



CHAPTER - 1

SOLID STATE

Solids.

Solids are a form of matter in which atoms or molecules are trapped locally by chemical bonds or forces between molecules called "intermolecular forces." Solid materials are generally strong, durable, and have a stable volume.

CHARACTERISTICS OF A SOLID STATE

Exact weight, volume and shape

Short intermolecular range.

Strong intermolecular forces

The fixed location of the existing particles and can only move about their central location.

Incompressible and durable

Amorphous and Crystalline Solids

In crystalline solids the particles are arranged in a 3-dimensional order. The particles have equal intermolecular forces. They have sharp melting point and are anisotropic. They are called true solids. Example: Benzoic acid, Diamond.

Application of diamond:

It is widely used in making beautiful jewellery

Amorphous means shapeless. This word is derived from Greek. It has an irregular arrangement of solid particles. The intermolecular forces are not equal. Also, the distance between particles varies. They have an undefined geometric shape. They are also called supercooled liquids. They are isotropic. Example: Naphthalene, glass

Application of glass:

It is widely used in construction of building

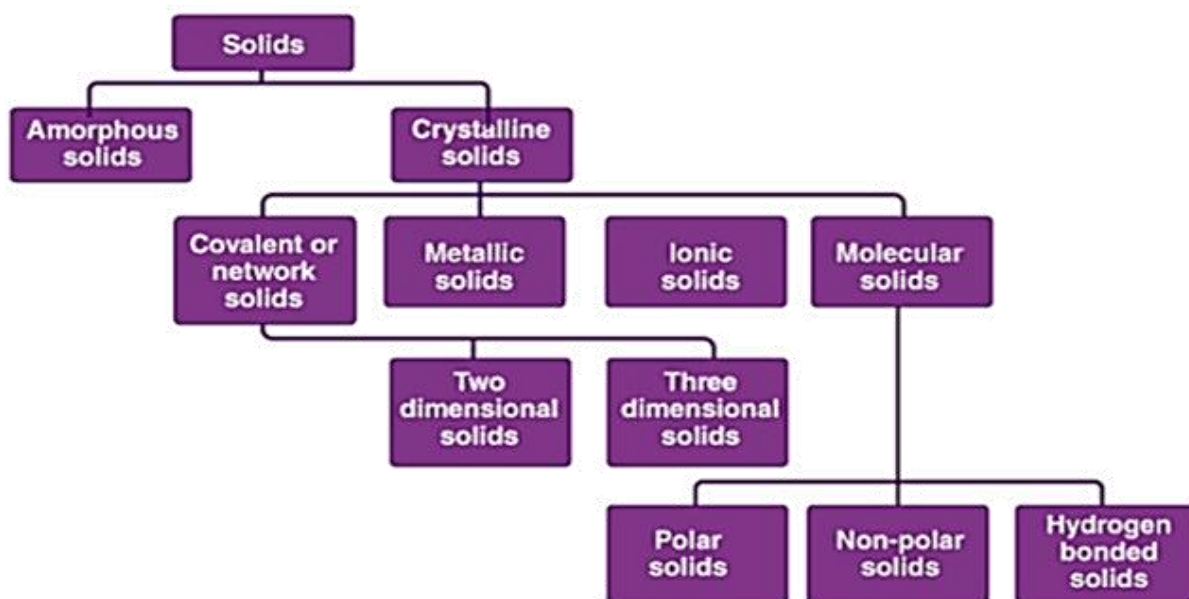
It is also used for packaging cosmetics like cosmetics box and packing of food like food jar

PROPERTY	CRYSTALLINE SOLIDS	AMORPHOUS SOLIDS
Shape	Definite shape	Irregular shape
Melting Point	Sharp melting point	Gradually soften over a range of temperature
Cleavage property	Crystalline solids tend to split into two pieces with plane surfaces.	Amorphous solids give irregular shape that means they break into two pieces with irregular shape.
Heat of fusion	Have definite heat of fusion	Do not have definite heat of fusion.
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids
Order in arrangement of constituent particles	Long range order	Short range order

Classification of crystalline solids:

Crystalline solids can be divided into four types on the basis of the natural intermolecular potential:

1. Ionic solid
2. A solid or solid network
3. Solid molecular weight
4. Solid metals



Crystal lattices and Unit Cells

The main components of crystalline solids are the normal state and the repetitive pattern of the composite particles.

Crystal Lattice

Crystals are made up of three-dimensional patterns. Thus, a crystal lattice is a set of endless, organized points related to each other by temporary symmetry. Drawings of such patterns are called lattices. The lattice is made up of three interlocking planes.

Features of crystal lattice

- Each point in the lattice is called a lattice point or lattice point.
- Each point represents a single particle, such as an atom, a molecule, or an ion.
- The lattice point is combined with straight lines to extract the geometry of the lattice.

Cell Unit

The smallest repeating unit of the crystal lattice is the unit cell, the building block of a crystal.

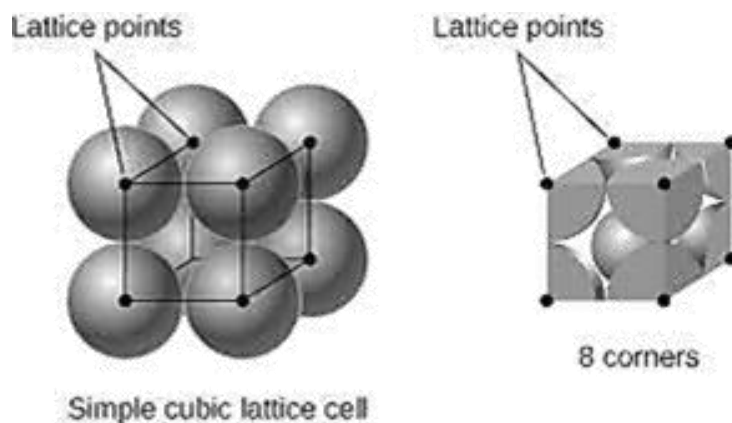
CELL UNIT TYPES

- Primitive Unit Cell - Particles are present only in the corner of the cell unit.
- Body-Centred Unit Cell - One part of the particle is located in the body surface and in eight corners
- Face Centred Unit Cell - Particles are located in eight corners and are located in the center of the face.
- End centred Unit Cell - Particles are in eight corners and two facing areas.

S. No.	Crystal System	Edge length	Angles	Unit cell found	Examples
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	SC, BCC, FCC (3)	NaCl, ZnS, Fe, Al, Cu, C (diamond), CsCl, Na_2O , CaF_2 , KCl, Pb, Alum.
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SC, BC (2)	Sn (white tin), SnO_2 , TiO_2 , ZnO_2 , NiSO_4 , urea.
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SC, BC, FC, EC (4)	Rhombic sulphur, BaSO_4 , KNO_3 , PbCO_3 , CaCO_3 (aragonite)
4	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$ $\beta \neq 120^\circ, \neq 90^\circ, \neq 60^\circ$	SC, EC (2)	Monoclinic sulphur, PbCrO_4 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	SC (1)	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3
6	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$ $\gamma = 120^\circ$	SC (1)	Graphite, ZnO, CdS, Mg, PbI_2 , SiC.

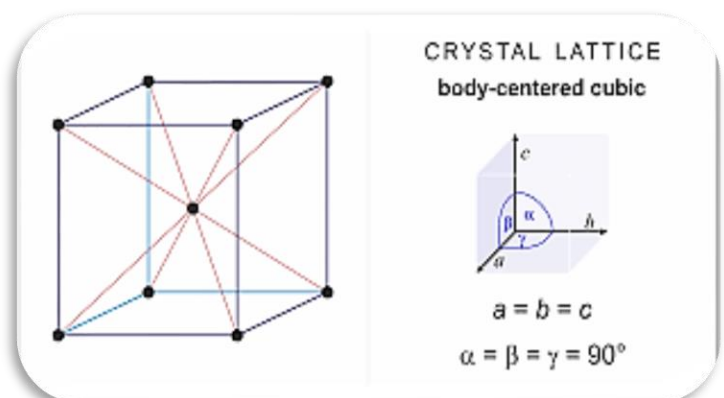
Number of Atoms in a Unit Cell

Primitive Unit Cell - The primitive cubic unit cell has atoms in its corner only. Each atom in the corner is divided between eight unit units of four cell units in the same layer as the four unit units of the upper or lower layer. Thus, only $1/8$ of the atoms actually belong to the unit of a particular cell.



Body Centred Unit Cell

A cubic unit centred on the body has atom in each corner and one atom in its center.



Number of atoms in a BCC cell:

(i) $8 \times 1/8$ corners atomic = 1 atom

(ii) 1 physical atom = 1 atom

Total number of atoms per cell unit = 2 atoms

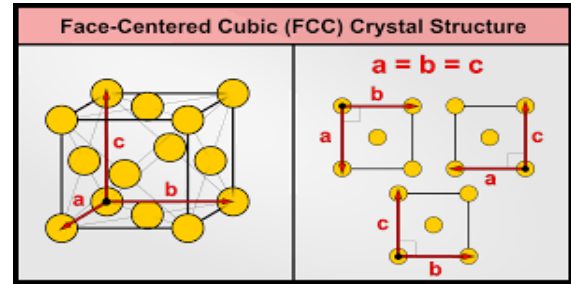
Face Centred Unit Cell

A surface-based cubic unit cell contains atoms in all corners and in the center of each cube surface. The atom present in the surface area is divided between 2 adjacent units and only 1/2 of each atom of each cell.

(i) 8 existing atoms $\times$ 1/8 existing atom = 1 atom

(ii) 6 faces - medium atom $\times$ 1/2 atoms per unit = 3 atoms

Atoms per unit = 4 atoms



End Centred Unit cell

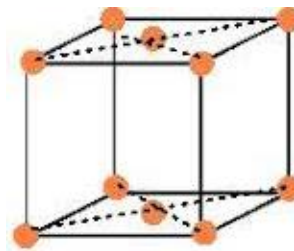
The center of the cell in the middle is made up of atoms in each corner and in the center of the two facing faces. The atom present in the surface area is divided between 2 adjacent units and only 1/2 of each atom of each cell.

Number of atoms in the cell of the central unit

(i) 8 existing atoms $\times$ 1/8 existing atom = 1 atom

(ii) 2 faces are focused on each other $\times$ 1/2 atoms per cell unit = 1 atom

Atoms of each unit = 2 atoms



End Centered Unit Cell

Closed Packed Structures

In solid materials, composite particles are packed close together, leaving a small empty space.

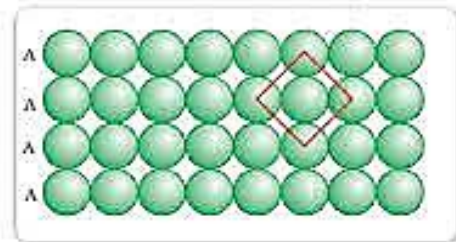
In packing close to one size, the spheres are arranged in a line so that the adjacent atoms are joined together. The contact number is defined as a number of nearby particles. In the case of a one-size-fits-all package, the link number is equal to two.



Fig. : Close packing of spheres in one dimension

(b) Close packing in two Dimensions

In close two-dimensional packaging, a line of closed spheres is stacked to obtain a two-dimensional pattern.

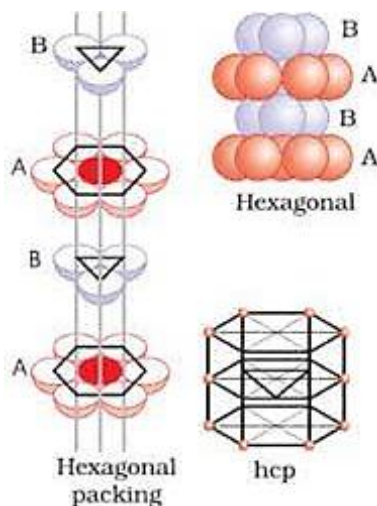


(a)



(b)

(c). Close packing in three dimension

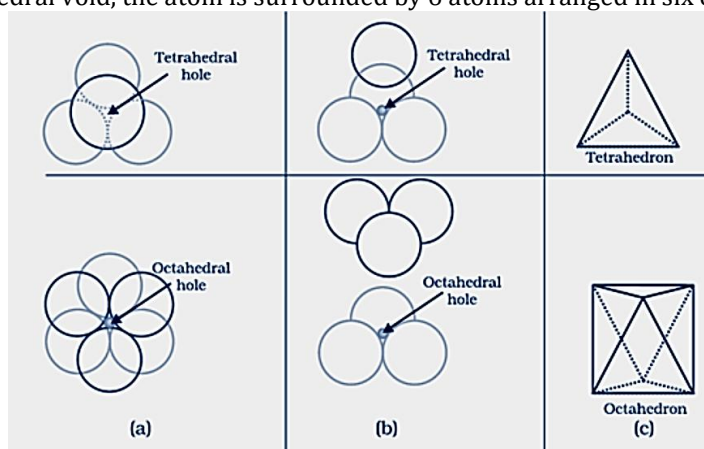


Voids: Voids literally means spaces between partial particles. It defines a space as an empty space in a unit cell or an empty space in a cell unit. Spaces in solid conditions mean the empty space between the particles that are part of a full structure nearby.

Types of voids	
Tetrahedral voids	
Octahedral voids	

Tetrahedral Voids: In a tetrahedral space, an atom is surrounded by 4 atoms placed on the four corners of the tetrahedron.

Octahedral voids: In the octahedral void, the atom is surrounded by 6 atoms arranged in six octahedron chambers.

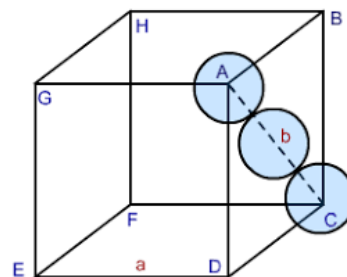


Packing Efficiency

The percentage of total particle-filled space is called the efficiency of the packaging or part of the total space filled.

Packing efficiency in hcp and ccp Structures:

Hexagonal close packing (hcp) and cubic close packing (ccp) have similar packaging properties.

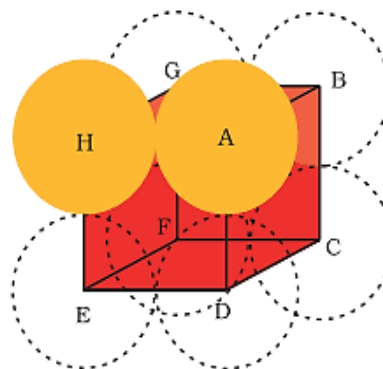
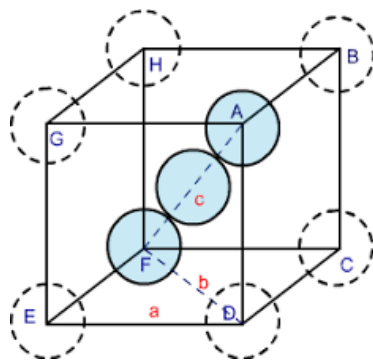


Packing Efficiency in Body-Centred Unit Cell

In a cubic unit cell, one atom is found in the center of the body outside the cube corners.

Packing Efficiency in simple Cubic Lattice

In a simple cubic unit cell, atoms are found in the corners of the cube.



Calculation involving unit cell dimension

A cell unit can be defined as a three-dimensional structure consisting of one or more atoms. We can determine the volume of this cell unit by knowing the size of the cell unit.

Weight of cell unit = number of atoms per cell unit $\times$ weight of each atom = $z \times m$

There, z = the number of atoms in a cell unit, m = The weight of each atom

Bulk atoms can be supplied with the help of Avogadro number and molar mass such as:

M / N_A

When M = molar weight

N_A = Avogadro number

Volume of a cell unit, $V = a^3$

$\Rightarrow$ Cell unit density = cell unit weight / unit cell capacity

$\Rightarrow$ Cell unit density = $m / V = z \times m / a^3 = z \times M / a^3 \times N_A$

Imperfections in Solids

Although solid crystals have a short distance and a long line arrangement in the arrangement of the particles they form, yet the crystals are not perfect. Crystalline solids are made up of a large number of small particles. These particles have a defect in them. This happens when the crystalline process takes place at a very real level.

Defects: Defects in particle structure are known as defects.

Types of defects:

Point defect, line defect

Point defect: irregularities or deviation from the correct arrangement near a point or atom in a crystal object is known as a point element.

Line defect: irregularities or deviations from good alignment across all lattice point lines.

STRUCTURE OF SOME CRYSTALS						
S. No.	Crystal	C.N		Z	Structural arrangement	E.g.
		Cation	Anion	Total Formula Unit		
1	NaCl	6	6	$Na^{+} = 4$ $Cl^{-} = 4$	Na^{+} = at All octahedral voids $Cl^{-} \rightarrow$ FCC	LiCl
2.	ZnS (wurtzite)	4	4	$Zn^{2+} = 6$ $S^{2-} = 6$	$Zn^{2+} =$ At $\frac{1}{2}$ TV $S^{2-} =$ HCP	Ag I
3.	ZnS (Blende)	4	4	$Zn^{2+} = 4, S^{2-} = 4$	$Zn^{2+} =$ At $1/2$ of TV S_2^2 FCC	CuCl, CuBr CuI, Cds
4.	CaF ₂ (Fluorite)	8	4	$Ca = 4, F^{-} = 8$	$Ca^{2+} =$ FCC, $F^{-} =$ All TV	BaF SrF
5.	Na ₂ O	4	8	$Na^{+} = 8, O^{2-} = 4$	$Na^{+} =$ All TV, $O^{2-} =$ FCC	
6.	CsCl	8	8	$Cs^{+} = 1, Cl^{-} = 1$	$Cr^{+} =$ Body Center $Cl^{-} =$ At corners	CsC, N CsI, Cas

Types of point defect:

1. **Stoichiometric defect:** Stoichiometric defect is an internal defect in which the ratio of cations to anions remains exactly the same as represented by the molecular formula. They are also called intrinsic or thermodynamic defect. There are two types of stoichiometric defects: Space and interstitial deformity.

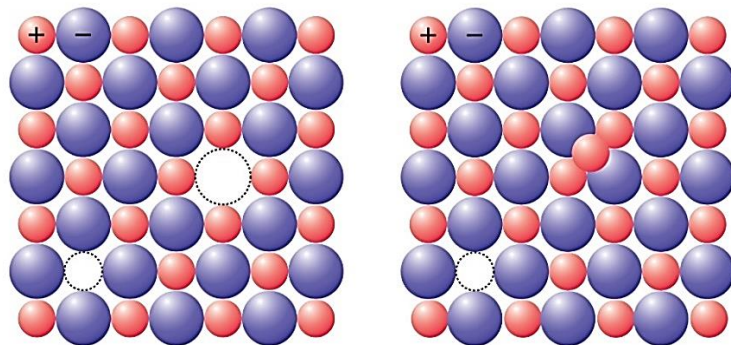
→ **Vacancy defect** - a gap in space where the atom is not in its lattice areas which causes that lattice area to be empty and creates a space problem.

→ **Interstitial defect** - When certain particles (atoms or molecules) replace interstitial, the crystal is said to have interstitial defects.

Space and interstitial defects as described above can be shown by strong non-ionic substances.

There are two types of stoichiometric feature: schottky and frenkel defect (indicated by ionic solids)

→ **Schottky Defects:** Schottky defects occur when equal numbers of cations and anions are not in the lattice. But for ionic compounds, we need to measure the electrical neutrality of the compound so that an equal amount of anions and cations are not present in the compound. Reduce object congestion. In this case, the size of the cations and anions is almost the same.



(a) Schottky defect

(b) Frenkel defect

→ **Frenkel defect** - Frenkel defect occurs when the ion is not in its actual lattice position and takes up any interstitial position.

2. **Impurity defect:** These problems arise when foreign atoms are present in the lattice space instead of the host atom. Or it exists on an unoccupied interstitial site for example n - semiconductor type, p - semiconductor type. Example - If the molten NaCl containing a small amount of SrCl_2 is crystalline, other Na^+ ion sites are used by Sr^{2+} . Each Sr^{2+} replaces two Na^+ ions. It stays in one ion zone and the other site remains empty. The cationic gaps produced are equal in value to Sr^{2+} ions



Cation vacancy in NaCl

3. **Non-Stoichiometric defect:** Nonstoichiometric defects are defects in crystal structures that interfere with crystal stoichiometry. Effect on Stoichiometry. They do not affect compound stoichiometry. They changed the stoichiometry of the compound.

These problems are of two types: excess iron and a lack of iron.

- ➔ **Excess iron deficiency** - It is a severe ion damage when deviation from the normal structure occurs due to the absence of iron ions in the two lattice zones. Let's take an example: When NaCl crystal is heated in sodium vapor! It changes color to yellow.
- ➔ **Metal defect defect** - a) In the event of a metal deficiency, the cation is not in its lattice position. To maintain electrical neutrality, one of the adjacent metal ions receives additional direct charge.
- (b) This type of feature occurs on computers when the instrument shows a variable valency e.g. Transition metal complexes such as NiO, FeO, FeS, etc.

Electrical Properties

Solids can be divided into three categories on the basis of their flow. These are:

Conductor - conductivities ranging from between 10^4 to $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$

Insulator - Conductivity ranging from 10^{-20} to $10^{-10} \text{ ohm}^{-1} \text{ m}^{-1}$.

Semiconductor - conductivities in the range from 10^{-6} to $10^{-4} \text{ ohm}^{-1} \text{ m}^{-1}$

Magnetic Properties

To study the magnetic field of the Magnetic field, materials are often placed in the same magnetic field and the magnetic field varies. There are five major types of magnetic behaviour:

- (i) **Diamagnetic Materials** - Diamagnetic objects are slightly driven by the magnetic field and do not retain the magnetic field when the outer field is removed.
Example - bismuth, copper, antimony.
- (ii) **Pararamagnetic Materials** - Pararamagnetic Appliances are less attracted to the magnetic field and do not retain the magnetic properties when removing the outer field.
For example - aluminum, gold, copper.
- (iii) **Ferromagnetic Materials** - Ferromagnetic materials are those devices that show the automatic magnetism of the net at the atomic level, even without the outer magnetic field. When placed on the surface of a magnetic field, ferromagnetic elements pull harder toward the field.
Iron, nickel, and cobalt are examples of ferromagnetic substances
- (iv) **Antiferromagnetic materials** - Materials that reflect antiferromagnetism are known as antiferromagnetic material. When these objects are stored in front of a strong magnetic field, they weaken the magnetic field toward the magnetic field. This is known as antiferromagnetism. Examples include hematite, metals such as chromium, alloys such as iron manganese (FeMn), and oxides such as nickel oxide (NiO).
- (v) **Ferrimagnetic Materials** - A ferrimagnetic material is a substance with atomic numbers with opposing magnetic moments, as in antiferromagnetism. As for ferrimagnetic materials, these times are not equal in size and therefore the automatic magnetization remains. Ferrimagnetism is often confused with ferromagnetism. An excellent example of a ferrimagnetic mineral is magnetite (Fe_3O_4). Two irons are trivalent, while one is divalent. Two trivalent ions are inversely proportional to each other and cancel out the other, so the net moment comes from the split metal ion.

SUMMARY

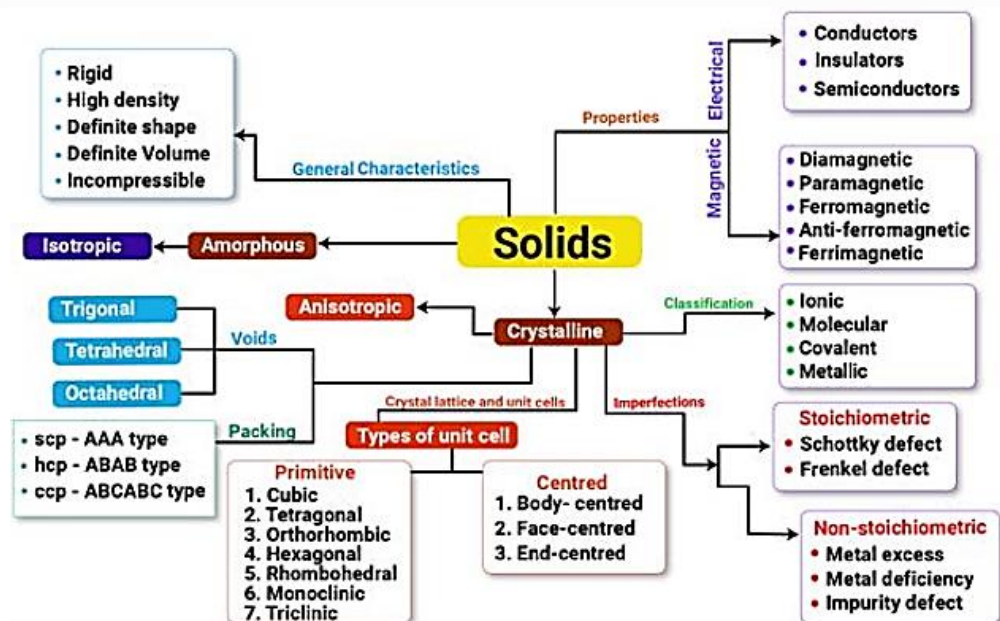
Solids have definite shape, definite volume and mass. This is because of fixed position of their constituent particles, short distances and strong interaction between them. In amorphous solids, the arrangement of constituent particles has only short range order and consequently they behave like super cooled liquids, do not have high melting points and are isotropic in nature. In crystalline solids there is long range order in the arrangement of their constituent particles. They have high melting points, are anisotropic in nature and their particles have characteristic shapes. Properties of crystalline solids depend upon the nature of interaction between their constituent particles. On the basis, they can be divided into four categories, namely: molecular, ionic, metallic and covalent solids. They differ widely in their properties.

The constituent particles in crystalline solids are arranged in a regular pattern which extends throughout the crystal. This arrangement is often depicted in the form of a three dimensional array of points which is called crystal lattice. Each lattice point gives the location of one particle in space. In all, fourteen different types of lattices are possible which are called Bravais lattices. Each lattice can be generated by repeating its small characteristics portion called unit cell. A unit cell is characterized by its edge lengths and three angles between these edges. Unit cells can be either primitive which have particles only at their body position or centred. The centred unit cells have additional particles at their body center, at the centre of each face or at the centre of two opposite faces. There are seven types of primitive unit cells. Taking centred unit cell also into account, there are fourteen types of unit cells in all, which result in fourteen Bravais lattices.

Close-packing of particles result in two highly efficient lattice, hexagonal close-packed and cubic packed. The latter is also called face-centred cubic lattice. In both of these packing 74% space is filled. The remaining space is present in the form of two types of voids-octahedral voids and tetrahedral voids. Other types of packing are not close-packings and have less efficient packing of particles. While in body-centred cubic lattice 68% space is filled, in simple cubic lattice only 52.5% space is filled.

Solids are not perfect in structure. There are different types of imperfections or defects in them. Point defects and line defects are common types of defects. Point defects are of three types – stoichiometry defects, impurity defects and non-stoichiometric defects. Vacancy defects and interstitial defects are the two basic types of stoichiometry point defects. In ionic solids, these defects are present as Frenkel and Schottky defects. Impurity defects are caused by the presence of an impurity in the crystal. In ionic solids, when the ionic impurity has a different valence than the main compound, some vacancies are created. Non-stoichiometric defects are of metal excess type and metal deficient type. Sometimes calculated amounts of impurities are introduced by doping in semiconductor that changes their electrical properties. Such materials are widely used in electronics industry. Solids show many types of magnetic properties like Para magnetism, diamagnetism, ferromagnetism, antiferromagnetism and ferromagnetism. These properties are used in audio, video and other recording devices. All these properties can be correlated with their electronic configuration or structures.

MIND MAP



MULTIPLE CHOICE QUESTIONS

1. Glass is a
(a) Liquid
(b) Solid
(c) Supercooled liquid
(d) Transparent organic polymer
2. Cation and anion combines in a crystal to form following type of compound
(a) Ionic (b) Metallic
(c) Covalent (d) Dipole-dipole
3. The ability of a substance to assume two or more crystalline structures is called
(a) Isomerism (b) Polymorphism
(c) Isomorphism (d) Amorphism
4. The number of carbon atoms per unit cell of diamond unit cell is
(a) 6 (b) 1
(c) 4 (d) 8
5. The fcc crystal contains how many atoms in each unit cell?
(a) 6 (b) 8
(c) 4 (d) 5
6. A solid compound XY has NaCl structure. If the radius of the cation is 100pm, the radius of the anion (Y-) will be
(a) 275.1 pm (b) 322.5 pm
(c) 241.5 pm (d) 165.7 pm
7. In the fluorine structure, the coordination number of Ca^{2+} ion is
(a) 4 (b) 6
(c) 8 (d) 3
8. The vacant space in bcc lattice unit cell is
(a) 48% (b) 923%
(c) 1032% (d) 1126%
9. Which of the following statement is correct
(a) The number of carbon atoms in a unit cell of diamond is 8
(b) The number of Bravais lattice in which a crystal can be categorised is 14
(c) The fraction of the total volume occupied by the atoms in a primitive cell is 0.48
(d) Molecular solids are generally volatile
10. The appearance of colour in solid alkali metal halides is generally due to
(a) Interstitial position (b) F-centres
(c) Schottky defect (d) Frenkel defect
11. Which of the following is not a characteristic property of solids?
(a) Intermolecular distances are short.
(b) Intermolecular forces are weak.
(c) Constituent particles have fixed positions.
(d) Solids oscillate about their mean positions.
12. Most crystals show good cleavage because their atoms, ions or molecules are
(a) Weakly bonded together
(b) Strongly bonded together
(c) Spherically symmetrical
(d) Arranged in planes
13. Which of the following is not a crystalline solid?
(a) KCl (b) CsCl
(c) Glass (d) Rhombic S
14. "Crystalline solids are anisotropic in nature. What is the meaning of anisotropic in the given statement?
(a) A regular pattern of arrangement of particles which repeats itself periodically over the entire crystal.
(b) Different values of some of physical properties are shown when measured along different directions in the same crystals.
(c) An irregular arrangement of particles over the entire crystal.
(d) Same values of some of physical properties are shown when measured along different directions in the same crystals.
15. A crystalline solid
(a) Changes abruptly from solid to liquid when heated
(b) Has no definite melting point
(c) Undergoes deformation of its geometry easily
(d) Has an irregular 3-dimensional arrangements
16. In Zinc blende structure
(a) Zinc ions occupy half of the tetrahedral sites
(b) Each Zn^{2+} ion is surrounded by six sulphide ions
(c) Each S^{2-} ion is surrounded by six Zn^{2+} ions
(d) It has fee structure
17. Alkali halides do not show Frenkel defect because
(a) Cations and anions have almost equal size
(b) There is a large difference in size of cations and anions
(c) Cations and anions have low coordination number
(d) Anions cannot be accommodated in voids
18. The fraction of the total volume occupied by the atoms present in a simple cube is
(a) $\pi/4$ (b) $\pi/6$
(c) $\pi/3\sqrt{2}$ (d) $\pi/4\sqrt{2}$
19. p-type semiconductors are formed When Si or Ge are doped with
(a) Group 14 elements (b) Group 15 elements
(c) Group 13 elements (d) Group 18 elements
20. Which of the following conditions favours the existence of a substance in the solid state?
(a) High temperature (b) Low temperature
(c) High thermal energy (d) Weak cohesive forces

21. How many lithium atoms are present in a unit cell with edge length 3.5 Å and density 0.53 g cm⁻³? (Atomic mass of Li = 6.94):
 (a) 2 (b) 1
 (c) 4 (d) 6
22. Fe₃O₄ (magnetite) is an example of
 (a) Normal spinel structure
 (b) Inverse spinel structure
 (c) Fluoride structure
 (d) Anti fluorite structure
23. Which of the following crystals does not exhibit Frenkel defect?
 (a) AgBr (b) AgCl
 (c) KBr (d) ZnS
24. NaCl type crystal (with coordination no.6 : 6) can be converted into CsCl type crystal (with coordination no.8 : 8) by applying
 (a) High temperature
 (b) High pressure
 (c) High temperature and high pressure
 (d) Low temperature and low pressure
25. In NaCl structure
 (a) All octahedral and tetrahedral sites are occupied
 (b) Only octahedral sites are occupied
 (c) Only tetrahedral sites are occupied
 (d) Neither octahedral nor tetrahedral sites are occupied
26. What is the effect of Frenkel defect on the density of ionic solids?
 (a) The density of the crystal increases
 (b) The density of the crystal decreases
 (c) The density of the crystal remains unchanged
 (d) There is no relationship between density of a crystal and defect present in it
27. To get n-type of semiconductor, germanium should be doped with
 (a) Gallium (b) Arsenic
 (c) Aluminium (d) Boron
28. Which of the following is not the characteristic of ionic solids?
 (a) Very low value of electrical conductivity in the molten state.
 (b) Brittle nature.
 (c) Very strong forces of interactions.
 (d) Anisotropic nature.
29. In a trigonal crystal
 (a) $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$
 (b) $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
 (c) $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
 (d) $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$
30. Polar crystals when heated produce small electrical current. The phenomenon is called
 (a) Ferroelectricity
 (b) Anti-ferroelectricity
 (c) Pyroelectricity
 (d) Piezoelectricity
31. Volume occupied by atoms in fcc is
 (a) 74% (b) 68%
 (c) 52.4% (d) 75%
32. Na and Mg crystallize in crystals of bcc and fcc form respectively and then the amount of Na and Mg atoms present in their respective crystal unit cells is:
 (a) 4 and 2 (b) 9 and 14
 (c) 14 and 9 (d) 2 and 4
33. Ferrous oxide has a cubic structure and each unit cell edge is 5.0 Å. Assuming the oxide density is 4.0 g / cm³, the amount of Fe²⁺ and O²⁻ ions in each unit cell will then be
 (a) Four Fe²⁺ and four O²⁻
 (b) Two Fe²⁺ and four O²⁻
 (c) Four Fe²⁺ and two O²⁻
 (d) Three Fe²⁺ and three O²⁻
34. Schottky defect in a crystal is observed when
 (a) The ion leaves its normal position and occupies an interstitial location
 (b) The unequal number of cation and anions are missing from the lattice
 (c) The density of the crystal increases.
 (d) An equal number of cations and anions are missing from the lattice.
35. For the orthorhombic system, axial ratios are $a \neq b \neq c$ and the axial angles are:
 (a) $\alpha = \beta = \gamma \neq 90^\circ$ (b) $\alpha \neq \beta \neq \gamma \neq 90^\circ$
 (c) $\alpha = \beta = \gamma = 90^\circ$ (d) $\alpha \neq \beta \neq \gamma = 90^\circ$
36. Which of the following transition metal oxides is paramagnetic?
 (a) TiO (b) VO
 (c) Cu₂O (d) Mn₂O₃
37. Which of the following transition metal oxides is not an insulator?
 (a) MnO (b) NiO
 (c) VO (d) Mn₂O₃
38. Coordination number in ccp and hcp arrangements of metal atoms are respectively.
 (a) 6, 6 (b) 12, 6
 (c) 8, 6 (d) 12, 12
39. Fe₃O₄ is ferrimagnetic at room temperature but at 850 K it becomes
 (a) Diamagnetic (b) Ferromagnetic
 (c) Non-magnetic (d) Paramagnetic
40. For tetrahedral coordination, the radius ration (r_+/r_-) should be
 (a) 0.155-0.225 (b) 0.225-0.414
 (c) 0.414-0.732 (d) 0.732-1

41. A compound formed by elements A and B crystallises in the cubic structure where A atoms are at corners of a cube and B atoms are at face centres. The formula of the compound is
 (a) AB₃ (b) A₂B
 (c) AB₂ (d) A₂B₃
42. How many space lattices are possible in a crystal?
 (a) 23 (b) 7
 (c) 230 (d) 14
43. Metallic lustre is explained by
 (a) Diffusion of metal ions
 (b) Oscillation of loose electrons
 (c) Excitation of free protons
 (d) Existence of bcc lattice.
44. The hardest substance among the following is
 (a) Be₂C (b) Graphite
 (c) Titanium (d) SiC
 (e) B₄C
45. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g? (Atomic mass of Na = 23, Cl = 35.5)
 (a) 5.14×10^{21} (b) 1.28×10^{21}
 (c) 1.71×10^{21} (d) 2.57×10^{21}
46. If Z is the number of atoms in the unit cell that represents the closest packing sequence....ABC ABC....the number of tetrahedral voids in the unit cell is equal to
 (a) Z (b) 2Z
 (c) Z/2 (d) Z/4
47. Which has no rotation of symmetry?
 (a) Hexagonal (b) Orthorhombic
 (c) Cubic (d) Triclinic
48. The interionic distance for cesium chloride crystal will be
 (a) a (b) a/2
 (c) $\sqrt{3} a/2$ (d) $2a/\sqrt{3}$
49. Which of the following metal oxides is antiferromagnetic in nature?
 (a) MnO₂ (b) TiO₂
 (c) VO₂ (d) CrO₂
50. The liquified metal expanding on solidification is
 (a) Ga (b) Al
 (c) Zn (d) Cu

ASSERTION AND REASON

1. Assertion: No compound has both Schottky and Frenkel defects.
 Reason: Both defects change the density of the solid.
 (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

- (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.

2. **Assertion:** Stability of a crystal is reflected in the magnitude of its melting.
Reason: The stability of a crystal depends upon the strength of the interparticle attractive force.
 (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
3. **Assertion:** Due to Frenkel defect, there is no effect on the density of the crystalline solid.
Reason: In Frenkel defect, no cation or anion leaves the crystal.
 (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
4. **Assertion:** On heating ferromagnetic or ferrimagnetic substances, they become paramagnetic.
Reason: The electrons change their spin on heating.
 (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
5. **Assertion:** In close packing of spheres, a tetrahedral void is surrounded by four spheres whereas an octahedral void is surrounded by six spheres.
Reason: A tetrahedral void has a tetrahedral shape whereas an octahedral void has an octahedral shape.
 (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.

TRUE AND FALSE

1. Amorphous solids are isotropic in nature.
 (a) True
 (b) False
2. A primitive unit cell contains constituent particles only at corners.
 (a) True
 (b) False
3. Cubic systems possess only primitive unit cell.
 (a) True (b) False.

PRACTICE QUESTIONS (MCQ)

1. Titanium metal has a density of 4.54 g/cm^3 and an edge length of 412.6 pm . In what cubic unit cell does titanium crystallise? ($T_i = 48$)
 (a) Fcc (b) Bcc
 (c) Simple cubic (d) None of these
2. MgO has a structure of NaCl and TiCl has the structure of CsCl. What are the coordination numbers of ions in each (MgO and TiCl).
 (a) 6, 6 (b) 7, 7
 (c) 8, 8 (d) 4, 4
3. A solid AB has the NaCl structure, If radius of cation A^+ is 120 pm , calculate the maximum possible value of the radius of the anion B^- .
 (a) 280 pm (b) 290 pm
 (c) 310 pm (d) 350 pm
4. The C.N. of the barium ion Ba^{2+} , in BaF_2 is 8. What must be the C.N. of F^- ion?
 (a) 2 (b) 4
 (c) 6 (d) 8
5. Sodium metal crystallises in body centred cubic lattice with cell edge = $4.29 \text{ \AA}$. What is radius of sodium atom?
 (a) $1.86 \text{ \AA}$ (b) $2.76 \text{ \AA}$
 (c) $1.08 \text{ \AA}$ (d) $2.90 \text{ \AA}$
6. Calculate the edge length of the unit cell of sodium chloride given density of NaCl is $2.17 \times 10^3 \text{ kg m}^{-3}$ and molecular weight $58.5 \times 10^{-3} \text{ kg mol}^{-1}$.
 (a) 524 pm (b) 564 pm
 (c) 565 pm (d) 545 pm
7. The effective radius of an iron atom is $1.42 \text{ \AA}$. It has a rock-salt structure. Calculate its density ($Fe = 56$).
 (a) 5.74 g/cm^3
 (b) 645 g/cm^3
 (c) 3.54 g/cm^3
 (d) 4.56 g/cm^3
8. In a CPS (close packed structure) of mixed oxides, it is found that lattice has O^{2-} (oxide ions), and one-half of octahedral voids are occupied by trivalent cations (A^{3+}) and one-eighth of tetrahedral voids are occupied by divalent cations (B^{2+}). Derive formula of the mixed oxide.
 (a) A_2BO_4 (b) AB_2O_4
 (c) A_3B_4O (d) None of these
9. If the length of body diagonal for CsCl, which crystallise into a cubic structure with Cl^- ions at the corner and Cs^+ ions at the centre of unit cell, is $7 \text{ \AA}$ and the radius of Cs^+ ion is $1.69 \text{ \AA}$, what is the radius of Cl^- ion?
 (a) $1.9 \text{ \AA}$ (b) $1.7 \text{ \AA}$
 (c) $1.8 \text{ \AA}$ (d) $2.0 \text{ \AA}$
10. Chromium metal crystallizes with a body centred cubic lattice. The length of the unit cell edge is found to be 287 pm . Calculate the atomic radius. What would be the density of chromium in g/cm^3 ?
 (a) 124.3 pm (b) 134.4 pm
 (c) 232.0 pm (d) 342.3 pm
11. A solid X melts slightly above 273K and is a poor conductor of heat and electricity. To which of the following categories does it belong:
 (a) Ionic solid (b) Covalent solid
 (c) Metallic (d) Molecular
12. In a crystal, the atoms are located at the position of:
 (a) Zero P.E. (b) Infinite P.E.
 (c) Minimum P.E. (d) Maximum P.E.
13. Amorphous solids :
 (a) Possess sharp melting points
 (b) Undergo clean cleavage when cut with knife
 (c) Do not undergo clean cleavage when cut with knife
 (d) Possess orderly arrangement over long distances
14. A compound formed by elements A and B has a cubic structure in which A atoms are at the corners of the cube and B atoms are at the face centres. Derive the formula of the compound.
 (a) AB (b) AB_2
 (c) AB_3 (d) AB_4
15. A cubic solid is made up of two elements X and Y. Atoms Y are present at the corners of the cube and atoms X at body centre. What is the formula of the compound?
 (a) XY (b) XY_2
 (c) X_2Y (d) XY_3
16. At room temperature, polonium crystallises in primitive cubic unit cell. If $a = 3.36 \text{ \AA}$, calculate the theoretical density of polonium. Molar mass M of polonium = 209 g/mol .
 (a) $9.15 \times 10^3 \text{ kg/m}^3$ (b) $8.12 \times 10^3 \text{ kg/m}^3$
 (c) $3.14 \times 10^3 \text{ kg/m}^3$ (d) $7.16 \times 10^3 \text{ kg/m}^3$
17. An organic compound crystallises in an orthorhombical cell in the ratio of 2:1. The dimensions of cell are 12.05 , 15.05 and $2.69 \text{ \AA}$ and density is 1.419 g/cm^3 , find molar density of the compound
 (a) 207 g/mol (b) 209 g/mol
 (c) 308 g/mol (d) 317 g/mol

18. Lithium forms body-centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be
 (a) 75 pm (b) 300 pm
 (c) 240 pm (d) 152 pm
19. Which among the following compounds can show the properties of a Ferroelectric substance?
 (a) CrO_2 (b) BaTiO_3
 (c) PbZrO_3 (d) MnO_2
20. Which of the following is not a crystal system?
 (a) Hexagonal (b) Cubic
 (c) Trigonal (d) Triclinic
21. Which type of crystalline solid is also called as giant molecules?
 (a) Metallic solids (b) Ionic solids
 (c) Covalent solids (d) Polar molecular solids
22. Silicon is found in nature in the forms of
 (a) body-centered cubic structure
 (b) hexagonal-closed packed structure
 (c) network solid
 (d) face-centered cubic structure
23. Copper crystallises in fcc lattice with a unit cell edge of 361 pm. The radius of copper atom is
 (a) 181 pm (b) 108 pm
 (c) 128 pm (d) 157 pm
24. The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of anion is
 (a) 288 pm (b) 398 pm
 (c) 618 pm (d) 144 pm
25. Which of the following are responsible for high electrical and thermal conductivity of a metal?
 (a) Ions
 (b) Covalent bonds
 (c) Free H^+ ions
 (d) Free and mobile electrons
26. Which type of solids are formed by three-dimensional arrangement of cations and anions bound by strong electrostatic force?
 (a) Polar molecular solids
 (b) Ionic solids
 (c) Covalent solids
 (d) Metallic solids
27. The molecules in polar molecular solid are held together by
 (a) dipole-dipole interaction

- (b) London forces
 (c) ionic bond
 (d) metallic bond

- Q28. The radius ratio in CsCl is 0.93. The expected lattice structure is
 (a) Tetrahedral
 (b) Square planar
 (c) Octahedral
 (d) Body centred cubic
29. The cubic unit cell of Al has an edge length of 405 pm. Its density is 2.7 g/cm^3 . The cubic unit cell is
 (a) Face centred
 (b) Body centred
 (c) Primitive
 (d) Edge centred
 (e) Simple
30. The radius of Na^+ and Cl^- ions are 95 pm and 181 pm respectively. The edge length of NaCl unit cell is
 (a) 276 pm
 (b) 138 pm
 (c) 552 pm
 (d) 415 pm

ASSERTION AND REASON

1. **Assertion:** The total number of atoms present in a simple cubic unit cell is one.
Reason: Simple cubic unit cell has atoms at its corners, each of which is shared between eight adjacent unit cells.
 (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
2. **Assertion:** Graphite is a good conductor of electricity however diamond belongs to the category of insulators.
Reason: Graphite is soft in nature on the other hand diamond is very hard and brittle.
 (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.

3. **Assertion:** Total number of octahedral voids present in unit cell of cubic close packing including the one that is present at the body center, is four.

Reason: Besides the body center there is one octahedral void present at the center of each of the six faces of the unit cell and each of which is shared between two adjacent unit cells.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
4. **Assertion:** The packing efficiency is maximum for the fcc structure.
Reason: The coordination number is 12 in fcc structures.
 (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.

TRUE AND FALSE

1. A particle present at the body centre is not shared by any other unit cell.
 (a) True (b) False
2. The unit cell of a face-centred cubic system contains 2 atoms.
 (a) True (b) False
3. The percentage of the occupied space in a face-centred unit cell is 74 %
 (a) True (b) False
4. In hcp, the arrangement is of the type A B C A B C...
 (a) True (b) False

SOLUTIONS MULTIPLE CHOICE

1. (c) supercooled liquid
 Glass is an example of amorphous solid. It is also known as supercooled liquid. Glass have short range order of constituents.
2. (a) Ionic
 Cation is a positively charged species and anion is a negatively charged species. We know that opposite charges always attract each other and this force of attraction is called the electrostatic force of attraction. It leads to the formation of ionic compounds. An example of an ionic compound is sodium chloride (NaCl).
3. (b) Polymorphism
 The phenomenon of occurrence of a substance in two or more crystalline structures is called polymorphism.
4. (d) 8
 In the diamond cubic unit cell, there are eight corner atoms, six face centered atoms and four more atoms inside the structure.
 $\therefore$ Number of atoms present in a diamond cubic unit cell
 $= 1 + 3 + 4 = 8$ atoms
5. (c) 4
 The face-centred cubic (FCC) has a coordination number of 12 and contains 4 atoms per unit cell. The atoms in the corner are shared by 8 unit cells and contribute to $1/8$ of themselves to the crystal lattice.
6. (c) 241.5 pm

In NaCl coordination number of each type of ion in solid is 6 and radius ratio is $r^+/r^- = 0.414$.
 Given the radius of cation $r^+ = 100$ pm.
 So, radius of anion $r^- = 100/0.414 = 241.5$ pm.

7. (c) 8
 In fluorite structure each Ca^{2+} ion is surrounded by eight F^- ions. Thus, the coordination number of Ca^{2+} is eight. In fluorite structure each FX^- ion is surrounded by four Ca^{++} ions whereas each Ca^{++} is surrounded by eight FX^- ions, giving a body centred cubic arrangement. Thus the coordination number of $Ca^{++} = FX^-$ are 8 and 4.
8. (c) 32%
 Packing fraction of BCC unit cell is 68%. Therefore, the vacant space in BCC unit cell is 32%.
9. (c) The fraction of the total volume occupied by the atoms in a primitive cell is 0.48
10. (b) F-centres
11. (b) Intermolecular forces are strong in solids.
12. (d) Crystals show good cleavage because their constituent particles are arranged in planes.
13. (c) Glass is amorphous solid.
14. (b) Crystalline solids are anisotropic in nature that is some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals.

15. (a) In crystalline solid there is perfect arrangement of the constituent particles only at 0 K. As the temperature increases the chance that a lattice site may be unoccupied by an ion increases. As the number of defects increases with temperature solid changes into liquid.

16. (a) ZnS has a ccp structure. S^{2-} ions are present at the corners of the cube and centre of each face. Zn^{2+} ions occupy half of the tetrahedral sites. Each Zn^{2+} ion is surrounded by four S^{2-} ions and each S^{2-} ion is surrounded by four Zn^{2+} ions.

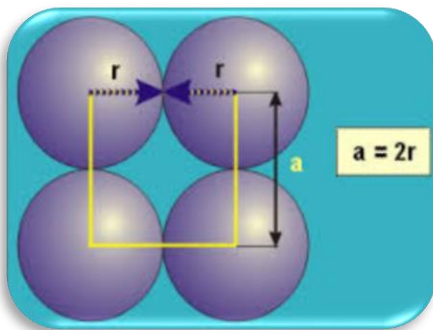
17. (a) Frenkel defect is not shown by alkali metals because cations and anions have almost same size and cations cannot be accommodated in interstitial sites.

18. (b) Let the edge length of the cube be a and the radius of the atom be r .

Now, in simple cube, number of atoms present = $1/8 \times 8 = 1$

So, volume occupied by atoms = $1 \times \frac{4}{3}\pi r^3$

Now, in simple cube atoms at corners will be touching each other.



$$\Rightarrow a = 2r \Rightarrow r = \frac{a}{2}$$

$$\text{Volume of cube} = a^3$$

So, fraction of total volume occupied = Volume of atoms / Volume of unit cell

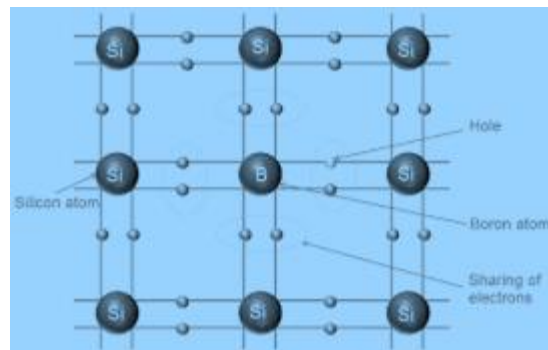
So, fraction of total volume occupied (Atomic Packing fraction) = $\frac{4/3\pi r^3}{a^3}$

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

$$\text{Atomic Packing fraction} = \frac{4}{3} \times \pi \times \frac{1}{8}$$

$$\text{Atomic Packing fraction} = \frac{\pi}{6}$$

19. (c) For Si or Ge to be a p-type semiconductor, they have to be doped with trivalent elements. This will lead to electron scarcity, which is called as hole. For this reason, the elements should be of Group 13.



20. (b) At low temperature substance exists in solid state due to decrease in molecular motion which leads to strong cohesive forces i.e., forces which hold the constituent particles together.

$$\begin{aligned} 21. (a) \quad d &= \frac{z \times m}{N_A \times a^3} \\ Z &= \frac{d \times N_A \times a^3}{m} \\ &= \frac{0.53 \times 6.023 \times 10^{23} \times (3.5 \times 10^{-8})^3}{6.94} \\ &= 2 \end{aligned}$$

22. (b) Fe_3O_4 is an example of inverse spinel. In Fe_3O_4 , oxide ions constitute fcc lattice and dipositive ions are present in octahedral holes and tripositive ions are equally distributed between tetrahedral and octahedral holes. A unit cell of Fe_3O_4 contain $4O^{2-}$, $2Fe^{3+}$ and $1Fe^{2+}$ ions.

23. (c) Condition for Frankel defects in an ionic crystal is- The size difference between the ions should be large.

Smaller ion (cation) move to interstitial site.

Frenkel defect generally appears in ZnS, AgBr, AgI, AgCl etc.

Alkali metal shows Schottky defect. Here KBr exhibits Schottky defect. However, it does not show Frankel defect. ZnS has a large size difference between the ions.

24. (b) The coordination number of a crystal can be increased by applying pressure on it. So, NaCl type crystal can be converted into CsCl type crystal by applying pressure on it.

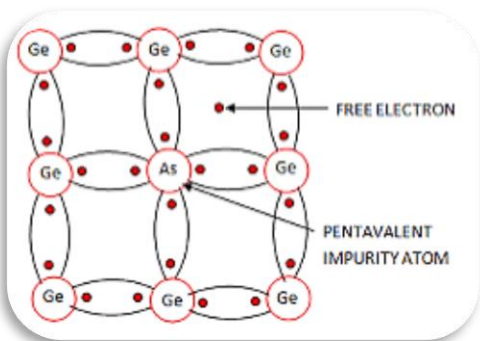
25. (b) In NaCl, Cl^- occupies all corner and face-centered sites and Na^+ occupies all octahedral sites.

26. (c) In Frenkel defect, an ion is displaced from its lattice place to an interstitial place. So, there is no loss or gain of ions in lattice structure.

It involves only the migration of the ions within the crystal, thus preserving both volume and mass.

Therefore, there is no any change in density of the crystal.

27. (b) For germanium to be a N-type semiconductor, it should be doped with group 15 elements. This will lead to excess of electrons.
In the given options, only element which belongs to group 15 is Arsenic.



28. (a)
29. (a) $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$
30. (c) Piezoelectric effect Certain crystal produce electric signals on application of pressure. This phenomenon is called piezoelectricity or piezoelectric effect.

Ferroelectric effect In some crystals the dipoles are permanently aligned up even in the absence of electric field and the direction of polarisation can be changed by applying an electric field. This phenomenon is known as ferroelectricity or ferroelectric effect.

Anti-ferroelectric effect In some crystals there is no net dipole moment inspite of the presence of small dipoles and therefore, they do not exhibit ferroelectric character. This phenomenon is known as anti-ferroelectricity or anti-ferroelectric effect.

Pyroelectric effect Some of the polar crystals when heated produce electric current. This phenomenon is called pyroelectricity or pyroelectric effect.

31. (a) 74%
[HINT]: packing fraction = $4\pi r^3/a^3$
32. (d) 2 and 4
The bcc cell consists of 8 atoms at the corners and one atom at center.
 $\therefore$ Number of atoms (n) = $\left(8 \times \frac{1}{8}\right) + 1 = 2$.
The fcc cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.
 $\therefore$ Number of atoms (n) = $8 \times \frac{1}{8} + \left(6 \times \frac{1}{2}\right) = 4$.
33. (a) Four Fe^{2+} and four O^{2-}
We have given
Density,

$$\text{Volume of the unit cell} = (5 \times 10^{-8})^3 = 1.25 \times 10^{-22} \text{ cm}^3$$

$$\text{Density of FeO} = 4 \text{ g cm}^{-3}$$

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

$$4 = \frac{z \times 72}{(5 \times 10^{-8})^3 \times 6.02 \times 10^{23}}$$

$$Z = \frac{4 \times 12.25 \times 10^{-22} \times 6.02 \times 10^{23}}{72} = 4.18 \cong 4$$

Each unit cell has four units of FeO. So it has four Fe^{2+} and four O^{2-} ions.

34. (d) The equal number of cation and anions are missing from the lattice
Schottky defect is observed when equal number of cations and anions are missing from the lattice. This defect changes the density as a pair of ions are missing from the lattice.

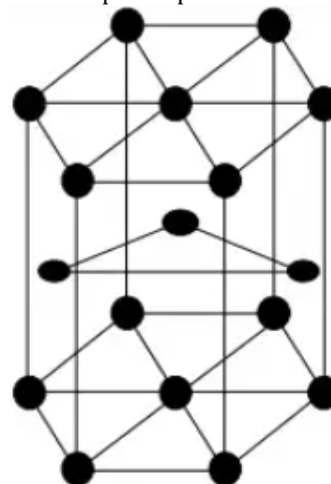
35. (c) $\alpha = \beta = \gamma = 90^\circ$

36. (b) VO

37. (c) VO

38. (d) 12, 12

It can be seen from the figure that the coordination number of hcp or ccp is 12.



39. (d) Paramagnetic
 Fe_3O_4 is ferrimagnetic at room temperature because in its crystals magnetic numbers of Fe (II) and Fe (III) ions are unequal in magnitude and aligned in antiparallel direction. But when heated at 850 K the arrangement randomized and substance becomes paramagnetic.
40. (b) 0.225-0.414
41. (a) AB₃
A atoms are at the corners of the cube. There are 8 corners and each contributes one eighth to the unit cell. Total number of A atoms = $8 \times \frac{1}{8} = 1$.
B atoms are at the face centres of the cube. There are 6 face centres and each contributes one half to the unit cell. Total number of B atoms = $6 \times \frac{1}{2} = 3$.

The formula of the compound is AB₃

42. (d) 14
There are 14 kinds of space lattices are possible for crystals these are called as Bravais lattice.
43. (b) Oscillation of loose electrons
The metallic lustre of a metal is due to the oscillation of loosely bound electrons.

When light falls upon the electrons, they absorb energy and are set into oscillation, and they emit radiations which are responsible for the metallic lustre.
44. (e) B₄C
Boron Carbide is one of the hardest known materials, behind cubic boron nitride and diamond. Boron carbide, (B₄C). crystalline compound of boron and carbon. It is an extremely hard synthetically produced material that is used in abrasive and wear. Resistant products, in lightweight composite materials, in tank arm and in, bulletproof vests. It is synthetically made in the manner to be hardest.
45. (d) 2.57×10^{21}
NaCl $\Rightarrow$ Cl⁻ occupies corners and face centres $\Rightarrow$ Effectively 4Cl⁻ ions
Na⁺ occupies octahedral voids.
 $\Rightarrow$ Effectively 4Na⁺ ions.
 $\Rightarrow$ 1 unit cell has effectively 4 molecules of NaCl.
mass of unit cell = $\frac{4 \times \text{mass (NaCl)}}{6.023 \times 10^{23}} = \frac{4 \times 58.5}{6.023 \times 10^{23}}$
 $\Rightarrow$ No. of unit cell in 1g = $\frac{1\text{g}}{\frac{4 \times 58.5}{6.023 \times 10^{23}}} = 2.57 \times 10^{21}$ unit cells
46. (b) 2Z
Number of tetrahedral voids in the unit cell = 2 ' number of atoms = 2Z.
47. (d) Triclinic
48. (c) $\sqrt{3} a/2$
As CsCl is body centred cubic,
So, $r = \sqrt{\frac{3}{4}} a$
49. (a) MnO₂
50. (a) Ga
Liquified Ga expand on solidification. Ga is less electropositive in nature. It has the weak metallic bond so, it expand on solidification.

ASSERTION AND REASON

1. (d) 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.

2. (a) The stability of a crystal depends upon the strength of the interparticle attractive force.

The melting point of a solid depends on the strength of the attractive force acting between the constituent particles.

Therefore, the stability of a crystal gets reflected in magnitude of its melting point.

Hence, both Assertion and Reason are correct and Reason is the correct explanation for Assertion.
3. (a) In a Frenkel defect an ion leaves its position in the lattice and occupies normally vacant interstitial position.
4. (a) All magnetically ordered solids (ferromagnetic and antiferromagnetic solids) transform to the paramagnetic state at high temperature due to the randomisation of spins.
5. (c) Tetrahedral void is so called because it is surrounded by four spheres tetrahedrally while octahedral void is so called because it is surrounded by six spheres octahedrally.

TRUE AND FALSE

1. (b) In crystalline solids, particles are arranged in a regular manner. In crystalline solid the arrangement is orderly. So when we go in any direction, the arrangement will be different. Therefore, physical properties like electrical conductance are different in different directions.
2. (a) In a primitive unit cell the constituent particles, whether atoms, molecules, or ions, are only located at the corners of the unit cell. Any particle at the corner of a unit cell contributes one-eighth of itself to one unit cell. Now in a cube, there are a total of eight corners.
3. (b) All three angles intersect at right angles and are of equal length. Crystal shapes of a cubic system based on inner structure (square) include octahedron, cube, and Hexahedron. Example: Silver, Garnet, Gold, and Diamond For cubic unit cells, primitive, body-centered, and face-centered arrangements are possible.

PRACTICE SOLUTIONS

1. (a)

$$\text{Density } d = \frac{zM}{a^3 N_0}$$

$$d = 4.54 \text{ g/cm}^3, M = 48 \text{ g mol}^{-1}, Z = ? \quad N_0 = 6.023 \times 10^{23} \text{ mol}^{-1}$$

If value of z is known, structure can be decided

$$Z = \frac{d N_0 a^3}{M} = \frac{4.54 \times 6.023 \times 10^{23} (412.6 \times 10^{-10})^3}{48} = 4$$

Thus, titanium has **face-centred cubic** structure.

2. (c)

C.N. of Na^+ in $\text{NaCl} = 6$
 C.N. of Cl^- in $\text{NaCl} = 6$
 Hence C.N. of Mg^{2+} is also = **6** and that of O^{2-} = **6 in MgO**
 We know in CsCl
 C.N. of $\text{Cs}^+ = 8$
 C.N. of $\text{Cl}^- = 8$

3. (b)

We know for the NaCl structure, for maximum of radius of B^- , the ratio r^+ / r^- should be minimum for octahedral void i.e. 0.414.
 radius of cation/radius of anion = 0.414

$$\frac{r_{\text{A}^+}}{r_{\text{B}^-}} = 0.414$$

$$r_{\text{B}^-} = \frac{r_{\text{A}^+}}{0.414} = \frac{120}{0.414} = 290 \text{ pm.}$$

4. (b)

C.N. of barium ion tells us that it is surrounded by eight fluoride ions (charge $8 \times (-1) = -8$). In order to balance out the eight negative charges, we need four barium ion (charge $4 \times (+2) = +8$). Hence, the C.N. of F^- ions must be **4**.

5. (a)

In 'BCC' structure.
 body diagonal = $4 \times r_{\text{Na}} = \sqrt{3} \times a$
 $\therefore 4 \times r_{\text{Na}} = \sqrt{3} \times 4.29$
 $r_{\text{Na}} = 1.86 \text{ \AA}$

6. (b)

NaCl is face-centred cubic lattice so that number of NaCl molecules in a unit cell (z) = 4.

We know density $d = \frac{zM}{a^3 N_0}$

where a = length of the unit cell

$$\text{Volume} = a^3 = \frac{Mz}{dN_0}$$

$$= \frac{4 \times 58.8 \times 10^{-3}}{2.17 \times 10^3 \times 6.02 \times 10^{23}} = 1.79 \times 10^{-28} \text{ m}^3$$

$$a = 5.64 \times 10^{-10} \text{ m}$$

$$a = 5.64 \text{ \AA} = \mathbf{564 \text{ pm}}$$

7. (a) Due to rock-salt (fcc) structure, number of atoms in a unit cell (z) = 4.

$$\text{Thus, } d (\text{density}) = \frac{zM}{a^3 N_0}$$

$$= 2\sqrt{2} \quad r = 2\sqrt{2} \times 1.42 \times 10^{-8} \text{ cm}$$

$$4 \times 56$$

$$\therefore d = \frac{6.02 \times 10^{23} \times (2\sqrt{2} \times 1.42 \times 10^{-8})^3}{4 \times 56} = \mathbf{5.743 \text{ g/cm}^3}$$

8. (a)

Number of octahedral voids per ion in lattice = 1
 Hence,
 number (aof trivalent cations (A^{3+}) = $1 \times \frac{1}{2} = \frac{1}{2}$
 number of tetrahedral voids per ion in lattice = 2
 Hence,

$$\text{number of divalent cations } (\text{B}^{2+}) = 2 \times \frac{1}{8} = \frac{1}{4}$$

Thus, formula is $\text{A}_{1/2} \text{B}_{1/4} \text{O}$ or $\mathbf{A_2BO_4}$.

9. (c)

For CsCl structure, body diagonal = $2r_+ + 2r_-$
 $7 \text{ \AA} = 2 \times 1.69 \text{ \AA} + 2r_-$
 $3.5 \text{ \AA} = 1.69 \text{ \AA} + r_-$
 $r_- = 3.5 \text{ \AA} - 1.69 \text{ \AA} = 1.81 \text{ \AA}$

10. (a)

Mass of the unit cell = $1.73 \times 10^{-22} \text{ g}$
 Volume of the unit cell = $(287 \times 10^{-10})^3 \text{ cm}^3$
 $= 2.364 \times 10^{-23} \text{ cm}^3$
 Density = 7.32 g/cm^3
 In BCC structure body diagonal is 4 times the atomic radius.

• Atomic radius = 124.3 pm

11. (d)

12. (c)

13. (c)

14. (c)

As A atoms are present at the 8 corners of the cube, therefore numbers of atoms of A in the unit cell

$$= \frac{1}{8} \times 8 = 1$$

As B atoms are present at the face centres of the 6 faces of the cube, therefore, numbers of atoms of

$$\text{atoms of B in the unit cell} = \frac{1}{2} \times 6 = 3$$

$$\therefore \text{Ratio of atoms A : B} = 1 : 3$$

Hence, the formula of the compound is $\mathbf{AB_3}$

15. (a)

As atoms Y are present at the 8 corners of the cube, therefore, numbers of atoms of Y in the unit cell = $1/8 \times 8 = 1$

As atoms X are present at the body centre. therefore, numbers of atoms of X in the unit cell = 1

$\therefore$ ratio of atoms X : Y = 1 : 1

Hence, the formula of the compound is XY

16. (a) a primitive cubic unit cell contains atoms only at the 8 corners with each corner contributing $1/8^{\text{th}}$ of an atom. Hence, $n = 8 \times (1/8) = 1$
 Volume, $V = a^3 = (3.36 \times 10^{-10} \text{ m})^3$
 Density = $nM/N_A V = 9.15 \times 10^3 \text{ kg/m}^3$
17. (b) Density, $\rho = a^3 \times N_A \times M$
 Given,
 Orthorhombic system has different edge length, width and height
 $\therefore a = 12.05 \text{ \AA} = 12.05 \times 10^{-8} \text{ cm}$
 $b = 15.05 \text{ \AA} = 15.05 \times 10^{-8} \text{ cm}$
 $c = 2.69 \text{ \AA} = 2.69 \times 10^{-8} \text{ cm}$
 $\therefore$ System has 2 molecules per unit cell,
 $\therefore Z = 2$
 and $N_A = 6.023 \times 10^{23}$
 Now, molecular mass will be
 $M = (\rho \times a \times b \times c \times N_A) / Z$
 $M = 1.419 \times 12.05 \times 10^{-8} \times 15.05 \times 10^{-8} \times 2.69 \times 10^{-8} \times 6.023 \times 10^{23} / 2$
 $M = 2084.6 \times 10^{-1} = 209 \text{ g/mol}$
18. (d) For BCC structure $\sqrt{3}a = 4r$
 $r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 351 = 152 \text{ pm}$
19. (b) At the Curie temperature (around 120°C) paraelectric BaTiO_3 transforms into a ferroelectric structure. Ferroelectricity is the characteristic of certain substances that possess a spontaneous electric field which can be reversed by applying an external electric field.
20. (a) Hexagonal is not a crystal system. Their crystal system are cubic, tetragonal, rhombohedral or trigonal, orthorhombic or rhombic, monoclinic, triclinic and hexagonal.
21. (b) Covalent solids consists of a long chain of covalent bonds between the adjacent molecules throughout the crystal. Hence, they are called giant molecules. They are hard and brittle in nature.
22. (c) Silicon due to its catenation property form network solid. Catenation is the ability of an atom to form bonds with other atoms of the same element. The compounds of silicon are reactive and not stable.
23. (c) As given that copper crystallizes is FCC lattice (Face centred cubic). In FCC atoms are present on the corners of the cubic, unit cell as well as on the face centres of each face.
 The atoms on the face diagonal will be touching each other. Let, the radius of the atom be r and edge length of the cube be a .
 Face diagonal of cube $= \sqrt{2}a$
 $\Rightarrow r + 2r + r = \sqrt{2}a$

$$\Rightarrow r = \sqrt{2}a / 4 = a / 2\sqrt{2} = 361 / 2\sqrt{2} \text{ pm} = 128 \text{ pm}$$

24. (d) for fcc,
 $2r_+ + 2r_- = a \sqrt{2} \quad + 2r_- = 508 \text{ pm} \quad + 2r_- = 144 \text{ pm}$
25. (d) Each atom of a metal gives one or more electrons towards the sea of mobile electrons it is surrounded by which ultimately contributes to the electrical and thermal conductivity of the metal.
26. (b) Ionic solids are made up of three dimensional arrangement of cations and anions bound by strong electrostatic force
27. (a) The force responsible for holding together the molecules of polar molecular solids is dipole-dipole force of attraction. Polar molecular solids are non-conductors of electricity.
28. (d) The ratio of the radius of the cation to the radius of the anion is called radius ratio. From this ratio the structure of lattice can be determined by using the following table
- | r_c/r_a | Arrangement |
|---------------|--------------------|
| 0.155 – 0.225 | Planar triangular |
| 0.225 – 0.414 | tetrahedral |
| 0.414 – 0.732 | Octahedral |
| 0.732 – 1.0 | Body centred cubic |
29. (a) Theoretical density of crystal, $\rho = \frac{nM}{N_0 a^3} \text{ g/cm}^3$
 Given, $\rho = 2.70 \text{ g/cm}^3$, $a = 405 \times 10^{-10} \text{ cm}$, $M = 26$
 $\Rightarrow n = \frac{\rho N_0 a^3}{M} = \frac{2.70 \times 6.022 \times 10^{23} \times (405)^3 \times 10^{-30}}{26}$
 $\Rightarrow n = 4$
 So, it is a face centered cubic cell.
30. (c) For NaCl type crystal structure,
 $A = 2r_{\text{Na}^+} + 2r_{\text{Cl}^-} = 2 \times 95 + 2 \times 181 \text{ pm} = 552 \text{ pm}$

ASSERTION AND REASON

1. (a) In simple cubic unit cell, total no. of atoms $= 8 \times 1/8 = 1$
2. (b) Graphite can conduct electricity because of the delocalised (free) electrons in its structure. These arise because each carbon atom is only bonded to 3 other carbon atoms. However, in diamond, all 4 outer electrons on each carbon atom are used in covalent bonding, so there are no delocalised electrons. Hence both assertion and reason are correct but reason does not explain assertion.
3. (c) "Besides the body centre there is one octahedral void at the centre of each 12 edges which is shared between four adjacent unit cells."

Thus, Octahedral voids present at the body centre of the cube =1

12 octahedral voids located at each edge and shared between four unit cells = $(12 \times 1/4) = 3$

Total number of octahedral voids =4

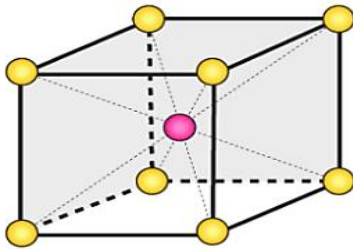
4. (b)

TRUE AND FALSE

1. (a)

A BCC unit cell has atoms at each corner of the cube and an atom at the centre of the structure. The diagram shown below is an open structure. According to this structure, the atom at the body centre wholly belongs to the unit cell in which it is present.

- In BCC unit cell every corner has atoms.
- There is one atom present at the centre of the structure.
- Below diagram is an open structure.
- According to this structure atom at the body centres wholly belongs to the unit cell in which it is present



Body-centred Cubic Unit Cell (BCC)

2. (b) 8 atoms are present at 8 corners of an fcc unit cell. Each atom contributes one eighth to the unit cell. Total contribution = $8 \times 1/8 = 1$ atom is present at 6 corners of an fcc unit cell. Each atom

contributes one-half to the unit cell. Total contribution = $6 \times 1/2 = 3$

The total number of atoms in one fcc unit cell = $1 + 3 = 4$.

The number of atoms contained in one face-centered cubic unit cell of monoatomic substance is 4.

3. (a)

4. (b) When the tetrahedral voids of the second layer are covered by the spheres of the third layer. So that the spheres of the third layer are exactly aligned with those of the first layer, We get a pattern of spheres that are repeated in alternate layers. This pattern can be written in the form of ABAB pattern. This structure is called a hexagonal close-packed (hcp) structure. Magnesium and zinc metals have this pattern.

