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CHEMISTRY

TARGET : JEE Advanced - 2021

CAPS – 23

Solid State

Answer Key

1.	(C)	**2.**	(A)	**3.**	(C)	**4.**	(C)	**5.**	(A)
6.	(B)	**7.**	(ABD)	**8.**	(ACD)	**9.**	(AB)	**10.**	(ABCD)
11.	(AC)	**12.**	(A)	**13.**	(A)	**14.**	(A)	**15.**	(B)
16.	(A)	**17.**	(A)	**18.**	(4.00)	**19.**	(4.00)	**20.**	(7.00)
21.	(2.367%)	**22.**	(0.0465 N_A)	**23.**	(D)	**24.**	(C)		

Solution

1. Sodium (Na = 23) crystallizes in bcc arrangement with the interfacial separation between the atoms at the edge 53.6 pm. The density of sodium crystal is

(A) 2.07 g/cc (B) 2.46 g/cc (C) 1.19 g/cc (D) none of these

Ans. **(C)**

Sol. a − 2r = 53.6 pm ...(i)

Also $4r = \sqrt{3}a$

$\Rightarrow a - \frac{\sqrt{3}}{2}a = 53.6$

$\Rightarrow a = \frac{53.6 \times 2}{2 - \sqrt{3}} = 400$ pm

$\Rightarrow$ Density$(\rho) = \frac{2 \times 23}{6.023 \times 10^{23} \times 4^3 \times 10^{-24}} = 1.19$ g/cc

2. An element X (atomic weight = 24 gm/mol) forms a face centered cubic lattice. If the edge length of the lattice is 4 × 10^{-8} cm and the observed density is 2.40 × 10^3 kg/m^3, then the percentage occupancy of lattice points by element X is (Use N_A = 6 × 10^{23})

(A) 96 (B) 98 (C) 99.9 (D) none of these

Ans. **(A)**

Sol. Theoretical density = $\frac{Z.M}{N_A.a^3}$

$= \frac{4 \times 24 \times 10^{-3}}{6 \times 10^{23} \times (4 \times 10^{-10})^3}$

= 2.5 × 10^3 kg/m^3

$\%\text{occupancy} = \frac{\text{observed density}}{\text{Ideal density}} \times 100$

$= \frac{2.4 \times 10^3}{2.5 \times 10^3} \times 100 = 96\%$

3. Metallic Gold crystallizes in fcc lattice and the length of cubic unit cell is 407 pm.

(Given: Atomic mass of Gold= 197, NA = 6×10^{23})

The density if it has 0.2% Schottky defect is (in gm/cm^3):

(A) 4.86 (B) 9.72 (C) 19.48 (D) 18.44

Ans. **(C)**

Sol. By using this formula

$$\rho = \frac{Z \times M}{N_A a^3}$$

Z = (4 – 0.2% of 4)

4. Select the correct statement(s).

(A) The co-ordination number of each type of ion in a CsCl crystal is twelve

(B) A metal that crystallizes in a bcc structure has a co-ordination number of twelve

(C) A unit cell of an ionic crystal shares some of its ions with other unit cells

(D) The length of the unit cell in NaCl is 552 pm (given that r_{Na^+} = 85 pm and r_{Cl^-} = 181 pm)

Ans. **(C)**

Sol. (a) The unit cell of CsCl has bcc arrangement of ions in which each ion has eight oppositely charged ions around it in the nearest neighbors.

(b) In bcc, coordination number of atoms is 8

(c) In a unit cell, a corner is shared in eight-unit cells and a face center is shared between two adjacent unit cells.

(d) In NaCl unit cell: $2(r_{Na^+} + r_{Cl^-}) = a \Rightarrow a = 2(85 + 181) = 532$ pm

5. A big RED spherical balloon (radius = 6a) is filled up with gas. On this balloon six small GREEN spherical balloons (radius = a) are stuck on the surface in a specific manner. As RED balloon is slowly deflated, a point comes when all these six GREEN balloons touch and green balloons arrange themselves in a 3-D closed packing arrangement. At that stage, the radius of the RED balloon would have reduced by approximately

(A) 14.5 times (B) 1.414 times (C) 6.0 times (D) 2.42 times

Ans. **(A)**

Sol. Red balloon is there in an octahedral void.

$\therefore$ $r_{red} = 0.414a$

$$\therefore \frac{(r_{red})_i}{(r_{red})_f} = \frac{6a}{0.414a} = 14.5$$

6. 100 cc of a piece of impure rock salt density 4 g/cc is dissolved in water and treated with excess of silver nitrate so that all chloride is precipitated as AgCl. If the number of moles of AgCl precipitated is 6, the percentage purity of the sample is

(A) 43.9 (B) 87.75 (C) 90 (D) 55.5

Ans. **(B)**

Sol. Mass of Rock Salt = $100 \times 4 = 400$ gm

Mass of NaCl present = $6 \times 58.5 = 351$ gm

% of NaCl in Rock Salt = $\frac{351}{400} \times 100 = 87.75$

MCQ

7. Pick out the correct statement(s).

(A) Due the presence of F-centers in crystals, the crystal attains paramagnetic character.

(B) Frenkel defect is a dislocation defect.

(C) In case of diamond that follows zinc blende structure, the number of carbon atoms per unit cell is four.

(D) Due to Schottky defect in crystals, the electrical neutrality is not affected.

Ans. **(ABD)**

Sol. • Crystals with F-centers − unpaired electrons are present and hence paramagnetic.

• In Frankel defect ions are dislocated from the normal sites to interstitial sites.

• The unit cell of diamond that follows ZnS structure, there are eight carbon atoms and not four.

• The electrical neutrality is maintained due to Schottky defects since pairs of ions are missing.

8. Select the correct statement(s).

(A) Co-ordination no. of Cs^+ and Cl^- are 8, 8 in CsCl crystal

(B) If radius ratio $(r_c/r_a) < 0.225$ then shape of compound must be linear

(C) If radius ratio (r_c/r_a) lies between 0.414 to 0.732 then shape of ionic compound may be square planer (Ex. $PtCl_4^{2-}$)

(D) If radius ratio is less than 0.155 then shape of compound is linear

Ans. **(ACD)**

Sol.

Limiting radius ratio	Co-ordination number	Shape	Examples
< 0.155	2	Linear	BeF_2
0.155-0.225	3	Trigonal planar	B_2O_3
0.225-0.414	4	Tetrahedral	ZnS
0.414-0.732	6	Octahedral	NaCl
0.732-0.999	8	Body centered cubic	CsCl

Cesium Chloride (CsCl) type structure: Cl has body-centered cubic (bcc) arrangement. Each Cs^+ ion is surrounded by 8 Cl^- ions and each Cl^- ion is surrounded by 8 Cs^+ ions, i.e., this structure has 8: 8 co-ordination.

9. Select the correct statement(s).

(A) CsCl changes to NaCl structure on heating

(B) NaCl changes to CsCl structure on applying pressure

(C) Co-ordination number decreases on applying pressure

(D) Co-ordination number increases on heating

Ans. **(AB)**

Sol. Coordination number decreases on heating and increases on applying pressure. Coordination number of CsCl is 8:8 and NaCl is 6:6.

10. Amorphous solids

(A) do not have sharp melting points.

(B) are isotropic.

(C) have same physical properties in all directions.

(D) are supercooled liquids.

Ans. **(ABCD)**

Sol. Properties of amorphous solids.

11. Which is/are correct statement about zinc blende structure?

(A) The number of first neighbors of S^{2-} is 4.

(B) The maximum distance between Zn^{2+} is $\frac{a\sqrt{3}}{2}$, where 'a' = edge length of unit cell.

(C) If all tetrahedral voids occupied by Zn^{2+} then C.N. of S^{2-} is 8.

(D) If all tetrahedral voids occupied by Zn^{2+} then C.N. change from 4 : 4 to 8 : 8.

Ans. **(AC)**

Sol. Zn^{2+} occupies alternate tetrahedral voids and S^{2-} occupies FCC.

Paragraph for Q. 12 to Q. 14:

In HCP as well as CCP, only 74% of the available space is occupied by spheres. The remaining space is vacant and constitute interstitial voids or spaces. There are two types of interstitial space, tetrahedral and octahedral voids, in three-dimensional close packing. In a close packing, the number of tetrahedral voids is double the number of spheres. Radius of the tetrahedral voids relative to the radius of the sphere is 0.225, that is, for tetrahedral voids $\frac{r_{void}}{r_{sphere}} = 0.225$. In a close packing, the number of octahedral voids is equal to the number of spheres. Radius of the octahedral void relative to the radius of the sphere is 0.414 that is, for octahedral void $\frac{r_{void}}{r_{sphere}} = 0.414$.

12. In a compound of XY_2O_4, oxide ions are arranged in CCP and cations X are present in octahedral voids. Cations Y are equally distributed between octahedral and tetrahedral voids. The fraction of the octahedral voids occupied is

(A) $\frac{1}{2}$ (B) $\frac{1}{4}$ (C) $\frac{1}{8}$ (D) $\frac{1}{6}$

Ans. **(A)**

Sol. $O \rightarrow CCP \Rightarrow 8 \times \frac{1}{8} + \frac{1}{2} \times 6 = 4$

According to the formula, effective number of Y atoms per unit cell will be 2 and the number of X atoms per unit cell will be 1. The possible arrangement is, Y $\rightarrow$ 1 effective O.V., 1 effective T.V. X−1 effective O.V. Total effective O.V.per unit cell=4

Fraction = $\frac{2}{4} = \frac{1}{2}$

13. In a solid, oxide ions are arranged in CCP, cations A occupy $\frac{1}{6}$ of the tetrahedral voids and cations B occupy $\frac{1}{3}$ of the octahedral voids. The formula of the compound is

(A) ABO_3 (B) AB_2O_3 (C) A_2BO_3 (D) $A_2B_2O_3$

Ans. **(A)**

Sol. The effective number of oxide ions = 4 (CCP structure)

Effective number of cations $A = \frac{1}{6} \times \text{No. of Tetrahedral voids} = \frac{1}{6} \times 8 = \frac{4}{3}$

Effective number of cations $B = \frac{1}{3} \times \text{Octahedral voids} = \frac{1}{3} \times 4 = \frac{4}{3}$

Formula is $A_{\frac{4}{3}}B_{\frac{4}{3}}O_4 = ABO_3$

14. Mineral having the formula AB_2 crystallizes in cubic packed lattice, with A atoms occupying the lattice points. The coordination number of A atoms, that of B atoms and percentage of tetrahedral voids occupied by B atoms are respectively.

(A) 8, 4, 100% (B) 2, 6, 75% (C) 3, 1, 25% (D) 6, 6, 50%

Ans. **(A)**

Sol. As given,

Number of atoms = 4 (for ccp crystal)

Formula = 4AB2 = A4B8

$\therefore$ CN of A = 8 [CN of A = Number of B atoms]

CN of B = 4 [CN of B = Number of A atoms]

In given arrangement, all tetrahedral Voids are occupied (fluorite type structure).

Paragraph for Q. 15 to Q. 17:

Diamond is a crystalline allotrope of carbon, which crystallizes in a 3-dimensional lattice. Each carbon forms four bonds with other carbon atoms. The unit cell of the diamond lattice can be thought of containing carbon atoms present at all CCP positions as well in alternate tetrahedral voids. Assuming contact between nearest atoms, answer the following:

15. Number of carbon atoms per unit cell of diamond structure is

(A) 4 (B) 8 (C) 12 (D) data insufficient

Ans. **(B)**

Sol. No. of carbon atoms in diamond = $8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) + 4 = 8$

16. What is the fraction of length covered along the body diagonal of the cubic unit cell by carbon atoms?

(A) 0.50 (B) 0.34 (C) 0.75 (D) 0.25

Ans. **(A)**

Sol. Since each body diagonal can have two atoms, but in case of diamond, atoms are present only in alternate tetrahedral voids. Hence, each body diagonal will have only one atom, hence only 50 % is covered.

17. How much fraction of area of one face is covered by atoms?

(A) $\frac{3\pi}{32}$ (B) $\frac{6\pi}{32}$ (C) $\frac{9\pi}{32}$ (D) $\frac{3\pi}{64}$

Ans. **(A)**

Sol. Fraction of area covered = $\frac{\text{area of all spheres in one face}}{\text{area of face}} = \frac{2\pi r^2}{\left(\frac{8r}{\sqrt{3}}\right)^2} = \frac{3\pi}{32}$

NUMERIC

18. In seven possible crystal system how many crystal systems have more than one Bravais lattice?

Ans. **(4.00)**

Sol. The following are the crystal structures with more than one Bravais lattice.

1. Cubic - 3
2. Tetragonal - 2
3. Orthorhombic - 4
4. Monoclinic - 2

19. Ionic solid $Na^+ A^-$ crystalline in rock salt type structure. 2.592 gm of ionic solid salt NaA dissolved in water to make 2 litre solution. The pH of this solution is 8. If distance between cation and anion is 300 pm. Calculate density of ionic solid (in gm/cm^3).

(Given: $pK_w = 13$, $pK_a(HA) = 5$, $N_A = 6 \times 10^{23}$)

Ans. **(4.00)**

Sol. $\left[OH^-\right] = \sqrt{\frac{CKw}{Ka}}$

$10^{-5} = \sqrt{\frac{2.592}{M \times 2} \times \frac{10^{-13}}{10^{-5}}}$

M = 129.6

$d = \frac{ZM}{a^3 \times N_A} = \frac{4 \times 129.6}{(600 \times 10^{-10})^3 \times 6 \times 10^{23}} = 4$

20. In a solid 'AB' having NaCl structure, A atoms are in FCC. If all the face centered atoms along one of the axes are removed, then what will be the sum of atoms in a unit cell of compound AB?

Ans. **(7.00)**

Sol. A = 8 × (1/8) + 4 × (1/2) = 3

B = 12 × (1/4) + 1 = 4

Total atoms = 3 + 4 = 7

21. A strong current of trivalent gaseous boron passed through a germanium crystal decreases the density of the crystal due to part replacement of germanium by boron and due to interstitial vacancies created by missing Ge atoms. In one such experiment, one gram of Germanium is taken, and the boron atoms are found to be 150 ppm by weight when the density of the Ge crystal decreases by 4%. Calculate the percentage of missing vacancies due to germanium which are filled up by boron atoms.

Atomic wt. Ge = 72.6, B = 11

Ans. **(2.367%)**

Sol. Let x moles of Ge atoms are replaced by B atoms.

Moles of B atoms in the final crystal = x

Now, according to the question, the final weight of crystal = 0.96 g

Out of which, weight of boron atoms = $\frac{150}{10^6} \times 0.96 = 1.44 \times 10^{-4}$ g

Moles of Boron atom in the final crystal = $\frac{1.44}{11} \times 10^{-4}$

Thus, $x = \frac{1.44}{11} \times 10^{-4}$

Now, weight of Ge in the final sample = 0.96 − 1.44 × 10^{-4} = 0.959856 g

Thus, loss in weight of Ge = 1 − 0.959856 = 401.44 × 10^{-4} g

Thus, moles of Ge missing = $\frac{401.44 \times 10^{-4}}{72.6}$

Thus, percentage of Ge replace by B = $\frac{\frac{1.44}{11} \times 10^{-4}}{\frac{401.44 \times 10^{-4}}{72.6}} \times 100 = 2.367\%$

22. It is believed that non-stoichiometric compound $Fe_{0.93}O$ forms by doping of Fe^{3+} ions in FeO crystal by replacement of Fe^{2+}. Calculate the total no. of cationic vacancies if now all the Fe^{2+} ions are replaced by Si^{4+} ions in 0.1 mole of $Fe_{0.93}O$. (Give your answer in multiple of N_A)

Ans. **(0.0465 N_A)**

Sol. Let 1 mole of the given compound has x mole Fe^{3+} and (0.93 – x) moles Fe^{2+}. Then, by charge balance,

3x + 2(0.93 – x) = 2

x + 1.86 = 2

x = 0.14

Moles of Fe^{2+} = 0.79

Now, moles of Si^{4+} added = $\frac{n_{Fe^{2+}}}{2} = \frac{0.79}{2} = 0.395$

Thus, total cation vacancy per mole of compound = (1 – 0.14 – 0.395) N_A = 0.465 N_A

Thus, total cation vacancy for 0.1 mole of compound = 0.0465 N_A

23. Match the following.

Column-I [Bravais Lattice (s)]	Column-II (Crystal System)
(A) Primitive, face centered, body centered, end centered	(P) Cubic
(B) Primitive, face centered, body centered	(Q) Orthorhombic
(C) Primitive, body centered	(R) Hexagonal
(D) Primitive only	(S) Tetragonal

(A) A $\rightarrow$ S; B $\rightarrow$ P; C $\rightarrow$ R; D $\rightarrow$ Q (B) A $\rightarrow$ P; B $\rightarrow$ Q; C $\rightarrow$ R; D $\rightarrow$ S

(C) A $\rightarrow$ R; B $\rightarrow$ P; C $\rightarrow$ S; D $\rightarrow$ Q (D) A $\rightarrow$ Q; B $\rightarrow$ P; C $\rightarrow$ S; D $\rightarrow$ R

Ans. **(D)**

Sol. Match the Bravais lattice with corresponding crystal unit system.

24. Match the following.

Column-I (Structure)	Column-II (Voids occupied)
(A) Rock salt	(P) 100% tetrahedral voids occupied by cation
(B) Zinc blende	(Q) 100% tetrahedral voids occupied by anion
(C) Fluorite	(R) 100% octahedral voids occupied by cation
(D) Anti fluorite (Na_2O)	(S) 50% tetrahedral voids occupied by cation

(A) A $\rightarrow$ S; B $\rightarrow$ P; C $\rightarrow$ Q; D $\rightarrow$ R (B) A $\rightarrow$ P; B $\rightarrow$ R; C $\rightarrow$ S; D $\rightarrow$ Q

(C) A $\rightarrow$ R; B $\rightarrow$ S; C $\rightarrow$ Q; D $\rightarrow$ P (D) A $\rightarrow$ Q; B $\rightarrow$ P; C $\rightarrow$ S; D $\rightarrow$ R

Ans. **(C)**

Sol. Factual