$ (C) $\frac{1}{2},\frac{1}{2}$ (D) $\frac{1}{4},\frac{1}{8}$

SOLUTIONS

1. Ans. (A, B, D)

Sol.

Element	X	Y	Z
Packing	FCC	BCC	Primitive
Edge	L_x	L_y	L_z
Relation between edge length and radius	$L_x = 2\sqrt{2}r_x$	$L_y = \frac{4}{\sqrt{3}}r_y$	$L_z = 2r_z$
Packing fraction	$\frac{\pi}{3\sqrt{2}}$	$\frac{\sqrt{3}\pi}{8}$	$\frac{\pi}{6}$

Now, $r_y = \frac{8}{\sqrt{3}} r_x$ & $r_z = \frac{\sqrt{3}}{2} r_y = \frac{\sqrt{3}}{2}\times\frac{8}{\sqrt{3}} r_x \Rightarrow r_z = 4r_x$

So, $L_x = 2\sqrt{2}\, r_x$, $L_y = \frac{4}{\sqrt{3}}\times\frac{8}{\sqrt{3}} r_x$, $L_z = 8r_x$

$L_x = 2\sqrt{2}\, r_x$, $L_y = \frac{32}{3} r_x$, $L_z = 8r_x$

So, $L_y > L_z > L_x$

Density $\frac{4M_x}{L_x^3}$, $\frac{2\times M_y}{L_y^3}$

Now, $3M_x = \frac{3M_y}{2}$ or $M_x \times 2 = M_y$

$$\frac{\text{density}(x)}{\text{density}(y)} = \frac{4M_x}{2M_y}\times\frac{L_y^3}{L_x^3} = \frac{4M_x}{4M_x}\times\frac{\left(\frac{32}{3}\right)^3}{\left(2\sqrt{2}\right)^3}$$

Hence d(x) > d(y)

2. Ans. (B)

Sol. Atom 'X' occupies FCC lattice points as well as alternate tetrahedral voids of the same lattice

$\Rightarrow \frac{1}{4}$th distance of body diagonal

$= \frac{\sqrt{3}a}{4} = 2r_x$

$\Rightarrow a = \frac{8r_x}{\sqrt{3}}$

Number of atoms of X per unit cell

= 4 + 4 = 8

(FCC lattice points) (Alternate tetrahedral voids)

% packing efficiency = $\dfrac{\text{Volume occupied by X}}{\text{Volume of cubic unit cell}} \times 100$

$$= \frac{8 \times \frac{4}{3}\pi (r_X)^3}{a^3} \times 100 = \frac{8 \times \frac{4}{3}\pi (r_X)^3}{\left(\frac{8r_X}{\sqrt{3}}\right)^3} \times 100$$

$$= \left(8 \times \frac{4}{3} \times \pi \times \frac{1}{8^3} \times 3\sqrt{3}\right) \times 100 = \frac{\sqrt{3}\pi}{16} \times 100 = 34\%$$

Hence, option (B) is the most appropriate option

3. **Ans. (B)**

Sol. Packing fraction (P.F.) $= \dfrac{1 \times \frac{4}{3}\pi r_-^3 + 3 \times \frac{4}{3}\pi r_+^3}{a^3}$

$\dfrac{r_+}{r_-} = 0.414$ (square planar void), a = $2r_-$

We get,

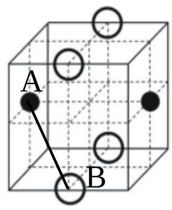
P.F. = $\dfrac{\frac{4}{3}\pi\left(r_-^3 + 3r_+^3\right)}{8r_-^3} = \left[\dfrac{\pi}{6}\left(1 + 3(0.414)^3\right)\right] = 0.63$

4. **Ans. (A, C)**

Sol. (A) $Z_M = 2 \times \frac{1}{2} = 1$

$Z_X = 4 \times \frac{1}{4} = 1$

∴ Empirical formula is MX



(B) Coordinate numbers of both M and X is 8.

(C) Bond length of M – X bond

= AB = $\sqrt{3}.\frac{a}{2} = 0.866ba$

(D) $r_M : r_X = \left(\sqrt{3} - 1\right) : 1$ = 0.732 : 1.000

5. **Ans. (3)**

Sol. $X^{\Theta} \Rightarrow$ O.V.

$M^+ \Rightarrow$ FCC

	M^+	X^-
(i)	4	1
(ii)	4–3	3+1
(iii)	4 – 3 – 1	3+1
(iv)	1	3

Z = $\dfrac{3}{1} = 3$

6. Ans. (2)

Sol. Formula of density = $\frac{Z \times M}{N_A \times a^3}$

For FCC unit cell Z = 4

Edge length a = 4 × 10^{-8} cm

$$M = \frac{d \times N_A \times a^3}{Z} = \frac{8 \times 6 \times 10^{23} \times 64 \times 10^{-24}}{4} \text{ gm/mol}$$

No. of atoms = $\frac{wt(gm)}{\text{molar mass}} \times N_A = \frac{256 \times 10 \times 6 \times 10^{23}}{8 \times 6 \times 16} = 2 \times 10^{24}$ (Value of N = 2)

7. Ans. (B, C, D)

Sol. CCP is ABC ABC ..... type packing

(A) In topmost layer, each atom is in contact with 6 atoms in same layer and 3 atoms below this layer.

(B) Packing fraction = $\frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3}$ = (0.74)

(C) Each FCC unit has effective no of atoms = 4

Octahedral void = 4

Tetrahedral void = 8

(D) $4r = a\sqrt{2}$

8. Ans. (A)

Sol. Effective number of O^{-2} = 4

Effective number of Al^{+3} = 4 m

Effective number of Mg^{+2} = 8 m

⇒ By charge balance 12 m + 16 n = 8

3 m + 4 n = 2

Possible value of m and n from given equation are

$m = \frac{1}{2}$; $n = \frac{1}{8}$