PERFECT CHEMISTRY-I Std XII Sci.

Atomic Structure of Water Molecule

STD.XII Sci. Perfect Chemistry - I

Eleventh Edition: March 2016

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Preface

In the case of good books, the point is not how many of them you can get through, but rather how many can get through to you.

"Std. XII Sci. : PERFECT CHEMISTRY - I" is a complete and thorough guide critically analysed and extensively drafted to boost the students confidence.

The book is prepared as per the Maharashtra State board syllabus and provides answers to all **textual and intext questions**. Sub-topic wise classified 'question and answer format' of this book helps the student to understand each and every concept thoroughly. Neatly labelled diagrams have been provided wherever required.

National Council Of Educational Research And Training (NCERT) questions and problems based on Maharashtra board syllabus have been provided along with solutions for a better grasp of the concept and preparing the students on a competitive level.

 Additional information about a concept is provided in the form of **Do You Know, Enrich Your Knowledge and Notes**. Definitions, statements and laws are specified with italic representation. Formulae are provided in chapters which involve numericals to help the students to tackle difficult problems. Solved problems are provided to understand the application of different concepts and formulae. **Brain Teasers** and **Check Your Grasp** cover brain-storming questions. **Quick Review** has been provided which gives an overview of the chapter. **Additional Theory Questions** have been provided to help the student gain insight on the various levels of theory-based questions.

Multiple Choice Questions help the students to test their range of preparation and the amount of knowledge of each topic.

 The journey to create a complete book is strewn with triumphs, failures and near misses. If you think we've nearly missed something or want to applaud us for our triumphs, we'd love to hear from you.

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 A book affects eternity; one can never tell where its influence stops.

Best of luck to all the aspirants!

Yours faithfully, Authors

PAPER PATTERN

Distribution of Marks According to Type of Questions

Topicwise Weightage

Contents

*Note: All the Textual questions are represented by * mark. All the Intext questions are represented by # mark.*

Target Indian Publications Publications O 1 Solid State

Syllabus

1.0 Prominent scientists

1.1 Introduction

Q.1. Under what conditions does a substance exist in solid state?

- **Ans:** i. Matter can exist in three states namely, solid, liquid and gas. Under a given set of conditions of temperature and pressure, the most stable state of a substance depends upon the net effect of two opposing forces: intermolecular forces and thermal energy.
	- ii. Intermolecular forces tend to keep the constituent particles (atoms, ions or molecules) closer, whereas thermal energy tends to keep them apart by making them move faster.
	- iii. The competition between molecular interaction energy due to intermolecular forces and thermal energy determines whether a given substance under a given set of condition is a gas, a liquid or a solid.
	- iv. At sufficiently low temperature, the thermal energy is low and molecular forces are very strong. As a result, the intermolecular forces keep the constituents so close that they cling to one another and occupy fixed positions and the substance exists in solid state.

- **Ans:** i. Matter can be changed from one state to another by changing temperature and pressure.
	- ii. Matter exists in solid state at relatively lower temperature.
	- iii. When the solid is heated to its melting point, thermal energy overcomes the intermolecular forces of attraction. The solid melts and changes into liquid. The liquid on heating to its boiling point vapourizes to form gas.
	- iv. When gases are cooled under high pressure, they condense into liquid state. The liquid thus formed on cooling changes into solid.

Solid state $\frac{\text{heat}}{\text{cool}}$ Liquid state $\frac{\text{heat}}{\text{cool}}$ Gaseous state

Q.3. Define a solid.

Ans: *A solid is defined as that form of matter which possesses rigidity and hence possesses a definite shape and a definite volume.*

***Q.4. Give characteristics of solid state.**

- **Ans:** The solid state is characterized by the following properties:
	- i. Solids have definite mass, volume, shape and density. Usually, the density of solid state is greater than the density of liquid and gaseous state. Water and mercury are exceptions. The density of ice (solid state of water) is lower than the density of liquid state of water. The density of mercury (which exists in liquid state) is very high $(13.6 \text{ g} \text{ mL}^{-1})$.
	- ii. Solids are usually hard, incompressible and rigid. Some solids like sodium, potassium and phosphorous are exceptions; they are soft. Solids cannot be compressed because the intermolecular distance of separation between neighbouring molecules is very small.
	- iii. In a solid state, intermolecular forces of attraction between the constituent particles are stronger than those present in liquid and gaseous states.
	- iv. All pure solids have characteristic melting points which depend on the extent of intermolecular forces present in the solid state. Stronger the intermolecular forces of attraction, higher is the melting point of the solid. Weaker the intermolecular forces of attraction, the lower is its melting point. Hence, depending on the intermolecular forces of attraction, melting points of the different solids range from almost absolute zero (helium) to a few thousand Kelvin (diamond).
	- v. The intermolecular forces of attraction hold the constituent particles of the solids tightly. Hence the particles cannot change their positions and remain stationary at one position. Therefore, solids cannot flow like liquids.

Check Your Grasp

Why do solids have a definite volume? (NCERT)

The intermolecular forces between the constituent particles (atoms, ions or molecules) of solid state are very strong. Therefore, they are strongly held at fixed positions and particles cannot separate from one another. Hence, solids have a definite volume.

1.2 Classification of solids

***Q.5. Give the classification of solids.**

Ans: Solids are classified as crystalline and amorphous on the basis of the presence or absence of orderly arrangement of their constituent particles (atoms, ions or molecules).

i. Crystalline solids: *A crystalline solid is a homogeneous solid in which the constituent particles (atoms, ions or molecules) are arranged in a definite repeating pattern.* Crystalline solids are further classified as:

a. Isomorphous form:

 1. *Two or more substances having the same crystal structure are said to be isomorphous (isosame, morphous-form) and the phenomenon is called isomorphism.*

- 2. The constituent atoms of isomorphous substances are in the same atomic ratio. The molecular formula and chemical properties of the isomorphous substances are similar.
- 3. Following are some examples of pairs of isomorphous substances and their atomic ratios:

 4. Some substances are not isomorphous eventhough they have same atomic ratio, similar molecular formula and similar chemical properties. This is because they have different crystal structures.

eg. Sodium chloride (NaCl) and potassium chloride (KCl)

b. Polymorphous / Allotropic form:

- 1. *A single substance that crystallises in two or more forms under different conditions is called polymorphous* (poly-many, morphous-form) and the phenomenon is called **polymorphism**.
- 2. The polymorphic forms are also called allotropic forms.
	- **eg**. i. Diamond, graphite and fullerene are three polymorphic forms of carbon.
		- ii. Rhombic sulphur and monoclinic sulphur are two allotropes of sulphur.
		- iii. Silicon dioxide and calcium carbonate also have allotropes.
- **ii. Amorphous solids / Psuedo solids / Super cooled liquids:** *The substances that appear like solids but do not have well developed perfectly ordered crystalline structure are called amorphous (no form) solids.*
	- **eg.** Tar, glass, plastic, rubber, butter, etc.

***Q.6. Explain crystalline solids and amorphous solids.**

Ans: i. Crystalline solids:

- a. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. These tiny crystals are called unit cells.
- b. A unit cell is a basic repeating structural unit of a crystalline solid.
- c. Crystalline solids have long range order which means that there is a regular pattern of arrangement of particles (atoms, ions or molecules) which repeats itself periodically over the entire crystal.
- **eg.** Sodium chloride and quartz

ii. Amorphous solids:

- a. The arrangement of constituent particles (atoms, molecules or ions) in amorphous solids has only short range order.
- b. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only.
- c. Such portions are scattered and in between, arrangement is disordered.
- **eg.** glass, rubber, plastics and amorphous silicon.

#Q.7. Explain the terms anisotropy and unit cell.

Ans: i. Anisotropy:

- a. *The ability of crystalline solids to change values of physical properties when measured in different directions is called anisotropy.*
- b. For crystalline solids, the physical properties like refractive index, electrical conductance, dielectric constant, etc., are different in different directions.

 As the direction changes (MN, OP, QR, etc.), the composition of the medium changes. This results in anisotropy.

- **ii. Unit cell:**
	- a. Crystalline solids are aggregates of many small, tiny crystals. These tiny crystals are called unit cells.
	- b. *A unit cell is a basic repeating structural unit of a crystalline solid.*

Q.8. *Distinguish between crystalline solids and amorphous solids. Give examples. OR Distinguish between crystalline solids and amorphous solids. [March 2013, 14]

Ans:

- **Q.9. Classify the following as amorphous or crystalline solids: Polyurethane, naphthalene, benzoic acid, teflon, potassium nitrate, cellophane, polyvinyl chloride, fibre glass, copper. (NCERT)**
- **Ans:** Amorphous solids: Polyurethane, teflon, cellophane, polyvinyl chloride, fibre glass. Crystalline solids: Benzoic acid, potassium nitrate, copper, naphthalene.

***Q.10. What is a glass?**

Ans: i. Silicon dioxide is fused with sodium oxide and boron oxide to form an optically transparent material known as glass. The colour of glass is due to addition of a trace amount of transition metal oxide.

- ii. Different types of glass are manufactured by changing its composition. Almost eight hundred different types of glasses are manufactured. Quartz glass is obtained from only silicon dioxide.
- iii. Pyrex glass is obtained by fusing together 60 to 80% $SiO₂$, 10 to 25% B₂O₃ and remaining amount of Al_2O_3 .
- iv. When 75% SiO₂ is fused with 15% Na₂O and 10% CaO, sodalime glass is obtained.
- v. Red glass contains trace amount of gold and copper. Yellow glass contains $UO₂$.
- vi. Blue glass contains CoO or CuO. Green glass contains $Fe₂O₃$ or CuO.

Q.11. Why is glass considered a super cooled liquid? (NCERT)

Ans: Glass is an amorphous solid. These amorphous solids do not have regular arrangement of constituent particles for a longer distance, unlike the crystalline solids. The structure of the amorphous solids resemble that of liquids, due to which they exhibit the property of liquids such as fluidity. Thus, these amorphous solids tend to float very slowly under gravity. They do not melt at definite sharp melting point, rather gradually soften with the increase in temperature. Thus, glass is considered as a pseudo solid or super cooled liquid.

Check Your Grasp

What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass? (NCERT)

Quartz is a crystalline solid with long range order whereas glass is an amorphous solid with short range order. When quartz is heated, it can be converted into glass at some temperature.

1.3 Classification of crystalline solids

Q.12. Name the different types of crystalline solids on the basis of different forces present in them.

- **Ans:** Depending upon the nature of intermolecular forces present in the constituent particles, crystalline solids are classified into the following four classes:
	- i. Molecular solids ii. Ionic solids iii. Metallic solids iv. Covalent solids
		-

Q.13. Explain the following terms:

-
-
-

***vii. Covalent solids**

Ans: i. Molecular solids:

- a. *Molecular solids are those solids in which the constituent particles are molecules of the same compound.*
- b. These are further subdivided into the following three categories:
- 1. Polar molecular solids
- 2. Non-polar molecular solids
- 3. Hydrogen bonded molecular solids

ii. Polar molecular solids:

- a. In these crystalline solids, the constituent particles are covalently bonded polar molecules like $HC1, SO₂, etc.$
- b. Polar molecules possess permanent dipole moment and in solid state they are held together by strong dipole-dipole interaction.
- c. There is a separation of positive and negative charges because of the polar nature of molecule. Hence, the polar molecules arrange themselves in such a way that opposite charges of the neighbouring molecules are brought closer.

Characteristics:

- a. They are soft.
- b. They do not conduct electricity.

- c. The melting points of the solids are relatively low, as the bonding is relatively weak.
- **eg.** Solid SO₂, solid NH₃ and solid HCl.
- ***i. Molecular solids ii. Polar molecular solids**
- **iii. Non-polar molecular solids *iv. Hydrogen bonded molecular solids**
- ***v. Ionic solids *vi. Metallic solids**

- a. They comprise of either atoms or molecules formed by non-polar covalent bonds.
- b. In these solids, the atoms or molecules are held by weak dispersion forces or London forces.

Characteristics:

- a. They are soft.
- b. They do not conduct electricity.
- c. They have very low melting points (lower than polar molecular solids) and are usually in liquid or gaseous state at room temperature and pressure. Iodine (I_2) exists in solid state even at room temperature.
- **eg.** Non-polar molecules like CO_2 , H_2 , CH_4 and weakly polar molecules like CO and other hydrocarbons form non-polar molecular solids at relatively lower temperatures.

iv. Hydrogen bonded molecular solids:

- a. These crystalline solids consist of hydrogen atom covalently bonded to strongly electronegative atom like oxygen, nitrogen or fluorine.
- b. In these molecules, the hydrogen atoms acquire additional positive charge and form additional bond with strongly electronegative atoms in the vicinity. This additional bond is called **hydrogen bond.**

Characteristics:

- a. They do not conduct electricity.
- b. These solids exist as liquids or gases at room temperature and pressure.
- c. On cooling, the liquids solidify.
- eg. H_2O , NH₃.

v. Ionic Solids:

- a. *Ionic solids are crystalline salts formed by the three dimensional arrangement of cations and anions bound by electrostatic forces.*
- b. Two types of electrostatic forces are present. One is the force of attraction between the ions carrying opposite charges. The other is the force of repulsion between the ions carrying same charges.
- c. The arrangement of ions depends on following factors:
- 1. Sizes of the cation and anion
- 2. The charges on the ions
- 3. The ease of polarisability of the anion

Characteristics:

- a. These solids are hard and brittle in nature. They have high melting and boiling points.
- b. Since the ions are not free to move about, they are electrical insulators (non-conductors) in the solid state.
- c. However, in the molten or fused state or when dissolved in water, the ions become free to move about and thereby conduct electricity.
- d. When shearing force is applied, ionic crystals distort and the crystal structure is fractured.
- **eg.** NaCl, ZnS, CuCl, etc.

vi. Metallic solids:

- a. *Metallic solids are the crystalline solids formed by atoms of the same metallic element.*
- b. Metals are orderly collection of positive ions (called kernels) in the sea of delocalised electrons.
- c. These electrons are mobile and are evenly spread throughout the crystal. Each metal atom contributes one or more electrons towards the sea of mobile electrons.
- d. The force of attraction between positively charged metallic ion and negatively charged sea of delocalised electrons is called metallic bond. Metallic bonds are stronger than ionic and covalent bonds.

Characteristics:

- a. Metallic solids are good conductors of heat and electricity due to the presence of mobile electrons.
- b. Metallic solids are tougher than other solids due to presence of strong metallic bonds. The nature of metallic bonds is such that any shape can be given to the metallic article.
- c. The metallic solid contains several layers of the metallic ions arranged over one another. These layers can slide on other layers. Hence, the metallic solids are malleable and ductile. They can be hammered or rolled into thin sheets of desired thickness and can be drawn into thin wires of required size.
- d. Alloys can be formed by fusing the mixture of metals. Alloys show all properties of metals.
- e. Metallic solids posses metallic lustre due to which the surface appears grey or silvery.
	- **eg.** The surface of gold appears yellow whereas the surface of copper appears reddish.

vii. Covalent or network solids:

- a. *Covalent solids are those in which the constituent particles are non-metal atoms linked to the adjacent atoms by covalent bonds throughout the crystal.*
- b. A network of covalent bonds is formed and the covalent solids are also called **giant solids**.

Characteristics:

- a. Depending on the type of covalent bonding present between the atoms, covalent solids are either hard or brittle.
- b. They have extremely high melting points. Covalent solids are good conductors of electricity if mobile electrons are available, otherwise they are insulators.
- **eg.** Three allotropic forms of carbon i.e. diamond, graphite and fullerene.

***Q.14. Write a note on: i. Diamond ii. Graphite iii. Fullerene**

Ans: i. Diamond:

- a. Diamond is an allotrope of carbon. It is used in jewellery and is the most precious crystal.
- b. Covalent bonds between $sp³$ hybridized carbon atoms continue in all directions to form a giant network.
	- c. Diamond is very strong and hard due to presence of strong covalent bonds.
	- d. It is the hardest material and has very high melting point $(3550 °C)$.

ii. Graphite:

- a. Graphite is an allotrope of carbon in which each carbon atom is sp^2 hybridized and forms covalent bonds with three other sp^2 hybridised carbon atoms. This results in formation of interlinked six membered rings.
- b. π bonds are formed between carbon atoms by utilizing half filled unhybridised $2p_z$ orbital on each carbon atom. Layers of carbon atoms are formed.
- c. Electrons present in delocalized molecular orbitals can move freely and conduct electricity. Hence graphite is a good conductor of electricity.
- d. Graphite is sufficiently hard due to presence of relatively stronger covalent bonds. The adjacent layers of carbon atoms are held together by weak van der Waal's forces of attraction.
- e. The layers of carbon atoms in graphite can slide over other layers. Hence, graphite is used as lubricant for reducing friction.
- f. It is used in ribbons used for printing in computers and typewriters. It is also used in lead pencils.

iii. Fullerene:

- a. Fullerene is an allotrope of carbon. It is also called **Buckball** or **Buckminster fullerene**.
- b. When a high power laser was focused on carbon, fullerene was formed. It has formula C_{60} and shape of a soccer ball (hollow sphere).
- c. sp² hybridized carbon atoms occupy sixty equidistant places on this sphere. They form hexagons and pentagons.
	- d. Fullerenes are present in carbon soot.
	- e. Fullerene reacts with potassium to form $K_{35}C_{60}$. This compound is a superconductor of electricity at 18 K. It reacts with transition metal to form a catalyst.
	- f. Tubes made from fullerene and graphite are called nanotubes. These are used as high strength materials, electric conductors, molecular sensors and semiconductors.
- **Q.15. What is the hybridisation of carbon atom in diamond and graphite? 0.1 mole of Buckminster fullerene contains how many kg of carbon? [Atomic mass of carbon = 12] [Oct 2015]**
- Ans: Hybridisation of carbon atom in diamond is $sp³$ and that in graphite is $sp²$. The chemical formula of Buckminster fullerene is C_{60} .
- \therefore 1 mole of C₆₀ contains 60 moles of C. 0.1 mole of C_{60} will contain 6.0 moles of C.

Weight of C-atoms = Number of moles of $C \times$ atomic mass of C

- $= 6.0 \times 12$
- $= 72.0 g$
- = **0.072 kg**
- 0.1 mole of Buckminster fullerene contains **0.072 kg** of carbon.

Q.16. Ionic solids conduct electricity in molten state but not in solid state. Explain. (NCERT)

Ans: In ionic solids, constituent ions are held together by strong electrostatic forces of attraction and they are present in fixed position in crystal lattice. Therefore, they cannot move when an electric field is applied. However, in molten state the well defined arrangement of ions in the crystal is destroyed and the ions can move freely when electric field is applied. Hence, ionic solids conduct electricity in molten state.

Q.17. Classify the following solids into different types

- Ans: i. Amorphous solid Plastic
	- ii. Molecular solids $-P_4$ molecule, S_8 molecule, Iodine molecule, Tetra phosphorus decoxide
	- iii. Ionic solids Ammonium phosphate, NaCl, LiBr
	- iv. Metallic solids Brass, Rubidium
	- v. Covalent or Network solids Graphite, Diamond, Silicon, SiC.

Q.18. Explain

- **b.** the basis of differences between metallic and ionic crystals. (NCERT)
- ***ii. why ionic solids are hard and brittle. (NCERT)**

***iii. why solid ice is lighter than water.**

Ans: i. Metallic and ionic crystals:

a. Similarities:

- 1. Both ionic and metallic crystals have electrostatic forces of attraction.
- 2. In ionic crystals, these are between the oppositely charged ions. In metals, these are among the valence electrons (negatively charged) and the positively charged metal ions (kernels).
- 3. This is the reason why both metallic and ionic crystals have high melting points.
- 4. In both the cases, the bond is non-directional.

b. Differences:

- 1. In ionic crystals, the ions are not free to move. Hence, they cannot conduct electricity in the solid state. They can do so only in the molten state or in aqueous solution.
- 2. In metals, the valence electrons are free to flow. Hence, they can conduct electricity in the solid state.
- 3. Ionic bond is strong due to electrostatic forces of attraction.
- 4. Metallic bond may be weak or strong depending upon the number of valence electrons and the size of the kernels.
- 5. On application of shearing force, ionic crystals undergo distortion and fracture in the crystal structure while on application of shearing force, metals are not fractured, but rather the layers of metallic ions slide on one another.
- 6. Metallic solids are malleable (hammered into sheets) and ductile (drawn into thin wires) whereas ionic solids are neither malleable nor ductile.

ii. Ionic solids are hard and brittle:

 a. In ionic crystalline solids, constituent particles are positively charged cations and negatively charged anions placed at alternate lattice points.

 c. Since there are no free electrons, they are not malleable and on applying a shearing force, ionic crystals break into small units. Hence, they are brittle.

iii. Solid ice is lighter than water:

- a. The volume of a single water molecule (as obtained from the knowledge of the atomic radii of hydrogen and oxygen atoms) is found to be equal to 15×10^{-24} cm³.
- b. If it is assumed that all the water molecules in liquid state are closely packed, the total volume of 1 mole (i.e., 18 g) of water may be obtained by the multiplication of volume of one molecule of water with the Avogadro's number, 6.022×10^{23} .

Hence, the volume of 1 mole of water = 15×10^{-24} cm³ $\times 6.022 \times 10^{23} = 9$ cm³.

- c. It is found that the volume of 1 mole of water with density 1 g mL⁻¹ is equal to 18 cm³. It is evident that out of the total 18 cm³ (the molar volume of water), the actual volume occupied by water molecules is about 9 cm³ and the remaining half (i.e., 9 cm³) of the total volume is empty.
	- d. According to X-ray studies, the structure of solid ice is almost identical to that of liquid water. Intermolecular hydrogen bonding present in ice forms a hexagonal three dimensional crystal structure. About one half of the total space remains unoccupied. When ice melts, some of the hydrogen bonds are broken. Water molecules occupy some of the empty spaces.
	- e. Thus, the hexagonal crystalline structure of solid ice collapses and the liquid water molecules are more closely spaced. Due to this, the density of liquid water is higher than that of solid ice. Since solid ice is lighter than liquid water, ice floats on water.

Note: Usually the density of solid state is more than that of liquid state, but water is an exception.

1.4 Unit cell and two and three dimensional lattices

***Q.19. What is a unit cell? Explain Bravais lattices.**

- **Ans:** i. *A unit cell is the smallest repeating structural unit of a crystalline solid*. A crystalline solid can be obtained by repeating the unit cells (of the same crystalline substance) in space in all directions.
	- ii. The lines connecting centres of the constituent particles are drawn to represent a unit cell. The constituent particle can be an ion or an atom or molecule of the crystalline solid.
	- iii. The points at the intersection of lines which represent constituent particles are called **lattice points**. These lattice points are arranged in a definite repeating pattern. Any one lattice point is identical to the number of other lattice points.

iv. *Space lattice is the collection of all the points in the crystal having similar environment.*

Bravais Lattices:

- i. The three dimensional arrangement of lattice points represents a crystal lattice. Thus, *a crystal lattice is a regular arrangement of the constituent particles (atoms, ions or molecules) of a crystalline solid in three dimensional space.*
- ii. There are only 14 possible three dimensional lattices, as proved by the French mathematician, Bravais. These are called **Bravais Lattices.**
- iii. Lattice points when joined by straight lines gives the geometry of the lattice.
- iv. Shape of any crystal lattice depends upon the shape of the unit cell which in turn depends upon following two factors,
	- a. The length of the three edges: a, b and c.
	- b. The angles between the edges: α (between edges b and c), β (between edges a and c) and γ (between edges a and b).

Thus, a unit cell is characterised by six parameters a, b, c, α , β and γ . The complete crystal lattice can be obtained by extending the unit cell in all three directions.

Enrich Your Knowledge

Unit cells can be broadly classified into two categories:

i. Primitive unit cells: *When constituent particles are present only at the corner positions of a unit cell, it is called as primitive unit cell.*

These are also called simple unit cells. In all, there are seven types of primitive unit cells. They are cubic, tetragonal, orthorhombic, monoclinic, triclinic, hexagonal and rhombohedral.

ii. Centred unit cells: *When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a <i>centred unit cell*.

Centred unit cells are of three types:

- **a. Body-centred unit cells:** These unit cells contain one constituent particle (atom, molecule or ion) at its body-centre besides the ones present at its corners.
- **b.** Face-centred unit cells: These unit cells contain one constituent particle present at the centre of each face, besides the ones present at its corners.
- **c. End-centred unit cells:** In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

***Q.20. Explain with the help of diagram:**

- **i. Seven types of unit cells ii. Three types of cubic cells**
-
- **v. Two types of monoclinic unit cells vi. Triclinic unit cell**

-
- iii. Two types of tetragonal unit cells **iv.** Four types of orthorhombic unit cells
	-
- **vii. Primitive hexagonal unit cell**
- **Ans: i.** There are seven types of simple or primitive unit cells among crystals. These unit cells are characterized by the edges a, b and c and the angles α , β and γ . These are as follows:
	- **a.** Cubic lattice: All the three edges (sides) are of equal length and are at right angles to each other $(a = b = c, \alpha = \beta = \gamma = 90^{\circ})$.

- **c. Orthorhombic lattice:** It has three unequal edges (sides) which are at right angles to each other $(a \neq b \neq c, \alpha = \beta = \gamma = 90^{\circ}).$
- **d.** Monoclinic lattice: The three edges (sides) are of unequal lengths and two angles are of 90^o while the third angle is other than 90 $^{\circ}$ (a \neq b \neq c, α = β = 90 $^{\circ}$ and γ angle \neq 90 $^{\circ}$).
- **e. Triclinic lattice:** The three edges (sides) are of unequal lengths and all angles are different but none is perpendicular to any of the others $(a \neq b \neq c, \alpha \neq \beta \neq y \neq 90^{\circ})$.
- **f. Hexagonal lattice:** It has two edges (sides) of equal lengths and differs in the length of the third side. Two of its angles are 90° and one angle is 120° (a = b \neq c, α = β = 90° and γ = 120°).
- **g. Rhombohedral lattice:** The three edges (sides) are of equal lengths and all the three angles are equal, but not equal to 90 $^{\circ}$ (a = b = c, α = β = $\gamma \neq$ 90 $^{\circ}$).

 ii. Three types of cubic cells: The three types of cubic cells are:

iv. Four types of orthorhombic unit cells: The four types of orthorhombic unit cells are:

 a. Primitive or Simple orthorhombic b. Body centred orthorhombic c. End centred orthorhombic d. Face centred orthorhombic

Four Types of Orthorhombic Unit Cells ($a \neq b \neq c$, $\alpha = \beta = \gamma = 90^{\circ}$)

- **v. Two types of monoclinic unit cells:** The two types of monoclinic unit cells are:
	- a. Primitive or Simple monoclinic b. End centred monoclinic

 vi. Triclinic unit cell: vii. Primitive hexagonal unit cell:

Triclinic unit cell exists in only Hexagonal unit cell exists in only one type i.e., primitive. one type i.e., primitive.

Note:

Q.21. Give the significance of a lattice point. (NCERT)

Ans: Each lattice point represents one constituent particle of the solid, which may be an atom, a molecule or an ion.

Q.22. *Explain coordination number. OR

What is meant by the term 'coordination number'? (NCERT)

- **Ans:** i. *The coordination number of constituent particle of the crystal lattice is the number of particles surrounding a single particle in the crystal lattice.*
	- ii. In the crystal lattice having higher coordination number, the constituent particles are more tightly packed. Coordination number is also the measure of hardness of the crystal.

Enrich Your Knowledge

 Open structures are those structures where each small sphere represents only the centre of the particle occupying that position and not the actual size of the particle. In this structure, the arrangement of particles is easier to follow as shown in the following figures:

(a) Simple cubic (b) Face-centred cubic (c) Body-centred cubic

Space filling structures are those structures which show how the particles are packed within the solids.

Q.23. Calculate the number of atoms present per unit cell in:

- **i. Simple or primitive cubic lattice ii. Body-centred cubic lattice**
- **iii. Face-centred cubic lattice**
- **Ans: i. Simple or primitive cubic lattice:**
	- a. In simple cubic unit cell, eight constituent particles (spheres) are present at eight corners of unit cell.
	- b. Unit cells repeat in three dimensions to form the complete crystal. The constituent particles at the corners are shared by neighbouring unit cells.
	- c. A constituent particle present at a corner is shared by eight neighbouring unit cells. Its contribution to a unit cell is only 1/8.

d. Thus, the number of atoms present in each unit cell = 8 corner atoms $\times \frac{1}{8}$ atom per unit cell = 1

Thus, simple cubic lattice has one atom per unit cell.

ii. Body-centred cubic lattice (bcc):

- a. In body-centred cubic unit cell, eight constituent particles (spheres) are present at eight corners of unit cell. One constituent particle is present at the centre of the body of the unit cell.
- b. A constituent particle present at a corner is shared by eight neighbouring unit cells. Its contribution to a unit cell is only 1/8.

 $= 8$ corner atoms $\times \frac{1}{2}$ 8 atom per unit cell $= 1$

> c. The constituent particle present at the centre of the body of the unit cell is not shared by any other unit cell. Its contribution to a unit cell is l.

Thus, the number of atoms present at the centre of the cube $= 1$

d. The total number of atoms present in the unit cell = $1 + 1 = 2$ **Thus, body centred cubic has 2 atoms per unit cell.**

iii. Face-centred cubic lattice (fcc):

- a. In face-centred cubic unit cell, eight constituent particles (spheres) are present at eight corners of unit cell. Six constituent particles (spheres) are present at centres of six faces.
- b. A constituent particle present at a corner is shared by eight neighbouring unit cells. Its contribution to a unit cell is only 1/8.

 c. A constituent particle present at the centre of a face is shared by two neighbouring unit cells. Its contribution to a unit cell is only 1/2.

The number of atoms present at faces per unit cell = 6 atoms at the faces $\times \frac{1}{2}$ 2 atom per unit cell $=$ 3

d. The total number of atoms per unit cell = $1 + 3 = 4$

8

Thus, a face centred cubic unit cell has 4 atoms per unit cell.

 Note: The coordination number of the constituent particle in a cubic close-packed structure or face centred cubic lattice is **twelve** i.e., four spheres are present in the layer above, four spheres in the layer below and four spheres in the layer of the constituent particle.

***Q.24. Give the number of lattice points in one unit cell of the crystal structures. (NCERT)**

 i. Simple cubic ii. Face-centred cubic

 iii. Body-centred cubic iv. Face-centred tetragonal

Ans: i. Lattice points in simple cubic unit cell $= 8$ (at corners)

$$
\therefore
$$
 Lattice points per unit cell = 8 × $\frac{1}{8}$ = 1.

ii. Lattice points in face-centred cubic unit cell = 8 (at corners) + 6 (at centre of a face) = 14.

$$
\therefore
$$
 Lattice points per unit cell = 8 × $\frac{1}{8}$ + 6 × $\frac{1}{2}$ = 4.

iii. Lattice points in body-centred cubic unit cell = 8 (at corners) + 1 (at centre of the body)

$$
\therefore
$$
 Lattice points per unit cell = 8 × $\frac{1}{8}$ + 1 = 2

- iv. Lattice points in face-centred tetragonal crystal (unit cell) = 8 (at corners) + 6 (at centre of the face)
- \therefore Lattice points per unit cell = 8 $\times \frac{1}{2}$ 8 $+ 6 \times \frac{1}{2}$ 2 $= 4$

Check Your Grasp

Explain how much portion of an atom located at (i) corner and (ii) body-centre of a cubic unit cell is part of its neighbouring unit cell. (NCERT)

- i. An atom located at corner of a cubic unit cell is shared by eight neighbouring unit cells. Hence $1/8th$ of an atom located at corner of a cubic unit cell is part of its neighbouring unit cell.
- ii. An atom located at body-centre of a cubic unit cell is not shared by any other unit cell. Hence, it is not a part of the neighbouring unit cell.

1.5 Packing in solids

Q.25. Explain one dimensional close packing in solids.

Ans: In solids, the constituent particles are close packed, leaving minimum vacant space. Consider the constituent particles as identical hard spheres.

Close packing in one dimension:

 i. There is only one way of arranging spheres in a one dimensional close packed structure, that is to arrange them in a row, touching one another as shown in the figure.

- ii. In this arrangement, each sphere (except the two spheres at the end) is in contact with two of its neighbours.
- iii. Thus, in one dimensional close packed arrangement, the coordination number of the spheres (particles) is 2.

Q.26. Explain:

 i. Square close packing in two dimensions

- **ii. Hexagonal close packing in two dimensions.**
- **Ans:** Two dimensional close packed structures can be generated by stacking (placing) the rows of one dimensional close packed spheres. This can be done in two different ways.

i. Square close packing (AAAA type arrangement):

- a. The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row.
- b. Thus, all the spheres of different rows are aligned horizontally as well as vertically.
- c. If the first row is called as 'A' type row, the second row being exactly the same as the first one, is also of 'A' type.
- d. The planar two dimensional arrangement is called **AAAA type** of arrangement.
- e. In this arrangement, each sphere is in contact with four of its neighbours. Thus, the **coordination number of the sphere is four**.
- f. If the centre of these 4 immediate neighbouring spheres are joined, a square is formed. Hence, this packing is called **square close packing in two dimensions** and it occupies 52.4 % of available space.

- a. The second row may be placed above the first one in staggered manner such that its spheres fit in the depressions of the first row.
- b. If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type.
- c. When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of 'A' type. The spheres of similarly placed fourth row will be aligned with those of the second row ('B' type).

- d. Hence, this arrangement is of **ABAB type**.
- e. Each sphere is in contact with six of its neighbours and therefore the **coordination number of the sphere is six.**
- f. The centres of these six spheres are at the corners of a regular hexagon. Hence, this packing is called **hexagonal close packing in two dimensions** and it occupies 60.4 % of available space. Hence, packing is more efficient than that in square close packing in two dimensions.

***Q.27. Explain with the help of neat diagrams AAAA and ABAB and ABCABC type of three dimensional packings.**

Ans: i. AAAA type of three dimensional packing:

- a. AAAA type of three dimensional packing is obtained by placing layers (of AAAA type of planar two dimensional crystal structure) one over the other. All the spheres of the successive layers are placed exactly above the spheres of the lower layers.
- b. This results in perfect horizontal and vertical alignment between spheres of various layers. The unit cell has **simple cubic structure** as shown in figure (a).
- c. This arrangement has more empty space.
- d. In this arrangement, the coordination number is **six**. Each sphere is in contact with four spheres in the layer, one above and one below the layer.

- **ii. ABAB type of three dimensional packing:** In this type (ABAB) of crystal structure, packing is more efficient than simple cubic structure.
	- a. Three dimensional packing can be obtained by placing layers (of ABAB type of planar two dimensional crystal structure) one over the other.
	- b. The spheres of second layer are placed into depressions between the spheres of the first layer.
	- c. The first layer is designated as A type and second layer is designated as B type for convenience eventhough both the layers are of ABAB type.
	- d. This arrangement of two layers is AB type shown in figure (a) and its top view is shown in figure (b).

e. In this arrangement,

- 1. Tetrahedral voids are formed by three spheres in the first layer and one sphere in the second layer. This happens when the sphere of second layer covers the triangular open space of first layer. Due to this, only half the number of triangular open spaces of first layers are covered.
- 2. Tetrahedralvoids are also formed by three spheres in the second layer and one sphere in the first layer.
- 3. Octahedral voids are formed by three spheres in the first layer and three spheres in the second layer. This happens when the three spheres of second layer covers the triangular open space of first layer. Due to this, the remaining half the number of triangular open spaces of first layers are covered.
- f. Thus, formation of tetrahedral voids involves four spheres and formation of octahedral voids involves six spheres.
- g. A tetrahedron can be formed by connecting the centres of four spheres involved in the formation of tetrahedral voids. An octahedron can be formed by connecting the centres of six spheres involved in the formation of octahedral voids.
- h. For N close packed spheres, the number of octahedral voids is N and the number of tetrahedral voids is 2N.
- i. Third layer can be placed over the second layer in two ways:
- 1. The spheres of the third layer can be placed into tetrahedral voids to form ABAB type structure.
- 2. The spheres of the third layer can be placed into octahedral voids to form ABCABC type structure.
- j. **Placing the spheres of the third layer into the tetrahedral voids:**
	- In ABAB type structure, there is horizontal and vertical alignment between the spheres of first layer and third layer. Similarly there is horizontal and vertical alignment between the spheres of second layer and fourth layer. This arrangement is called **hexagonal close packed (hcp) structure**. This is shown in the following figure:

iii. ABCABC type of three dimensional packing: OR Placing the spheres of the third layer into octahedral voids:

- a. The spheres of the third layer can be placed into octahedral voids. The arrangement of third layer is different from that of first and second layers. Hence, third layer is designated as C layer and the structure is called ABCABC type.
- b. When fourth layer is placed, there is horizontal and vertical alignment between the spheres of first layer and fourth layer. This is shown in figure (a).
- c. This arrangement is called **cubic close packed (ccp) structure**. It is same as face-centred cubic structure.
- d. In both arrangements (hcp and ccp), the coordination number is 12. Each sphere is in contact with 6 neighbouring spheres in its own layer, 3 spheres in the layer above and 3 spheres in the layer below. It is not possible to increase coordination number beyond 12. Hence, hcp and ccp packing are equally efficient.

- **iii. Tetrahedral void and octahedral void.**
- **Ans: i. Crystal lattice and unit cell:**

ii. Hexagonal close packing and cubic close packing:

iii. Tetrahedral voids and octahedral voids:

1.6 Density of unit cells

Q.29. Derive density formula for a simple cubic unit cell.

- **Ans:** i. Consider a unit cell of cubic crystal of edge length 'a' units and radius 'r' of each constituent particle then, $a = 2r$ (: Two constituent particles touch along the edge)
	- \therefore Volume of unit cell (V) = $a^3 = (2r^3) = 8r^3$

- ii. In a simple cubic unit cell, eight constituent particles are present at eight corners of unit cell.
- iii. A constituent particle present at a corner is shared by eight neighbouring unit cells. Its contribution to a unit cell is only $1/8^{th}$.
- \therefore The number of constituent particles present in each unit cell

= 8 corner atoms
$$
\times \frac{1}{8}
$$
 atom per unit cell = 1.

 iv. As the unit cell contains only one constituent particle and if the constituent particle is an atom, the mass of the unit cell is $\frac{\text{Atomic mass}}{\text{Avogadro number}} = \frac{\text{Atomic mass}}{6.022 \times 10^{23}} \text{ g}.$

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v. The density of the unit cell is given by the formula,

 vi. Thus, when atomic mass and atomic radius are known, the density of unit cell can be calculated. **Note:** If z is the number of atoms per unit cell, M is the atomic/molar mass, a is the edge length of unit cell and

 N_A is the Avogadro number (6.022 \times 10²³), then the density (d) of the unit cell is

$$
d = \frac{z.M}{a^3 \cdot N_A}
$$

Q.30. ***Calculate the percentage efficiency of packing in case of the following crystals: OR Calculate the efficiency of packing in case of a metal crystal for: (NCERT)**

 i. Simple cubic ii. Body centred cubic

Simple Cubic Cell

a

 iii. Face centred cubic with all atoms touching one another.

Ans: i. Simple cubic unit cell:

- a. In a simple cubic lattice, the atoms are located only on the corners of the cube. The particles touch each other along the edge.
- b. Thus, the edge length or side of the cube 'a', and the radius of each particle, 'r' are related as $a = 2r$
- c. The volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$
	- d. Since a simple cubic unit cell contains only 1 atom,

The volume of one atom (occupied space) = $\frac{4}{3}$ 3 πr^3

e. Packing efficiency = $\frac{\text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100\%$

$$
= \frac{4/3\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100
$$

$$
= 52.36 \% \approx 52.4 %
$$

 f. The packing efficiency of simple cubic metal crystal is **52.4 %.** Thus, simple cubic crystal has minimum packing efficiency. Since almost half the space is empty, the simple cubic crystalline solid is loosely bonded.

ii. Body centred cubic unit cell:

- a. In a body-centred cubic unit cell, eight constituent particles (spheres) are present at eight corners of unit cell and are shared by eight neighbouring unit cells. Each constituent particle present at the corner contributes only $1/8^{th}$ to the unit cell.
- b One constituent particle is present at the centre of the body of the unit cell. It is not shared by any other unit cell. Its contribution to a unit cell is 1.
- c. Thus, the number of constituent particles or atoms present in bcc unit cell is

8 corner atoms $\times \frac{1}{2}$ 8 atom per unit cell $+1$ body centre atom $= 2$.

d. If the length of face diagonal AB is 'b', the length of body diagonal AD is 'c' and \triangle ABC and ABD are right angled triangles, $L(AB)^2 = L(AC)^2 + L(BC)^2$ $b^2 = a^2 + a^2 = 2a^2$ and $L(AD)^2 = L(AB)^2 + L(BD)^2$ $c^2 = b^2 + a^2 = 2a^2 + a^2 = 3a^2$ (: $b^2 = 2a^2$) \therefore c = $\sqrt{3}a$ But the length of body diagonal AD is also equal to 4r, where, r is the radius of atom. \therefore c = $\sqrt{3}a = 4r$ \therefore $a = \frac{4}{\sqrt{2}} r$ 3 **Body Centered Cubic Unit Cell** D $\mathcal{C}_{0}^{(n)}$ A a b a B r \mathbf{c}^{\prime}

The volume of cube $= a³ =$ $\left(\frac{4}{5}\right)^3$ $\left(\frac{4}{\sqrt{3}} \mathbf{r}\right)^2 = \frac{64 \mathbf{r}^3}{3\sqrt{3}}$

e. Volume of one atom of radius r is $\frac{4}{3}\pi r^3$ 3 π Since bcc unit cell contains 2 atoms,

$$
\therefore \qquad \text{Volume of two atoms} = 2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3
$$

This is the occupied volume.

f. Packing efficiency =
$$
\frac{\text{Volume occupied by 2 atoms}}{\text{Volume of bcc unit cell}} \times 100 = \frac{\frac{8}{3}\pi r^3}{\frac{64r^3}{3\sqrt{3}}} \times 100 = 68.04 \%
$$
.

 The packing efficiency of bcc unit cell is **68.04 %.** The volume unoccupied (or empty space) is $100 - 68 \% = 32 \%$.

iii. Face centred cubic unit cell (cubic close packing):

a. In a face-centred cubic unit cell, eight constituent particles (spheres) are present at the eight corners of unit cell and are shared by eight neighbouring unit cells. Each constituent particle at the corner contributes only $1/8th$ to the unit cell.

8

 b. Six constituent particles (spheres) are present at the centres of six faces of the unit cell. Each of these constituent particle is shared by two neighbouring unit cells. Thus, its contribution to a unit cell is only 1/2.

Thus, the number of constituent particles or atoms present in fcc unit cell is

8 corner atoms \times 1/8 atom per unit cell + 6 atoms at the faces \times 1/2 atom per unit cell = 4

- c. If the edge length is 'a', the length of hypotenuse AB is 'b' and the triangle ABC is right angled triangle, $L(AB)^2 = L(AC)^2 + L(BC)^2$ $b^2 = a^2 + a^2 = 2a^2$
	- d. But the length of the hypotenuse AB is also equal to 4r, where r is the radius of atom.
- \therefore b² = 2a² = (4r)² $= 16r^2$: $a^2 = 8r^2$ $a = \sqrt{8} r = 2\sqrt{2} r$

Volume of unit cell = $a^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}r^3$

e. The volume of one atom of radius r is $\frac{4}{3}$ 3 πr^3 . A fcc unit cell contains 4 atoms.

$$
\therefore
$$
 Volume occupied by 4 atoms is $4 \times \frac{4}{3} \pi r^3$ or $\frac{16}{3} \pi r^3$.

 \therefore The packing efficiency of fcc unit cell is **74.0 %.** The packing efficiency is maximum in fcc. unit cell.

The volume unoccupied (or empty space) is $100 - 74.0 \% = 26 \%$.

Note: Both fcc (ccp) and hcp have same packing efficiency. Hence, hcp has a packing efficiency of 74.0 % and space unoccupied (or empty space) is 26.0 %.

Check Your Grasp

How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain. (NCERT)

Since, $d = \frac{2.1W}{a^3.N_A}$ z.M a^3 . N

On rearranging, we get, atomic mass (M) = $d.a^3.N_A$ z

- On substituting the values of density (d), dimension/edge length (a), Avogadro number (N_A) and number of atoms per unit cell (z), we get atomic mass of an unknown metal.
- If a is taken in cm and M is molar mass in g mol⁻¹, the above expression becomes, $d = \frac{Z \times M}{a^3 \times N_A} g cm^{-3}$ $\frac{z \times M}{a^3 \times N_A}$ g cm⁻ \times
- In terms of SI units, if M is in kg mol⁻¹ and a is in meters, then, $d = \frac{z \times M}{a^3 \times N_A}$ kg m⁻³ \times
- \bullet In case of ionic compounds $A⁺B⁻$ having fcc structure like NaCl, Edge (a) = $2 \times$ Distance between A^+ and B^- ions

1.7 Packing in voids of ionic solids

Do You Know?

- ľ i. When particles are closely packed resulting in either cubic close packed (ccp) or hexagonal close packed (hcp) structure, two types of voids are generated i.e. tetrahedral void and octahedral void.
- ii. While number of octahedral voids present in lattice is equal to number of close packing particles, the number of tetrahedral voids generated is twice this number. Let the number of close packed spheres be N, then;

The number of octahedral voids generated $= N$ and the number of tetrahedral voids generated $= 2N$

- iii. In ionic solids, the bigger ions (usually anions) form close packed structure and smaller ions (usually cations) occupy the voids. If the latter ion is small enough then tetrahedral voids are occupied; but if it is bigger, then octahedral voids are occupied.
- iv. Not all octahedral or tetrahedral voids are occupied in a given compound. The fraction of tetrahedral or octahedral voids that are occupied depends upon the chemical formula.

eg. A compound is formed by two elements X and Y. Atoms of the element Y (anion) make ccp and those of the element X (cations) occupy all the octahedral voids. Then the formula of a compound is determined as: The ccp lattice is formed by the element Y.

Number of octahedral voids = Number of atoms of Y present in ccp

 Since all the octahedral voids are occupied by the atoms of X, their number would also be equal to that of the number of atoms of element Y. Thus, the atoms of elements X and Y are present in equal numbers.

- \therefore Ratio of X and Y = 1:1
- \therefore The formula of the compound = XY

***Q.31. Explain the packing and voids in ionic solids.**

- **Ans:** i. The constituent particles in ionic solids are the cations and anions. They carry positive and negative charge respectively. Electrical neutrality is maintained as the number of cations is equal to the number of anions. Due to this, charges are balanced.
	- ii. The structure of the unit cell depends on the relative sizes of cations and anions. Usually cation has relatively small size and occupies tetrahedral or octahedral voids.
	- iii. Tetrahedral void is occupied when the size of the cation is relatively small. Octahedral voids are occupied by bigger cations.
	- iv. Sometimes the size of the cations is so large that they cannot occupy octahedral voids. Then the structure of the unit cell is modified. The unit cell expands as the anions are separated from one another. This forms larger cubic hole which can accommodate larger cations.

***Q.32. Write a note on radius ratio rule of ionic compounds.**

- **Ans:** i. The stoichiometry and the size of the cation and anion determines the structure of ionic compounds.
	- ii. Smaller cations occupy tetrahedral voids and bigger cations occupy octahedral voids or cubic voids.
	- iii. The coordination number of the ion also determines the geometry of the unit cell.
- iv. The ratio of the radius of the cation (r^+) to the radius of the anion (r^-) is the radius ratio $\begin{pmatrix} r \ -r \end{pmatrix}$ r $^{+}$ - $\left(\frac{r^+}{r^-}\right)$. For a

given coordination number, the radius ratio has a limiting value.

- v. The ionic structure is unstable when the radius ratio is less than the expected value.
- vi. By using radius ratio rule, the structures of ionic solids can be predicted. This rule is not applicable to covalent compounds.

***Q.33. Explain how to deduce coordination number of cations.**

- **Ans:** i. *The coordination number of constituent particle of the crystal lattice is the number of particles surrounding a single particle in the crystal lattice.*
	- ii. In case of ionic crystals, coordination number of an ion in the crystal is the number of oppositely charged ions surrounding that ion.
	- iii. The stoichiometry and the size of the cation and anion determines the structure of ionic compounds.
	- iv. In ionic solids, the bigger ions (usually anions) form close packed structure and smaller ions (usually cations) occupy the voids. If the latter ion is small enough then tetrahedral voids are occupied; but if it is bigger, then octahedral voids are occupied. Generally, for an ionic crystalline structure to be stable, there is definite radius ratio (r^{+}/r^{-}) limit for a cation to fit perfectly in the lattice of anions. This also defines the coordination number of the cation.
- v. The limiting values of r^{\dagger}/r^{-} for the coordination number and the hole occupied by the cation are given in the following table:

1.8 Defects in crystal structure

Q.34. Define crystal defect.

Ans: *Any deviation or irregularity from the perfectly ordered arrangement of constituent particles in crystal is called crystal imperfection or defect.*

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Q.35. Why does crystal defect arise?

Ans: The defect may arise due to the heat absorbed by the crystals from the surrounding or due to the presence of impurities in the crystals and also due to the irregularities in the arrangement of constituent particles. When the rate of crystallisation is fast, more defects are present. When the rate of crystallisation is slowest, the defects are minimized. The physical and chemical properties of crystalline solids are affected due to presence of crystal defects.

Q.36. Define line defect.

Ans: *The defect due to irregularity in a complete line, i.e., a row of lattice points of constituent particles is called line defect.*

***Q.37. What are point defects?**

Ans: *The point defect is the defect due to a fault produced in the arrangement of a point i.e., a constituent particle like atom, ion or molecule in a crystalline solid.*

The point defects are classified into three types:

- **i. Vacancy defect or Schottky defect:**
	- a. *Sometimes during crystallisation some of the places of the constituent particles remain unoccupied and the defect generated is called vacancy defect.*
	- b. The unoccupied positions are called vacancies.
	- c. It results in the decrease in density of the substance.
	- d. In this defect, the electrical neutrality is maintained and equal number of cations and anions are missing.

- e. In Ionic compounds, this defect is known as **Schottky defect**.
- f. Ionic compounds in which the size of the cations is almost similar to that of anions shows vacancy defect.

eg. NaCl, KCl, CsCl, KBr, AgBr, etc.

ii. Interstitial defect or Frenkel defect:

- a. *When cation or anion from ionic solid leaves its regular site and moves to occupy a place between the lattice site called interstitial position, the defect is called interstitial defect or Frenkel defect.*
- b. Due to this defect, the density of the substance is not affected.
- c. Ionic compounds with large difference in the size of the cation and anion show interstitial defect.

d. Silver halides (AgCl, AgBr and AgI) and ZnS show interstitial defect. The cations Ag^+ and Zn^{2+} occupy the interstitial space as they have relatively smaller size.

Chapter 01: Solid State

iii. Impurity defect:

- a. *The impurity defect occurs when a regular cation of the crystal is replaced by some different cation.*
- b. If the impurity cation is substituted in place of regular cation, it is called **substitution impurity defect.**
- c. If the impurity is present in the interstitial positions, it is called **interstitial impurity defect.**
- d. When one metal is substituted by another metal, substitution alloy is formed.
	- **eg.** When copper metal is substituted by zinc metal in 3:1 ratio, brass is obtained.
- e. The impurity defect completely changes the original properties of crystalline solid.
- **Fig.1. Brass Alloy (showing substitution impurity defect)** Copper Zinc **Fig.2. Stainless Steel** –Iron Carbon

(showing interstitial impurity defect)

 eg. Iron is soft, malleable and ductile. Carbon is introduced as impurity to form stainless steel. It is an interstitial alloy and is hard, stronger, less ductile, shiny and has bright appearance.

1.9 Electrical properties

***Q.38. Explain band theory.**

- **Ans:** i. Band theory can explain the variation in electrical conductivity of metals, non-metals and semiconductors.
	- ii. It is based on the assumption that molecular orbitals are formed in the crystal by combination of atomic orbitals. The number of molecular orbitals increase with increase in the number of participating atomic orbitals.
	- iii. Due to this, the difference in energy levels decreases. When a very large number of molecular orbitals are formed, the energy gaps are so small that the energy levels merge to form a continuous band of molecular orbitals. This extends over entire crystal.
	- iv. Each atomic orbital contains electrons and corresponds to one energy level in the band. The electrons present in the higher energy level of band are free to move and they conduct electricity.
	- **eg.** a. Consider the formation of bands in magnesium which has atomic number 12 and electronic configuration $1s^2 2s^2 2p^6 3s^2$.
		- b. Two valence electrons are present in 3s atomic orbital. A large number of 3s atomic orbitals of several magnesium atoms combine to form a large number of bonding and antibonding molecular orbitals.
		- c. These molecular orbitals are so close to each other that they cannot be distinguished from one another. They collectively form a **band.**
		- d. The band formed by the overlap of filled 3s atomic orbitals is called **valence band**. The band formed by the overlap of empty 3p atomic orbitals is called **conduction band.**

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- v. In case of metals, the energy gap between valence band and conduction band is very small. Electrons can be excited from valence band into conduction band by providing very little energy. Electrons present in the conduction band can move freely from one end of the metal to other end. Hence, metals have good thermal and electrical conductivity.
- vi. In case of insulators, the energy gap between valence band and conduction band is large. Excitation of electrons from valence band into conduction band requires large amount of energy. This amount of energy is not available. Thus, electrons remain in the valence band and cannot move freely. Hence, insulators have poor thermal and electrical conductivity.

eg. copper, aluminium, etc.

ii. Insulators:

iii. Semiconductors:

- a. In insulators, the energy gap between valence band and conduction band is very large. Therefore, the empty bands are not accessible for conduction and hence, electrons from valence band cannot jump into the conduction band.
- b. Thus, the insulators have extremely low conductivity.
- **eg.** rubber, wood, plastics, glass, diamond, etc.

and insulators. These are called semi-metals or semiconductors. b. In semiconductors, the energy gap between the valence band and conduction band is small. Therefore, some of the electrons may jump from valence band to conduction band and some conductivity is observed.

- c. Conductivity of semiconductor increases with increase in temperature, because with increase in temperature, large number of electrons jump from valence band to conduction band.
- **eg.** silicon, germanium, etc.

***Q.40. Distinguish between conductor, insulator and semiconductor.**

Ans: Conductors Insulators Semiconductors i. Definition *A substance which conducts heat and electricity to a greater extent is called conductor. A substance which cannot conduct heat and electricity under any conditions is called insulator. A substance which has poor electrical conductance at low temperature, but higher conductance at higher temperature is called semiconductor.*

Do You Know?

- i. *The conductivity of semiconductor is too low, which can be increased by adding an appropriate amount of suitable impurity. This process is called doping.*
- ii. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium.
- iii. Such impurities introduce electronic defects in them. Electronic defects correspond to defects in ionic crystals due to the electrons.

***Q.41. What is semiconductor? (NCERT)**

Ans: *A substance which has poor electrical conductance at low temperature but higher conductance at higher temperature is called semiconductor.*

Q.42. *Describe the two main types of semiconductors. OR

 Describe the two main types of semiconductors and contrast their conduction mechanism. (NCERT) Ans: The two main types of semiconductors are as follows:

i. n-type semiconductor (Electron rich or donor impurities):

The electron rich (or donor) impurities provide electrons in the following way:

- a. Silicon and germanium belonging to group 14 of the periodic table have four valence electrons. In their crystals, each atom forms four covalent bonds with its neighbours.
- b. If some atoms with five valence electrons (of group 15) such as arsenic (As) or phosphorus (P) are added to the germanium crystal, a minute proportion of 'Ge' atoms are randomly replaced by 'As' atoms.
- c. As a 'Ge' atom is substituted by an atom of 'As', four of the electrons in arsenic form covalent bonds with surrounding 'Ge' atoms and the fifth electron remains free as shown in figure (a).
- d. Hence, an extra electron, (more than the number required for forming the four covalent bonds), gets introduced in the crystal. This extra electron which is not needed for bonding, becomes delocalised and thus helps in conducting electricity. Therefore, germanium containing traces of arsenic (or arsenic doped germanium) exhibits high electrical conductivity.
- e. This type of conduction is known as n-type semiconduction, where 'n' stands for negative because electrons are responsible for semiconducting behaviour. This is shown in figure (b). Doping of germanium or silicon with other group-15 elements such as P, Sb or Bi also give ntype semiconductors.

ii. p-type semiconductor (Electron deficient or acceptor impurity):

An electron deficient or acceptor impurity helps in conduction in the following way:

- a. Some atoms of germanium are doped with acceptor atoms having only three outer shell electrons such as Indium (of Group 13).
- b. Each indium atom uses its three electrons to form three bonds in the lattice and is unable to form fourth bond to complete the network structure of Ge. As a result, some sites normally occupied by electrons are left empty and gives rise to electrons deficiencies. The electron deficient sites are called electron vacancies or positive holes because the net charge at these sites is positive.
- c. When electric field is applied, a valence electron on adjacent Ge atom may gain sufficient energy to move into the hole. This forms a new positive hole on the adjacent Ge atom.
- d. The migration of positive hole continues and current is carried throughout the crystal. This is equivalent to moving an electron in the opposite direction, and therefore, current is carried. Thus, doping of germanium with traces of indium increases the electrical conductivity of the germanium crystal. This type of conduction is called p-type semiconduction because holes (positive in charge) appears to be responsible for the semiconducting properties. This is shown in figure (b).
- e. Doping of silicon or germanium with other group-13 elements such as B, Al or Ga also give p-type semiconductors.

***Q.43. Classify the following semiconductors into n- or p-type.**

Q.44. A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong? (NCERT)

Ans: To prepare n-type semiconductor, group 14 element (such as silicon or germanium having four valence electrons) is doped with group 15 element (such as arsenic or phosphorus having five valence electrons).

1.10 Magnetic properties

***Q.45. Explain the origin of magnetic properties in solids.**

Ans: Magnetic property of substance:

- i. Every substance has some magnetic properties associated with it. The origin of these properties depends on the electrons.
- ii. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from the following two types of motions:
	- a. Its orbital motion around the nucleus b. Its spin motion around its own axis.

- iii. Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment.
- iv. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it.
- v. On the basis of their magnetic properties, substances are classified into three categories:
	- a. Paramagnetic b. Diamagnetic c. Ferromagnetic

Q.46. *Explain: i. Paramagnetism ii. Diamagnetism iii. Ferromagnetism OR

Explain the following with suitable examples: (NCERT)

 i. Paramagnetism ii. Diamagnetism iii. Ferromagnetism

Ans: i. Paramagnetism:

- a. *The substances which have permanent magnetic dipoles and are attracted by the magnetic field are known as paramagnetic substances. The property thus exhibited is called paramagnetism.*
- b. Paramagnetic substances contain unpaired electrons. In such cases, the magnetic moments of electrons do not cancel each other.
- c. Thus, paramagnetic substances have a net magnetic moment associated with them. When placed in a magnetic field, they experience net force of attraction.
- d. Paramagnetic substances with greater number of unpaired electrons experience stronger pull in the magnetic field. Hence, as the number of unpaired electrons increases, the degree of paramagnetism increases.
	- eg. Oxygen, Cu^{2+} , Fe^{3+} , Cr^{3+} ions, etc.

ii. Diamagnetism:

- a*. The substances which are weakly repelled by the magnetic field are known as diamagnetic substances. The property thus exhibited is called diamagnetism.*
- b. In diamagnetic substances, all electrons are paired. Each orbital contains two electrons having opposite spins. Thus, the spins are paired. Such substances are weakly repelled by the magnetic field.
	- **eg.** Water, sodium chloride, benzene, etc.

iii. Ferromagnetism:

- a. *The substances which are strongly attracted by the magnetic field and show permanent magnetism even when the magnetic field is removed are known as <i>ferromagnetic substances*. *The property thus exhibited is called ferromagnetism.*
- b. Ferromagnetic substances contain a large number of unpaired electrons. They can be permanently magnetised. They posses very strong magnetic property. **eg.** Iron, cobalt, nickel, $CrO₂$, etc.

The electronic configuration of iron (atomic number 26) is $[Ar]$ 3d⁶ 4s². It contains four unpaired electrons. Hence, it is strongly ferromagnetic.

#Q.47. Identify the following substances as paramagnetic, diamagnetic or ferromagnetic.

i. Sodium $_{11}$ Na ii. Magnesium $_{12}$ Mg iii. $_{20}Ca^{2+}$ cation iv. $_{17}CI$ ⁻ anion **v.** Iron ${}_{26}Fe$ **vi.** ${}_{27}Co$ atom **vii.** ${}_{28}Ni$ atom Ans: Paramagnetic: Sodium ₁₁Na, Diamagnetic: $_{17}Cl^-$ anion, Magnesium $_{12}Mg$, $_{20}Ca^{2+}$ cation Ferromagnetic: Iron $_{26}Fe$, $_{27}Co$ atom, $_{28}Ni$ atom

Quick Review

 Classification of solids on the basis of the presence or absence of orderly arrangement of the constituent particles:

Classification of crystalline solids based on different binding forces:

Three types of cubic lattices:

Classification of solids based on response to magnetic field:

Important Formulae

1. Density of unit cell:

i. Mass of one atom =
$$
\frac{\text{Atomic mass}}{\text{Avogadro number}}
$$

ii. Volume of unit cell = a^3

iii. Density = $\frac{\text{Mass of unit cell}}{\text{Area of the total}}$ Volumeof unit cell

2. **Packing efficiency** =
$$
\frac{\text{Volume occupied by spheres in unit cell}}{\text{Var}(x)} \times 100
$$

Volumeof unit cell

Solved Examples

Type I: Problems based on density of unit cell

Example 1

A unit cell of iron crystal has edge length 288 pm and density 7.86 g cm–3. Find the number of atoms per unit cell and type of the crystal lattice.

Given: Molar mass of iron = 56 g mol⁻¹, Avogadro's number $N_A = 6.022 \times 10^{23}$ [Oct 2014] *Solution:* **Method 1:**

Given: Density (d) = 7.86 g cm⁻³, Edge length (a) = 288 pm = 288 × 10⁻¹² m = 2.88 × 10⁻⁸ cm Molar mass = 56 g mol⁻¹, Avogadro number N_A = 6.022×10^{23}

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**Example 2*

Unit cell of iron crystal has edge length of 288 pm and density of 7.86 g cm³ . Determine the type of crystal lattice (Fe = 56).

Solution: Refer example 1: Method 1

Example 3

An element having bcc geometry has atomic mass 50. Calculate the density of the unit cell, if its edge length is 290 pm. *Solution:*

Given: Edge length (a) = 290 pm = 290 \times 10⁻¹² m = 290 \times 10⁻¹⁰ cm Atomic mass $= 50$

Example 4

An element crystallizes in fcc structure with unit cell edge length of 200 pm. Calculate its density if 200 g of this element contain 24×10^{23} **atoms.**

Solution:

Example 5

The density of chromium metal is 7.29 g cm⁻³. If the unit cell is cubic with edge length of 289 pm, determine the type of unit cell (simple, body centred or face-centred) (Atomic mass $Cr = 52$ a.m.u). *Solution:*

Calculation: Mass of one Cr atom =
$$
\frac{\text{Atomic mass}}{\text{Avogadro number}} = \frac{52}{6.023 \times 10^{23}} = 8.63 \times 10^{-23} \text{ g}
$$

\nVolume of unit cell = $a^3 = (289 \times 10^{-10} \text{ cm})^3 = 2.414 \times 10^{-23} \text{ cm}^3$

\nDensity (d) = $\frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{\text{Number of atoms in unit cell} \times \text{Mass of one atom}}{\text{Volume of unit cell}}$

\n7.29 = $\frac{\text{Number of atoms in unit cell} \times 8.63 \times 10^{-23}}{2.414 \times 10^{-23}}$

\nNumber of atoms in unit cell = $\frac{7.29 \times 2.414 \times 10^{-23}}{8.63 \times 10^{-23}} = 2.04$

\nNumber of atoms in unit cell = $2.04 \approx 2$

\n \therefore Type of crystal lattice = **bcc**

\n**Ans:** Since the given unit cell contains 2 atoms, it has a **body centred cubic (bcc) structure.**

Example 6

An element crystallizes in bcc structure. The edge length of its unit cell is 288 pm. If the density of the crystal is 7.2 g cm^{-3} , what is the atomic mass of the element? *Solution:*

Given: Edge length (a) = 288 pm = 288 \times 10⁻¹² m = 288 \times 10⁻¹⁰ cm, Density (d) = 7.2 g cm⁻³ *To find:* Atomic mass *Formulae:* i. Mass of one atom = $\frac{\text{Atomic mass}}{\text{6}}$ Avogadro number ii. Volume of unit cell $= a³$ iii. Density = $\frac{\text{Mass of unit cell}}{\text{mass of unit cell}}$ Volumeof unit cell *Calculation:* Volume of unit cell = $a^3 = (288 \times 10^{-10} \text{ cm})^3 = 2.389 \times 10^{-23} \text{ cm}^3$ Density = $\frac{\text{Mass of unit cell}}{\text{mass of unit cell}}$ Volumeof unit cell $\therefore \qquad 7.2 \text{ g cm}^{-3} = \frac{\text{Mass of unit cell}}{2.380 \times 10^{-23} \text{ cm}^3}$ 2.389×10^{-23} cm \therefore Mass of unit cell = 7.2 × 2.389 × 10⁻²³ = 17.2 × 10⁻²³ g Since, the unit cell is bcc type, the number of atoms per unit cell is 2. \therefore Mass of one atom = $\frac{17.2 \times 10^{-23}}{2}$ 2 $\frac{\times 10^{-23}}{2}$ = 8.6 $\times 10^{-23}$ g atom⁻¹ Atomic mass = Mass of one atom \times Avogadro number $= 8.6 \times 10^{-23}$ g atom⁻¹ $\times 6.023 \times 10^{23}$ atom mol⁻¹ $= 51.8 \text{ g mol}^{-1}$ = **51.8 a.m.u. Ans:** The atomic mass of the given element is **51.8 a.m.u.**

Example 7

An element has a body centred cubic (bcc) structure with a cell edge of 288 pm. The density of element is 7.2 g cm–3. How many atoms are present in 208 g of this element? (NCERT) *Solution: Given*: Density (d) = 7.2 g cm⁻³, Edge length (a) = 288 pm = 288 \times 10⁻¹² m = 288 \times 10⁻¹⁰ cm. Mass of the element = 208 g *To find:* Number of atoms present in 208 g of the element

 1.2×10^{24} unit cells will contain $2 \times 1.2 \times 10^{24} = 2.419 \times 10^{24}$ atoms Ans: Number of atoms present in 208 g of the given element is 2.419×10^{24} atoms.

Example 8

Face centred cubic crystal lattice of copper has density of 8.966 g. cm⁻³. Calculate the volume of the unit cell. Given: Molar mass of copper is 63.5 g. mol⁻¹ and Avogadro number N_A is 6.022 \times 10^{23} mol⁻¹.

[Mar 2014]

Ans: The volume of the given unit cell is 4.70×10^{-23} cm³ **.**

Example 9

 X-ray diffraction studies show that copper crystallise in an fcc unit cell edge of 3.608×10^{-8} **cm. In a** separate experiment, copper is determined to have a density 8.92 g cm⁻³. Calculate the atomic mass of **copper. (NCERT)**

Solution:

Given: Edge length (a) = 3.608×10^{-8} cm, Density (d) = 8.92 g cm⁻³ *To find:* Atomic mass of copper *Formulae:* i. Mass of one atom = $\frac{\text{Atomic mass}}{\text{6}}$ Avogadro number ii. Volume of unit cell = a^3 iii. Density = $\frac{\text{Mass of unit cell}}{\text{mass of unit cell}}$ Volumeof unit cell *Calculation:* Volume of unit cell = $a^3 = (3.608 \times 10^{-8} \text{ cm})^3 = 4.697 \times 10^{-23} \text{ cm}^3$ Density = $\frac{\text{Mass of unit cell}}{\text{mass of unit cell}}$ Volumeof unit cell \therefore 8.92 g cm⁻³ = $\frac{\text{Mass of unit cell}}{4.607 \times 10^{-23} \text{ cm}^3}$ 4.697×10^{-23} cm \therefore Mass of unit cell = 8.92 × 4.697 × 10⁻²³ = 41.9 × 10⁻²³ g Since, the unit cell is fcc type, the number of atoms per unit cell is 4. \therefore Mass of one atom = $\frac{41.9 \times 10^{-23}}{4}$ 4 $\frac{\times 10^{-23}}{1}$ = 10.5 $\times 10^{-23}$ g atom⁻¹ Atomic mass = Mass of one atom \times Avogadro number $= 10.5 \times 10^{-23}$ g atom⁻¹ $\times 6.023 \times 10^{23}$ atom mol⁻¹ $= 63.24$ g mol⁻¹ = **63.24 a.m.u.**

Ans: The atomic mass of copper is **63.24 a.m.u.**

Example 10

Example 11

An element with molar mass 2.7×10^{-2} kg mol⁻¹ forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^3 kg m⁻³. What is the nature of the cubic unit cell? (NCERT) *Solution:*

Volume of unit cell = $a^3 = (408 \times 10^{-10} \text{ cm})^3 = 6.79 \times 10^{-23} \text{ cm}^3$

Density (d) =
$$
\frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{\text{number of atoms in unit cell} \times \text{mass of one atom}}{\text{Volume of unit cell}}
$$

2.7 = $\frac{\text{Number of atoms in unit cell} \times 4.48 \times 10^{-23}}{6.79 \times 10^{-23}}$
Number of atoms in unit cell = $\frac{2.7 \times 6.79 \times 10^{-23}}{4.48 \times 10^{-23}} = 4.09 \approx 4$
Time of crystal lattice = **free**

Type of crystal lattice = **fcc**

Ans: Hence, nature of cubic unit cell is **face-centred** or **cubic close packed.**

**Example 12*

Silver crystallizes in fcc structure with edge length of unit cell, 4.07×10^{-8} cm and if density of metallic silver is 10.5 g cm⁻³. Calculate the molecular mass of silver.

Solution:

Given: Edge length (a) = 4.07×10^{-8} cm, Density (d) = 10.5 g cm⁻³ *To find:* Molecular mass of silver *Formulae:* i. Mass of one atom = $\frac{\text{Atomic mass}}{\text{6}}$ Avogadro number ii. Volume of unit cell $= a³$ iii. Density = $\frac{\text{Mass of unit cell}}{\text{mass of unit cell}}$ Volumeof unit cell *Calculation:* Volume of unit cell = $a^3 = (4.07 \times 10^{-8} \text{ cm})^3 = 6.74 \times 10^{-23} \text{ cm}^3$ Density = $\frac{\text{Mass of unit cell}}{\text{mass of unit cell}}$ Volumeof unit cell $10.5 \text{ g cm}^{-3} = \frac{\text{Mass of unit cell}}{6.74 \times 10^{-23} \text{ cm}^3}$ 6.74×10^{-23} cm \therefore Mass of unit cell = 10.5 \times 6.74 \times 10⁻²³ = 70.8 \times 10⁻²³ g Since, the unit cell is fcc type, the number of atoms per unit cell is 4. \therefore Mass of one atom = $\frac{70.8 \times 10^{-23}}{1}$ 4 $\frac{\times 10^{-23}}{1}$ = 17.7 $\times 10^{-23}$ g atom⁻¹ Atomic mass = Mass of one atom \times Avogadro number $= 17.7 \times 10^{-23}$ g atom⁻¹ $\times 6.023 \times 10^{23}$ atom mol⁻¹ = 106.6 g mol⁻¹ Since silver is monoatomic, molecular mass of silver is equal to atomic mass of silver. \therefore Molecular mass of silver = 106.6 g mol⁻¹ **Ans:** The molecular mass of silver from the given data is **106.6 g mol–1**

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**Example 13*

Copper crystallizes into a fcc structure and the unit cell has length of edge 3.61×10^{-8} cm. Calculate the **density of copper if the molar mass of Cu is 63.5 g mol–1.**

Solution:

**Example 14*

Determine the density of cesium chloride which crystallizes in a bcc type structure with the edge length 412.1 pm. The atomic masses of Cs and Cl are 133 and 35.5 respectively. *Solution:*

Ans: The density of cesium chloride is **4.0 g cm⁻³.**

Example 15

Niobium crystallises as body centred cube (BCC) and has density of 8.55 kg dm³ . Calculate the atomic radius of niobium. (Given: Atomic mass of niobium = 93) [Mar 2015]

OR

*****Niobium is found to crystallise with bcc structure and found to have density of 8.55 g cm³ . Determine the atomic radius of niobium if its atomic mass is 93 a.m.u. (NCERT)**

Solution: Given: Atomic mass (M) = 93 Density (d) = $8.55 \text{ kg dm}^{-3} = 8.55 \text{ g cm}^{-3}$ *To find:* Atomic radius (r) *Formulae:* i. Mass of one atom = $\frac{\text{Atomic mass}}{\text{6}}$ Avogadro number ii. Density = $\frac{\text{Mass of unit cell}}{\text{mass of unit cell}}$ Volumeof unit cell *Calculation*: Unit cell of bcc type contains 2 atoms. iii. Volume of unit cell = a^3 Mass of unit cell of bcc type = $2 \times \frac{93}{6.023 \times 10^{23}}$ 6.023×10 $= 30.88 \times 10^{-23}$ g Density of niobium = 8.55 g cm⁻³ Density $=$ $\frac{\text{mass of unit cell}}{\text{mass of unit cell}}$ volumeof unit cell \therefore Volume of unit cell = 23 3 30.88×10 8.55gcm \overline{a} \overline{a} $\frac{\times 10^{-23}}{1} = 3.612 \times 10^{-23}$ cm³ Volume of unit cell = $a^3 = 3.612 \times 10^{-23}$ cm³ where, a is the edge length of unit cell \therefore a = $\sqrt[3]{3.612 \times 10^{-23}}$ $= 3.306 \times 10^{-8}$ cm $= 3.306 \times 10^{-10}$ m For bcc unit cell, $a = \frac{4r}{\sqrt{3}}$ Hence, $r = \frac{\sqrt{3}}{2}$ 4 $a = \frac{\sqrt{3}}{2}$ 4 \times 3.306 \times 10⁻¹⁰ $= 1.43 \times 10^{-10}$ m = **0.143 nm Ans:** Atomic radius of niobium is **0.143 nm. Note:** 1 pm = 1×10^{-12} m $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ \therefore 1 pm = 1×10^{-3} nm

 \therefore 143 pm = 143 × 10⁻³ nm = 0.143 nm

**Example 16*

An atom crystallises in fcc crystal lattice and has a density of 10 g cm⁻³ with unit cell edge length of 100 pm. **Calculate number of atoms present in 1 g of crystal.**

Solution:

Ans: Number of atoms present in 1 g of given crystal is 4×10^{23} atoms.

Example 17

Calculate the number of atoms present in 2 gram of crystal which has face-centred cubic (FCC) crystal lattice having edge length of 100 pm and density 10 g cm^{-3} . **. [Oct 2013]**

*Solution***:**

Ans: Number of atoms present in 2 g of given crystal is 8×10^{-3} atoms.

Example 18 Gold occurs as face centred cube and has a density of 19.30 kg dm⁻³. Calculate atomic radius of gold. **(Molar mass of Au = 197) [Mar 2013]** *Solution***:** *Given*: Density (d) = 19.30 kg dm⁻³ = 19.30 g cm⁻³ Molar mass of Au = 197 g/mol *To find*: Atomic radius of gold

Formulae: i. Mass of one atom =
$$
\frac{\text{Atomic mass}}{\text{Avogadro number}}
$$

\nii. Density = $\frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

\niii. Volume of unit cell = a^3

\n*Calculation*: Unit cell of fcc type contain = $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$ atoms

\nMass of unit cell of fcc type = $4 \times \frac{197}{6.023 \times 10^{23}} = 130.83 \times 10^{-23}$ g

\nDensity of gold = 19.30 g cm⁻³

\nMass of unit cell

\nDensity = $\frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

\n3. Volume of unit cell = $\frac{130.83 \times 10^{-23}}{19.30 \text{ g cm}^{-3}} = 6.78 \times 10^{-23} \text{ cm}^3$

\nVolume of unit cell = $a^3 = 6.78 \times 10^{-23} \text{ cm}^3$

\n4. a = $\sqrt[3]{6.78 \times 10^{-23}}$ m = 4.08 × 10⁻⁸ cm

\nwhere, a is the edge length of unit cell

\nFor fcc unit cell, $a = \sqrt[3]{8} \text{ cm}$

\n $r = \frac{a}{\sqrt{8}} = \frac{4.08 \times 10^{-8} \text{ cm}}{\sqrt{8}}$

\n $= 1.44 \times 10^{-8} \text{ cm}$

\n $= 1.44 \times 10^{-10} \text{ m}$

= **144 pm**

Ans: The atomic radius of gold is **144 pm**.

Note: All the above problems can alternatively be solved by using the formula: $d = \frac{2.1W}{a^3.N_A}$ $\frac{Z.M}{a^3.N_A}$. *(Refer example 1)*

Type II: Problems based on edge length of unit cell

Example 19

Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell? (NCERT)

Solution:

Given: Atomic radius (r) of gold = 0.144 nm *To find:* Edge length (a) of the unit cell *Formula:* $a = \sqrt{8} r = 2\sqrt{2} r$ *Calculation:* For fcc unit cell, $a = 2\sqrt{2}$ r = $2\sqrt{2} \times 0.144 = 0.407$ nm **Ans:** The length of a side of the cell is **0.407 nm**.

Example 20

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Type III: Problems based on formula of compound

Example 21

A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids? (NCERT)

Solution:

Example 22

A compound is formed by two elements M and N. The elements N formed ccp and atoms of M occupy 1/3 rd of tetrahedral voids. What is the formula of the compound? (NCERT)

Solution:

Given: Element N forms ccp lattice and element M occupy $1/3^{rd}$ of tetrahedral voids.

To find: Formula of the compound.

Calculation: Let the atoms N in ccp unit cell be 'n'.

 \therefore Number of tetrahedral voids = 2n

As 1/3 rd of the tetrahedral voids are occupied by atoms M,

: $n = 2 : 3$

Number of atoms $M = 2n \times \frac{1}{2}$ 3 $=\frac{2n}{2}$ 3

3

$$
\therefore
$$
 Ratio of M : N = $\frac{2n}{3}$

Ans: The formula of the compound is M_2N_3 .

Example 23

Ferric oxide crystallized in a hexagonal close packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide. (NCERT) *Solution:*

Given: Oxide (O^{2-}) ions form hcp lattice and ferric (Fe³⁺) ions occupy $2/3^{rd}$ of the octahedral voids. *To find:* Formula of the compound.

Calculation: Let the number of oxide ions (O^{2-}) in hcp unit cell = n

 \therefore Number of octahedral voids = n

As $\frac{2}{3}$ 3 rd of the octahedral voids are occupied by ferric ions, the number of ferric ions present 2 $2n$

$$
= n \times \frac{2}{3} = \frac{2}{3}
$$

$$
\therefore
$$
 Ratio of Fe³⁺ : O²⁻ = $\frac{2n}{3}$: n = 2 : 3

3

Ans: The formula of ferric oxide is $Fe₂O₃$.

Example 24

Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B? (NCERT) *Solution:*

Ans: The formula of the con

**Example 25*

Atoms C and D form fcc crystalline structure. Atom C is present at the corners of the cube and D is at the faces of the cube. What is the formula of the compound?

Solution:

Given: Atoms C and D form fcc lattice.

C is present at corners of the cube.

D is at the faces of the cube.

To find: Formula of the compound.

Calculation: As C is present at the 8 corners of the cube, number of atoms of C in the unit cell

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

As D atoms are present at the face centres of the 6 faces of the cube, the number of atoms of D in

the unit cell =
$$
\frac{1}{2} \times 6 = 3
$$

 \therefore Ratio of atoms C : D = 1 : 3.

Ans: The formula of the compound is CD_3 .

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**Example 26*

Practice Problems

Type I

- 1. An element occurs in bcc structure. It has a cell edge of 250 pm. Calculate its atomic mass if its density is 8.0 g cm^{-3} .
2. Tungsten has body centred cubic lattice. Each
- edge of the unit cell is 316 pm and density of the metal is 19.35 g cm^{-3} . How many atoms are present in 50 g of the element?
- 3. An element of density 6.8 g cm^{-3} occurs in bcc structure with cell edge of 290 pm. Calculate the number of atoms present in 200 g of the element.
- 4. A metal (atomic mass = 50) has a body centred cubic crystal structure. The density of the metal is 5.96 g cm⁻³. Find the volume of the unit cell.

Type II

5. An element crystallises in fcc type unit cell. Calculate the edge length of the unit cell. Given that atomic radius is 127.6 pm.

Type III

6. A solid is made of two elements X and Y. Atoms X are in fcc arrangement and Y atoms occupy all the octahedral sites and alternate tetrahedral sites. What is the formula of the compound?

Multiple Choice Questions

- 1. A compound alloy of gold and copper crystallizes in a cube lattice in which the gold atoms occupy the lattice points at the corners of cube and copper atoms occupy the centres of each of the cube faces. The formula of this compound is
	- (A) AuCu (B) AuCu₂
	- (C) AuCu₂ (D) AuCu₄

2. Which is NOT a property of solids?

- (A) Solids are always crystalline in nature.
- (B) Solids have high density and low compressibility.
- (C) The diffusion of solids is very slow.
- (D) Solids have definite volume.
- 3. Which is covalent solid?
	- (A) Fullerene (B) Diamond
- (C) Graphite (D) All of these
- 4. 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
- 5. Glass is
	- (A) microcrystalline solid
	- (B) super cooled liquid
	- (C) gel
	- (D) polymeric mixture
- 6. A solid having no definite geometry is called
	- $\frac{1}{2}$ (A) amorphous solid (B) crystalline solid
	- (C) anisotropic solid (D) allotropic solid
- 7. Which of the following is/are amorphous solids? (A) Rubber (B) Plastics
	- (C) Glass (D) All of these
- 8. In the molten or fused state, which is solids conduct electricity.
	- (A) polar molecular
	- (B) non-polar molecular
	- (C) hydrogen bonded molecular
	- (D) ionic
- 9. Which one of the following is a good conductor of electricity?
	- (A) Diamond (B) Graphite
	- (C) Silicon (D) Amorphous carbon
- 10. To prepare a n-type semiconductor, the impurity to be added to silicon should have the following number of valence electrons.

[Mar 2014]

- (A) 2 (B) 3
- (C) 4 (D) 5
- 11. The number of atoms present in a simple cubic unit cell is $\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1-\frac{1}{\sqrt{1$
	- (A) 4 (B) 3 (C) 2 (D) 1
- 12. The number of atoms in a face-centred cubic unit cell is ______.
	- (A) 4 (B) 5 $(C) 6$ (D) 2
- 13. The number of unit cells in 58.5 g of NaCl is nearly $\frac{1}{20}$.

 $(A) 6 \times 10$ (B) 3×10^{22} (C) 1.5×10^{23} (D) 0.5×10^{24}

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14. The number of octahedral sites per sphere in a fcc structure is

15. Body centred cubic lattice has a coordination number of

- 16. In body centred cubic structure the space occupied is about _______. **[Mar 2013]** (A) 68% (B) 53% (C) 38% (D) 32%
- 17. The number of atoms in 100 g of an fcc crystal with density $d = 10 g / cm^3$ and cell edge equal to 100 pm is equal to $\qquad \qquad$.

(A)
$$
4 \times 10^{25}
$$

\n(B) 3×10^{25}
\n(C) 2×10^{25}
\n(D) 1×10^{25}

- 18. Crystals can be classified into basic crystal lattices. (A) 3 (B) 7
	- (C) 14 (D) 4
- 19. In cubic closest packing (ccp) structure of NaCl, the coordination number of $Na⁺$ ion is

20. An element occurring in the bcc structure has 12.08×10^{23} unit cells. The total number of atoms of the element in these cell will be

- 21. Which of the following are the CORRECT axial distances and axial angles for rhombohedral system?
	- (A) $a = b = c$, $\alpha = \beta = \gamma \neq 90^{\circ}$
	- (B) $a = b \neq c, \alpha = \beta = \gamma = 90^{\circ}$
	- (C) $a \ne b \ne c$, $\alpha = \beta = \gamma = 90^{\circ}$
	- (D) $a \ne b \ne c, \alpha \ne \beta \ne \gamma \ne 90^{\circ}$
- 22. Which of the following parameters are CORRECT for triclinic lattice? **[Oct 2013]**
	- (A) $\alpha = \beta = \gamma = 90^{\circ}$ and $a = b = c$

(B)
$$
\alpha \neq \beta \neq \gamma = 90^{\circ}
$$
 and $a \neq b \neq c$

(C)
$$
\alpha = \gamma = 90^{\circ}, \beta \neq 90^{\circ} \text{ and } a \neq b \neq c
$$

(D) $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$ and $a \neq b \neq c$

- 23. The arrangement ABCABCABC is referred as \mathcal{L}_max
	- (A) octahedral close packing
	- (B) hexagonal close packing
	- (C) tetragonal close packing
	- (D) cubic close packing
- 24. Close packing is maximum in the crystal lattice of _______.
	- (A) simple cubic (B) face centred
	- (C) body centred (D) none of these
- 25. ABAB type represents an arrangement of layers called \qquad .
	- (A) hexagonal closed packing
	- (B) cubic closed packing
	- (C) body centred cubic packing
	- (D) face centred cubic packing
- 26. The coordination number of a metal crystallizing in a hexagonal close packed structure is $\qquad \qquad$.
	- (A) 4 (B) 12 (C) 8 (D) 6
- 27. Na and Mg crystallize in bcc and fcc type crystals respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is $\qquad \qquad$.
	- (A) 4 and 2 (B) 9 and 14
	- (C) 14 and 9 (D) 2 and 4
- 28. The empty space between the shared balls and hollow balls as shown in the diagram is called
	- $\frac{1}{2}$ (A) hexagonal void
	- (B) octahedral void
	- (C) tetrahedral void
-
- (D) double triangular void
- 29. In a closed packed lattice containing nparticles, the number of tetrahedral and octahedral voids respectively are $\qquad \qquad$.
	- (A) n, 2n (B) n, n (C) $2n, n$ (D) $2n, n/2$
- 30. A binary solid $(A⁺B⁻)$ has a zinc blende structure with B^- ions constituting the lattice and A^+ ions occupying 25% tetrahedral holes. The formula of solid is $\qquad \qquad$.
	- (A) AB (B) A_2B
	- (C) AB_2 (D) AB_4

[Mar 2015]

Chapter 01: Solid State

(A) germanium (B) boron

silicon with impurities of

- (C) arsenic (D) antimony
- 39. Which one of the following has Frenkel defect?
	- (A) Sodium chloride (B) Graphite
	- (C) Silver chloride (D) Diamond
- 40. The major binding force in diamond is _______. **[Oct 2014]**
	- (A) covalent bond
	- (B) ionic bond
	- (C) metallic bond
	- (D) coordinate covalent bond
- 41. The relation $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$ represents which crystal system? **[Oct 2015]** (A) Orthorhombic (B) Tetragonal
(C) Triclinic (D) Monoclinic (D) Monoclinic

Answers to Practice Problems

- 1. 37.64
- 2. 1.63×10^{23} atoms.
- 3. 2.4×10^{24} atoms.
- 4. 2.786×10^{-23} cm³
- 5. 360.9 pm
- 6. XY_2

Answers to Multiple Choice Questions

- 31. A solid has 3 types of atoms namely X, Y and Z. X forms a fcc lattice with Y atoms occupying all the tetrahedral voids and Z atoms occupying half the octahedral voids. The formula of the solid is
	- (A) X_2Y_4Z (B) XY_2Z_4
	- (C) X_4Y_2Z (D) X_4YZ_2
- 32. In octahedral holes (voids), a
	- (A) simple triangular void is surrounded by four spheres
	- (B) bi-triangular void is surrounded by four spheres
	- (C) bi-triangular void is surrounded by six spheres
	- (D) bi-triangular void is surrounded by eight spheres
- 33. An fcc unit cell of aluminium contains the equivalent of how many atoms?

34. The formula for determination of density of unit cell is $\qquad \qquad$.

(A)
$$
\frac{a^3 \times N_A}{z \times M} \text{g cm}^{-3}
$$

(B)
$$
\frac{z \times M}{z \times M} = \text{g cm}^{-3}
$$

(B)
$$
\frac{2 \times m}{a^3 \times N_A} \text{g cm}^{-3}
$$

(C)
$$
\frac{a^{3} \times M}{z \times N_{A}} g cm^{-3}
$$

(D)
$$
\frac{M \times N_{A}}{a^{3} \times z} g cm^{-3}
$$

- $a^3 \times z$ \times
- 35. Schottky defect defines imperfection in the lattice structure of a _______. (A) solid (B) liquid
	- (C) gas (D) plasma
- 36. Frenkel and Schottky defects are _______.
	- (A) impurity defects
	- (B) non-crystal defects
	- (C) crystal defects
	- (D) line defects
- 37. Which of the following defect, if present, lowers the density of the crystal?

- (A) Frenkel
- (B) Schottky
- (C) both (A) and (B)
- (D) none of these