

Perfect

Chemistry-I

Std. XII Science

Atomic Structure of Water Molecule



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STD. XII Sci.
Perfect Chemistry - I

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Salient Features:

- Exhaustive coverage of syllabus in Question Answer Format.
- Covers answers to all Textual Questions and numericals.
- Textual Questions are represented by * mark.
- Intext Questions are represented by # mark.
- Covers relevant NCERT Questions.
- Charts for quick reference.
- Simple and Lucid language
- Includes Board Question Paper of March 2013.

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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.

Chemistry is a science concerned with the composition, structure and properties of matter as well as the changes they undergo under different conditions. From the making of medicines to the manufacture of steel, to the thunder of clouds, everything is encapsulated in the study of physical chemistry. A science that calls for such deep knowledge of concepts and an intrinsic study of all aspects must obviously, not be easy to conquer. For this we bring to you “**Std. XII : PERFECT CHEMISTRY - I**” a complete and thorough book which analyses and extensively boosts confidence of the student.

Topic wise classified “question and answer” format of this book helps the student to understand each and every concept thoroughly. Important definitions, statements and laws are specified with italic representation. Solved problems are provided to understand the application of different concepts and formulae. Practice problems and multiple choice questions help the students, to test their range of preparation and the amount of knowledge of every topic.

And lastly, we would like to thank our publishers for helping us to take this exclusive guide to all students. There is always room for improvement and hence we welcome all suggestions and regret any errors that may have occurred in the making of this book.

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

Best of luck to all the aspirants!

Yours faithfully
Publisher

PAPER PATTERN

- There will be one written paper of 70 Marks in Chemistry.
- Duration of the paper will be 3 hours.
- Chemistry paper will have two parts viz: Part I of 35 marks and Part II of 35 marks
- Same Answer Sheet will be used for both the parts.
- In the question paper, for each part there will be 4 Questions.
- Students have freedom to decide the sequence of answers.
- The paper pattern as per the marking scheme for Part I and Part II will be as follows:

Question 1: (7 Marks)

There will be 7 multiple choice Questions (MCQs), each carrying 1 mark.

Total marks = 7

Question 2: (12 Marks)

There will be 8 Questions out of which 6 Questions are to be answered, each carrying 2 marks.

Total marks = 12

Question 3: (9 Marks)

There will be 4 Questions out of which 3 Questions are to be answered, each carrying 3 marks.

Total marks = 9

(There will be 3 Questions based on numericals from part I)

Question 4: (7 Marks)

There will be 2 Question out of which 1 Question has to be answered.

It will carry 7 marks.

Total Marks = 7

(There will be 2/3 marks Questions based on numericals from Part I)

Distribution of Marks According to Type of Questions

Type of Questions	Marks	Marks with option	Percentage (%)
Objectives	14	14	20
Short Answers	42	56	60
Brief Answers	14	28	20
Total	70	98	100

Contents

No.	Topic Name	Page No.	Marks Without Option	Marks With Option
1	Solid State	1	04	06
2	Solutions and Colligative Properties	52	05	07
3	Chemical Thermodynamics and Energetics	117	06	08
4	Electrochemistry	195	05	07
5	Chemical Kinetics	276	04	06
6	General Principles and Processes of Isolation of Elements	353	03	05
7	p-Block Elements	386	08	10
	Board Question Paper March 2013	472		

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

01 | Solid State

Syllabus

- 1.0 Prominent scientists
- 1.1 Introduction
- 1.2 Classification of solids
- 1.3 Classification of crystalline solids
- 1.4 Unit cell and two and three dimensional lattices
- 1.5 Packing in solids
- 1.6 Density of unit cells
- 1.7 Packing in voids of ionic solids
- 1.8 Defects in crystal structure
- 1.9 Electrical properties
- 1.10 Magnetic properties

1.0 Prominent Scientists

Scientists		Contributions
William Henry Bragg (1862-1942) (British physicist, chemist and mathematician)	i.	Derived the Bragg equation $n\lambda = 2d \sin\theta$ to explain why cleavage of crystal reflect x-ray beam of wavelength λ at an angle θ .
	ii.	Shared the Nobel Prize in 1915 with his son William Lawrence Bragg for determining crystal structures of NaCl, ZnS and Diamond.
William Lipscomb (1919-2011) (American inorganic and organic chemist)	i.	Determined structure of boron hydride using technique of x-ray crystallography.
	ii.	Received the Nobel Prize in chemistry in 1976 for his work on structure and bonding of boron hydride and its derivatives.
Isabella Karle (1921) (American X-ray crystallographer)	i.	Developed method for determining the molecular structure by x-ray diffraction.
	ii.	Worked on crystallography of materials in the field of organic chemistry and biochemistry.

1.1 Introduction

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

- Ans:**
- 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.
 - Intermolecular forces tend to keep the constituent particles (atoms, ions or molecules) closer, whereas thermal energy tend to keep them apart by making them move faster.
 - 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.
 - 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.

Q.2. Explain the conversion of states of matter from one form to the other with the changing conditions of temperature and pressure.

- Ans:**
- Any state of matter can be changed into another by effecting changes in conditions of temperature and pressure.
 - At relatively low temperature solid state is the common state of matter.
 - By raising the temperature of the solid to its melting point, sufficient energy is imparted into the solid to overcome the intermolecular forces of attraction and thereby to melt the solid and transform it into liquid state.
 - Liquids on heating to their boiling points evaporate and transform into gaseous state.
 - On the contrary, gases on cooling and subjecting to high pressure can be transformed into liquid which on further cooling, can be transformed into solid substance.
 - Solids are rigid and cannot be compressed like gases or poured like liquids as the positions of their constituent particles, atoms or molecules are constant and cannot be changed.

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:

- Solids of fixed composition have fixed mass, volume, shape and density. Generally, solid state is denser than the liquid and gaseous states of the same substance. However solid state of water, ice is lighter than the liquid state of water. Mercury exists in liquid state and it has relatively very high density (i.e. 13.6 g mL^{-1})
- Most of the solids are hard, incompressible and rigid. Some solids like sodium, potassium, phosphorous are soft. The intermolecular distance of separation between neighbouring molecules is the shortest in solid state. Hence solids cannot be compressed.
- Intermolecular forces of attraction between the constituent particles in a solid state are stronger as compared to liquid and gaseous states.
- 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).
- The constituent particles of the solids are held tightly by intermolecular forces of attraction. Hence the particles cannot change their positions and remain stationary at one position. Therefore, solids cannot flow like liquids.

Q.5. Why do solids have a definite volume? (NCERT)

Ans: 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.6. 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).

- 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:

- Two or more substances having the same crystal structure are said to be isomorphous form (iso-same, morphous-form) and the phenomenon is called isomorphism.
- Isomorphous substances contain constituent atoms of the substance in the same atomic ratio and have similar molecular formula and similar chemical properties.
- Some of the pairs of isomorphous substances are given below:
 - NaF and MgO (atoms in the ratio 1:1)
 - NaNO₃ and CaCO₃ (atoms in the ratio 1:1:3)
 - K₂SO₄ and K₂SeO₄ (atoms in the ratio 2:1:4)
 - Cr₂O₃ and Fe₂O₃ (atoms in the ratio 2:3)
- The same atomic ratio, similar molecular formula or similar chemical properties of two or more solids are not enough to claim that the substances are isomorphous.

Eg. Sodium chloride NaCl and potassium chloride KCl have almost all the properties identical, but their crystalline structures are different. Therefore, sodium chloride and potassium chloride are not isomorphous.

b. Polymorphous / Allotropic form:

1. A single substance that crystallises in two or more forms under different conditions is called polymorphous forms (poly-many, morphous-form) and the phenomenon is called polymorphism.
2. The polymorphic forms are also called allotropic forms.
3. Carbon has two polymorphic forms, graphite and diamond.
4. Sulphur also exists in two polymorphic forms rhombic and monoclinic.
5. Calcium carbonate and silicon dioxide also exist in nature in two polymorphic forms.

ii. Amorphous / Pseudo solids / Super cooled solids: 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.7. Describe the term 'amorphous'. Give a few examples of amorphous solids. (NCERT)

Ans: Refer Q.6. ii.

***Q.8. Explain crystalline solids and amorphous solids.**

Ans: i. Crystalline solids:

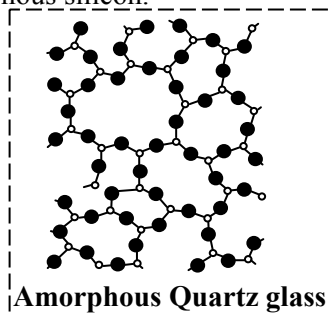
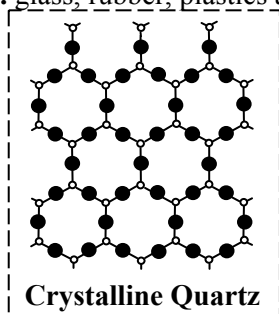
- a. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. These tiny crystals are called unit cells.
- b. A unit cell is a basic repeating structural unit of a crystalline solid.
- c. Crystalline solids have long range order which means that there is a regular pattern of arrangement of particles (atoms, ions or molecule) 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 such a solid 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.9. Distinguish between crystalline solids and amorphous solids. Give examples. OR**

Distinguish between crystalline solids and amorphous solids. [March 2013]

Ans:

	Property	Crystalline solids	Amorphous solids
1.	Shape	They have definite characteristic geometrical shape due to the orderly regular long range arrangement of constituent particles.	They have irregular shape and lack characteristic geometrical shape due to the short range orderly arrangement of constituent particles.
2.	Melting point	They have sharp and characteristic melting point.	They do not have sharp melting point. They gradually soften over a range of temperature.

3.	Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth.	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces.
4.	Heat of fusion	They have a definite and characteristic heat of fusion.	They do not have definite heat of fusion.
5.	Anisotropy	They are anisotropic, i.e. have different physical properties in different direction.	They are isotropic, i.e. have same physical properties in all directions.
6.	Nature	They are true solids.	They are pseudo solids or super cooled liquids.
7.	Order in arrangement of constituent particles	They have long range order.	They have only short range order.
8.	Eg.	Copper, silver, iron, zinc sulphide, common salt, potassium nitrate, etc.	Glass, rubber, plastics, etc.

#Q.10. Explain the term isomorphism, polymorphism, anisotropy and unit cell.

Ans: i. Isomorphism:

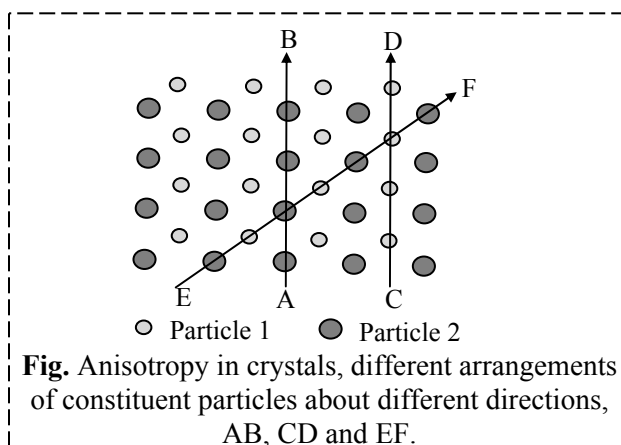
Refer Q. 6. i. a.

ii. Polymorphism:

Refer Q. 6. i. b.

iii. Anisotropy:

- The ability of crystalline solids to change values of physical properties when measured in different directions is called anisotropy.
- The physical properties like refractive index, electrical conductance, dielectric constant, etc. of crystalline solids change with the change in direction.
- The anisotropy in crystalline solid arises because the composition of solid changes with direction. From the figure, it is evident that the composition of the medium changes with the change of directions AB, CD, EF etc.



iv. Unit cell:

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

Q.11. 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.12. Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property? (NCERT)

Ans: As the solid has same value of refractive index along all directions, it is isotropic and hence amorphous. Being an amorphous solid, it would not show a clean cleavage when cut with a knife. Instead, it would break into pieces with irregular surfaces.

***Q.13. What is a glass?**

- Ans:**
- Glass is an optically transparent material produced by fusing together silicon oxide with sodium oxide, boron oxide and a trace amount of transition metal oxide is added to impart colour to the glass.
 - By changing its composition, almost eight hundred different types of glasses are manufactured. Quartz glass is obtained from only silicon dioxide.
 - Pyrex glass is obtained by fusing together 60 to 80% SiO_2 , 10 to 25% B_2O_3 and remaining amount of Al_2O_3 .
 - Soda lime glass is produced by fusing 75% SiO_2 , 15% Na_2O and 10% CaO .
 - Red glass contains trace amount of gold and copper.
 - Yellow glass contains UO_2 .
 - Blue glass contains CoO or CuO .
 - Green glass contains Fe_2O_3 or CuO .

1.3 Classification of Crystalline Solids

Q.14. Give the classification 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:

Molecular solids are those solids in which the constituent particles are molecules of the same compound.

These are further subdivided into the following categories:

a. Polar molecular solids:

- In these crystalline solids, the constituent particles are covalently bonded polar molecules like HCl , SO_2 etc.
- Polar molecules possess permanent dipole moment and in solid state they are held together by strong dipole-dipole interaction.
- 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:

- They are soft.
- They do not conduct electricity.
- The melting points of the solids are relatively low as the bonding is relatively weak.

Eg. Solid SO_2 , solid NH_3 and solid HCl .

b. Non polar molecular solids:

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

Characteristics:

- They are soft.
- They do not conduct electricity.
- They have very low melting points (lower than polar molecular solids) and are usually in liquid or gaseous state at room temperature and pressure.

Eg. Non polar molecules like CO_2 , H_2 , Cl_2 , CH_4 and weakly polar molecules like CO and other hydrocarbons form non-polar molecular solids at relatively lower temperatures. Iodine (I_2) exists in solid state even at room temperature while other solids are in gaseous state at normal temperature.

- c. **Hydrogen bonded molecular solids:**
1. These crystalline solids consist of hydrogen atom covalently bonded to strongly electronegative atom like oxygen, nitrogen or fluorine.
 2. 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:

1. They do not conduct electricity.
2. At normal temperatures and pressures, these solids exist as liquids or even gases.
3. The liquids solidify on cooling.

Eg. H₂O, NH₃

ii. **Ionic Solids:**

- a. All salts are crystalline in nature and are called ionic solids.
- b. These solids are formed by the three dimensional arrangement of cations and anions bounded by strong coulombic (electrostatic) forces. Ionic solids are formed by the force of attraction between ions of opposite charges and force of repulsion between ions of same charges.
- c. These two opposite forces result into well ordered three dimensional arrangement of ions in ionic solids, as shown in the following figure (a)

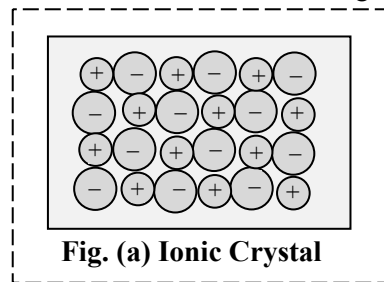


Fig. (a) Ionic Crystal

- d. The actual arrangement of ions depends on three factors,
 1. Sizes of the cation and anion.
 2. The charges on the ions.
 3. The ease with which the anion can be polarised.

Characteristics:

- a. These solids are hard and brittle in nature.
- b. They have high melting and boiling points.
- c. Since the ions are not free to move about, they are electrical insulators (non-conductors) in the solid state.
- d. However, in the molten or fused state or when dissolved in water, the ions become free to move about and thereby conduct electricity.
- e. On application of shearing force, ionic crystals undergo distortion and fracture in crystal structure.

Eg. NaCl, ZnS, CuCl, etc.

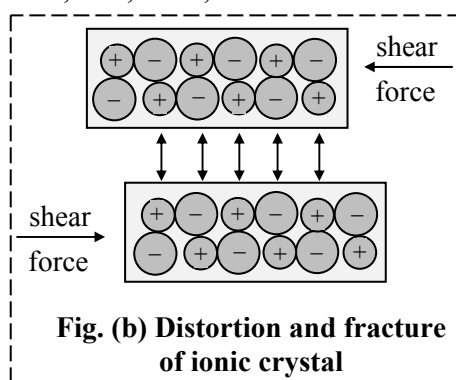
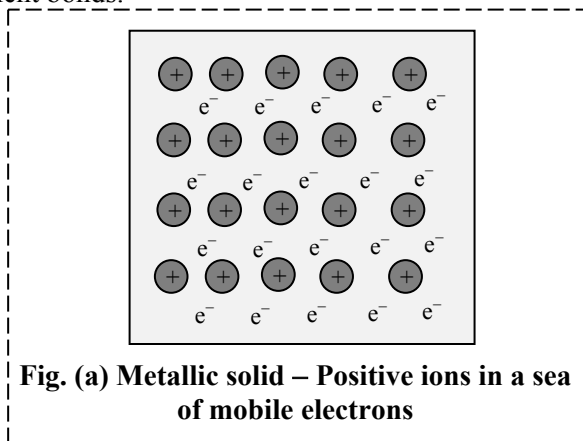


Fig. (b) Distortion and fracture of ionic crystal

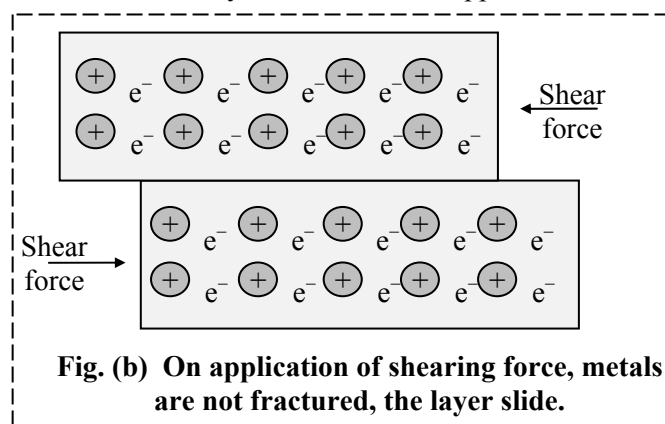
iii. Metallic solids:

- Metallic solids are the crystalline solids formed by atoms of the same metallic element.*
- Metals are orderly collection of positive ions (called kernels) in the sea of delocalised electrons.
- These electrons are mobile and are evenly spread throughout the crystal.
- Each metal atom contributes one or more electrons towards this sea of mobile electrons.
- 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:**

- Metallic bonds are tougher than other solids.
- The bonding in metals helps to acquire any shape to the metallic article.
- The metal is always present in the form of several layers arranged over one another. The layers of the metallic ions can slide on another layer.
- The metals are malleable and ductile i.e. they can be hammered or rolled into thin sheets of desired thickness and can be drawn into thin wires of required size.
- The mixture of metals can be fused together to form alloys, which exhibit all the properties of metals.
- The surfaces of all metals exhibit lustre of grey or silvery colour.

Eg. Gold metal exhibits yellow lustre and copper has reddish lustre.

**iv. Covalent or Network Solids:**

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

Characteristics:

- The solids may be hard or brittle depending on the type of covalent bonding between the atoms.
- They have extremely high melting points.
- Depending upon availability of mobile electrons, they are either good conductors of electricity or act as insulators.

Eg. Three allotropic forms of carbon i.e. diamond, graphite and fullerene.

***Q.15. Explain:**

- | | |
|----------------------------|---|
| i. Molecular solids | ii. Hydrogen bonded molecular solids |
| iii. Ionic solids | iv. Metallic solids |
| v. Covalent solids | |

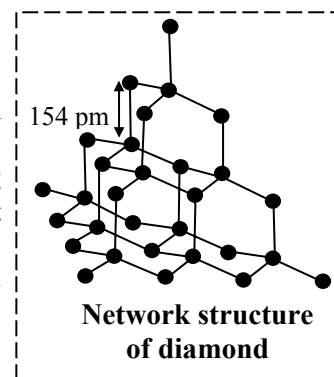
- Ans:**
- Molecular solids: *Refer Q.14. i.*
 - Hydrogen bonded molecular solids: *Refer Q.14. i. c.*
 - Ionic solids: *Refer Q.14. ii.*
 - Metallic solids: *Refer Q.14.iii.*
 - Covalent solids: *Refer Q.14. iv.*

***Q.16. Write a note on**

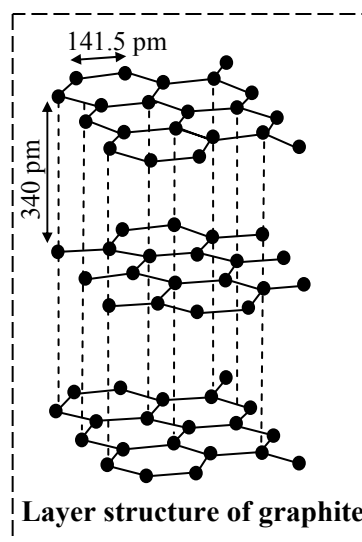
- | | |
|-------------------|---------------------|
| i. Diamond | ii. Graphite |
|-------------------|---------------------|

iii. Fullerene**Ans: i. Diamond:**

- It is the most precious crystal used in jewellery and it is an allotropic form of carbon.
- All carbon atoms in diamond are sp^3 hybridized and the bonding continues in all direction to form big giant network of covalent solid.
- The strong covalent bonds between sp^3 hybridised carbon atoms make diamond very strong and hard solid.
- It is the hardest material with very high melting point of 3550°C .

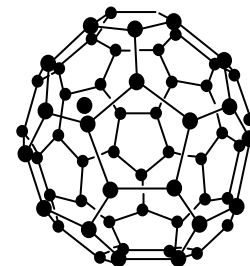
**ii. Graphite:**

- Graphite is another allotropic form of carbon.
- All carbon atoms in graphite are sp^2 hybridised. Each carbon atom is covalently bonded to three other sp^2 hybridised carbon atoms and form interlinked six membered rings of carbon atoms.
- The remaining half filled unhybridised $2p_z$ orbital is used for π bonding, so that layers of carbon atoms (i.e. graphite) are formed.
- Graphite has delocalized molecular orbitals and the delocalized electrons have the freedom to move in the delocalized molecular orbitals. Therefore, graphite is a good conductor of electricity.
- The adjacent layers of carbon atoms are held together by weak van der Waal's forces of attraction.
- The relatively stronger covalent bonds between sp^2 hybridised carbon atoms make graphite sufficiently hard.
- The layer of carbon atoms in graphite can slide over another layer. Due to this property, graphite is used as lubricant for reducing friction.
- It is used in ribbons used for printing in computers and typewriters and also used in lead pencils.



iii. Fullerene:

- Fullerene is an allotrope of carbon which was discovered when a high power laser was focused on carbon.
- The product formed is found to have formula C_{60} and has a shape of soccer ball i.e. hollow sphere.
- On this sphere, there are sixty equidistant places occupied by carbon atoms.
- Like graphite, all carbon atoms are sp^2 hybridized.
- The delocalized molecular orbitals are spread over the complete structure of the fullerene.
- The structure of fullerene is similar to that of a soccer-ball formed by arranging carbon hexagons and carbon pentagons to form hollow spheres to accommodate sixty carbon atoms present at the corners of hexagons and pentagons.
- Fullerenes are observed in carbon soot.
- Fullerene reacts with potassium to form a compound $K_{35}C_{60}$ which acts as super conductor of electricity at 18 K.
- It reacts with transition metal to form a catalyst.
- Tubes made from fullerene and graphite are called nanotubes. These are used as high strength materials, electric conductors, molecular sensors and semi conductors.



The structure of C_{60} ,
Buckminsterfullerene

Q.17. 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.18. What type of solids are electrical conductors, malleable and ductile? (NCERT)

Ans: Metallic solids are electrical conductors, malleable and ductile.

Q.19. Classify the following solids into different types

- | | | | |
|----------------------|--------------------------------|----------------------|-------------------------|
| *i. Plastic | *ii. P_4 molecule | *iii. S_8 molecule | |
| *iv. Iodine molecule | *v. Tetra phosphorous decoxide | | *vi. Ammonium phosphate |
| *vii. Brass | *viii. Rubidium | *ix. Graphite | *x. Diamond |
| *xi. NaCl | *xii. Silicon | xiii. SiC (NCERT) | xiv. LiBr (NCERT) |

- Ans:**
- Amorphous solid – Plastic
 - Molecular solids – P_4 molecule, S_8 molecule, Iodine molecule, Tetra phosphorous decoxide
 - Ionic solids – Ammonium phosphate, NaCl, LiBr
 - Metallic solids – Brass, Rubidium
 - Covalent or Network solids – Graphite, Diamond, Silicon, SiC.

Q.20. Explain:

- The basis of similarities and difference between metallic and ionic crystals. (NCERT)
- Ionic solids are hard and brittle. (NCERT)
- Solid ice is lighter than water.

Ans: i. Metallic and ionic crystals:

a. Similarities:

- Both ionic and metallic crystals have electrostatic forces of attraction.
- 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).
- This is the reason why both metallic and ionic crystals have high melting points.
- In both the cases, the bond is non-directional.

b. Differences:

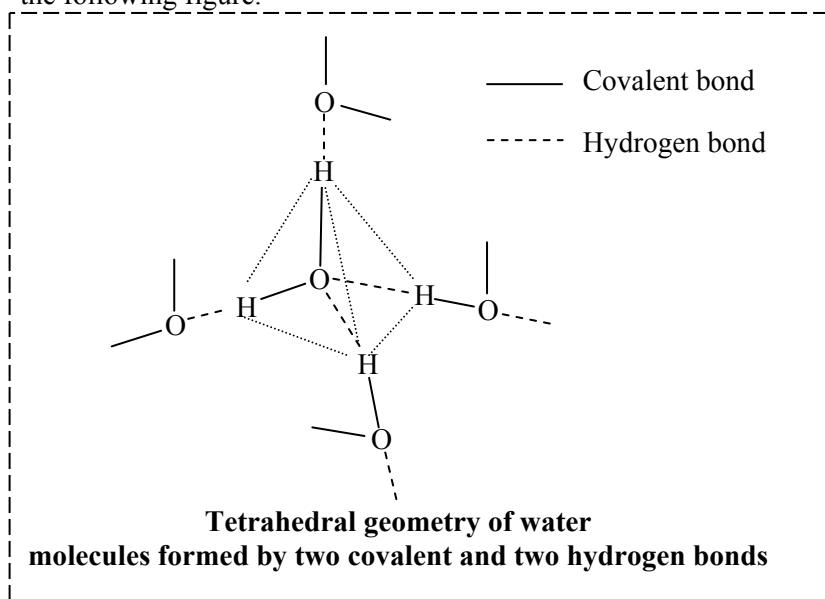
1. In ionic crystals, the ions are not free to move. Hence, they cannot conduct electricity in the solid state. They can do so only in the molten state or in aqueous solution.
2. In metals, the valence electrons are free to flow. Hence, they can conduct electricity in the solid state.
3. Ionic bond is 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.
- b. The ions are held by strong coulombic electrostatic forces of attraction compensating opposite forces. Hence they are hard.
- 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. Ice has hexagonal three dimensional crystal structure formed by intermolecular hydrogen bonding, which leave almost half the vacant space, unoccupied. X-ray studies of liquid water shows that structure of liquid water and solid ice are almost identical.
- b. However on melting of ice, some of the hydrogen bonds are broken and some of the empty spaces are occupied by water molecules and thereby density of liquid water becomes more than solid water (ice).
- c. As the hexagonal crystalline structure of solid ice collapses the liquid water molecules become more closely spaced.
- d. Generally density of solid state is always greater than the density of its liquid state but water has abnormal behaviour, since its liquid state has more density than its solid state. Hence ice floats on water due to more empty space in hexagonal structure of ice.
- e. Hydrogen bonding between water molecules forming tetrahedral arrangement of ice is shown in the following figure.

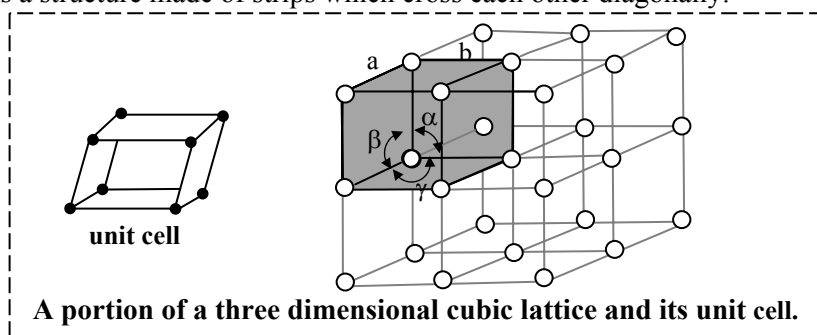


1.4 Unit cell and two and three dimensional lattices

*Q.21. What is a unit cell? Explain Bravais lattices.

Ans: A unit cell is the smallest repeating structural unit of a crystalline solid.

- When unit cells of the same crystalline substance are repeated in space in all directions, a crystalline solid is formed.
- For convenience, unit cell is drawn on paper by drawing lines connecting centres of constituent particles.
- Each point at the intersection of the lines in the unit cell represents constituent particles, i.e. an ion or an atom or molecule of the crystalline solid.
- Any point at the intersection of lines is called a lattice point.
- The particles in a crystal are arranged in a definite repeating pattern. Therefore, any one lattice point in the crystal is identical to the number of other lattice points in the crystal that have identical environments.
- The collection of all the points in the crystal having similar environment is called space lattice.
- Lattice means a structure made of strips which cross each other diagonally.



Bravais Lattices:

- The crystalline solids have definite orderly arrangement of their constituent particles in three dimensions.
- The positions of these particles in a crystal, relative to one another, are usually shown by points. The arrangement of an infinite set of these points is called space lattice.
- Each point in a lattice is called lattice point or lattice site.
- Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.
- 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.
- There are only 14 possible three dimensional lattices, as proved by the french mathematician, Bravais. These are called Bravais Lattices.
- Lattice points when joined by straight lines gives the geometry of the lattice.
- Shape of any crystal lattice depends upon the shape of the unit cell which in turn depends upon following two factors,
 - The length of the three edges, a, b and c.
 - The angles between the edges which are 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.

Q.22. How are unit cells classified?

Ans: 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 cells.

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 centred unit cell.

Centred unit cells are of three type:

a. **Body-centred unit cell:**

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.23. Explain with the help of diagram**

i. **Seven types of unit cells**

ii. **Three types of cubic cells**

iii. **Two types of tetragonal unit cells**

iv. **Four types of orthorhombic unit cells**

v. **Two types of monoclinic unit cells**

vi. **Triclinic unit cell**

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 are 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 ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$).

b. **Tetragonal lattice:**

The three edges (sides) are at right angles to each other but only two axes are equal ($a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$).

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

e. **Hexagonal lattice:**

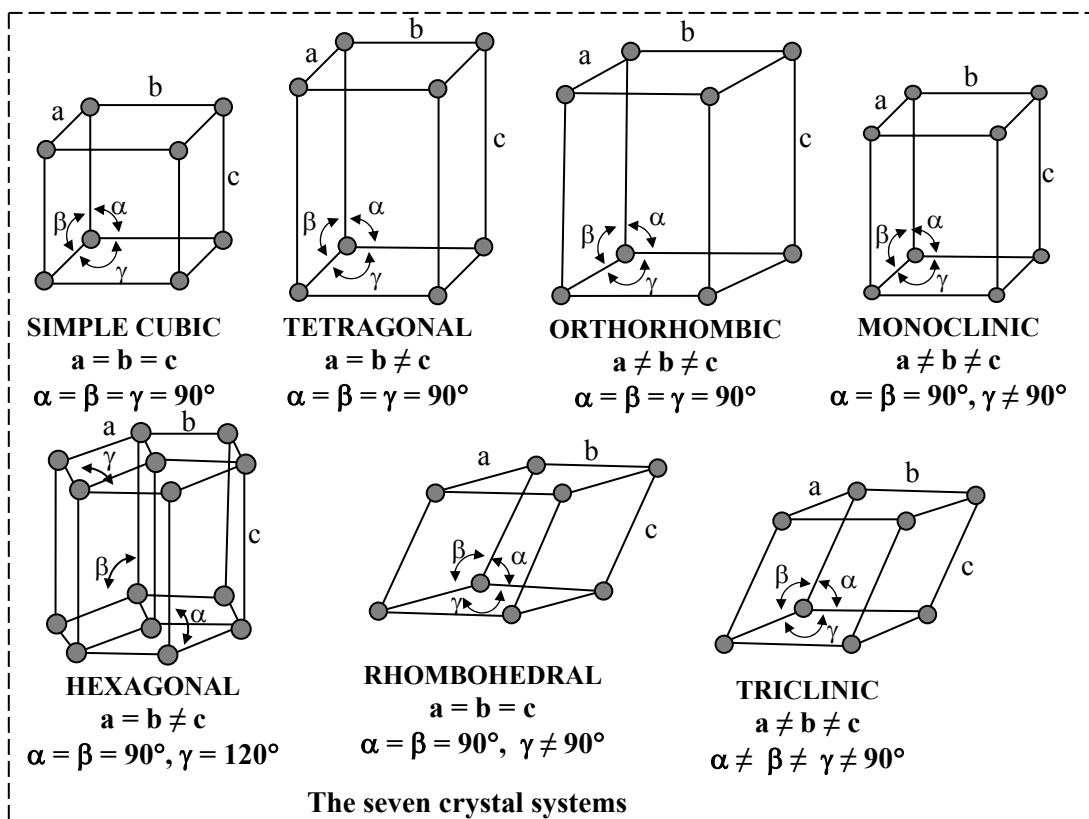
It has two edges (sides) of equal length and two angles of 90° and one angle of 120° ($a = b \neq c$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$).

f. **Rhombohedral lattice:**

The three edges (sides) are of equal lengths two axial angles are equal to 90° but the third is not equal to 90° ($a = b = c$, $\alpha = \beta = 90^\circ$, $\gamma \neq 90^\circ$).

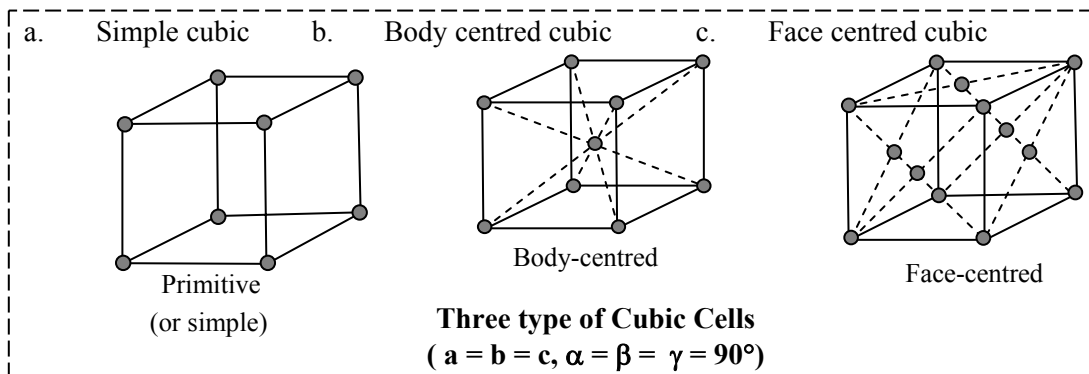
g. **Triclinic lattice:**

The three edges (sides) are of unequal lengths, and all angles are different but none is perpendicular to any of the others ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$).



ii. **Three types of cubic cells:**

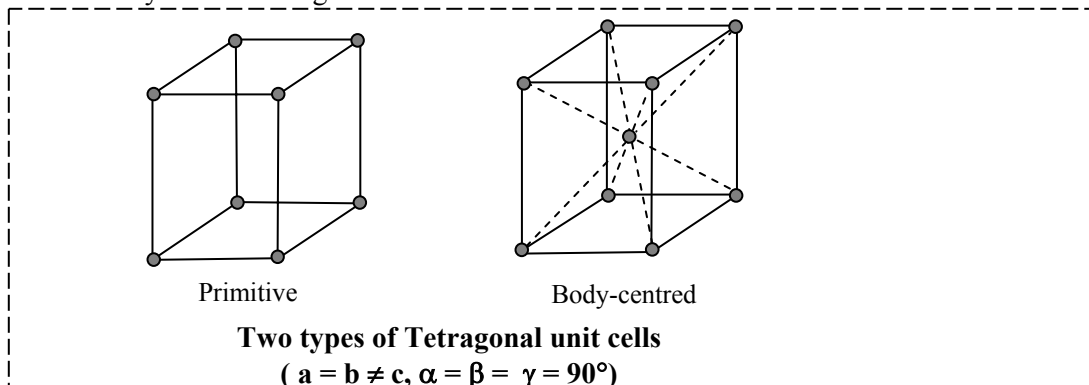
There are three types of cubic cells



iii. **Two types of tetragonal unit cells:**

There are two types of tetragonal unit cells

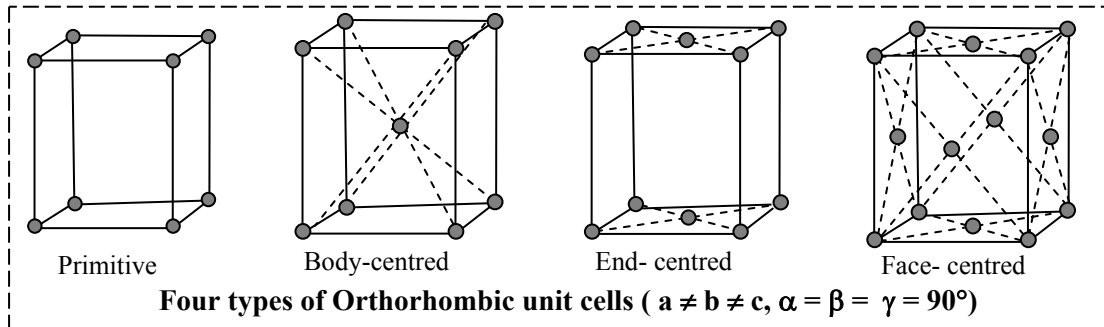
- a. Primitive or simple tetragonal
- b. Body centred tetragonal



iv. Four types of orthorhombic unit cells:

There are four types of orthorhombic unit cells

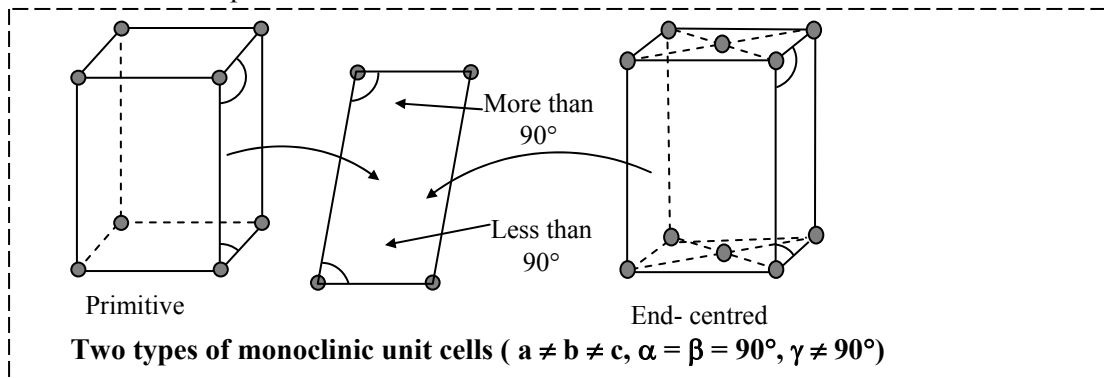
- a. Primitive or Simple orthorhombic
- b. Body centred orthorhombic
- c. End centred orthorhombic
- d. Face centred orthorhombic



v. Two types of monoclinic unit cells:

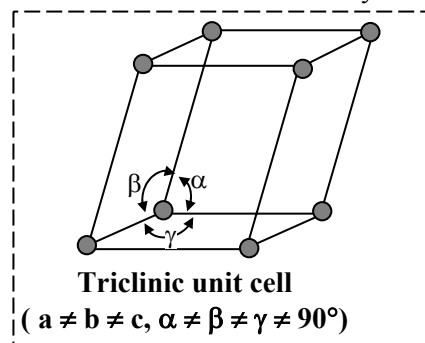
There are two types of monoclinic unit cells

- a. Primitive or Simple monoclinic
- b. End centred monoclinic



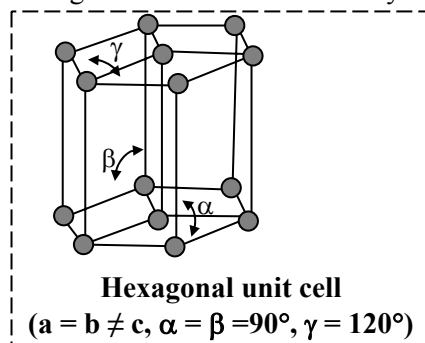
vi. Triclinic unit cell:

Triclinic unit cell exists in only one type i.e. Primitive



vii. Primitive hexagonal unit cell:

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



Note:

No.	Crystal system	Type	Edge length	Angle	Example
1.	Cubic	Simple/primitive	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Polonium
2.	Cubic	Body centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Fe, Rb, Na, Ti, W, U, Zr
3.	Cubic	Face centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Cu, Al, Ni, Au, Ag, Pt
4.	Tetragonal	Primitive	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SnO_2
5.	Tetragonal	Body centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO_2 , CaSO_4
6.	Orthorhombic	Primitive	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur
7.	Orthorhombic	Body centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO_3
8.	Orthorhombic	Face centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	BaSO_4
9.	Orthorhombic	End centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
10.	Monoclinic	Primitive	$a \neq b \neq c$	$\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$	Monoclinic sulphur
11.	Monoclinic	End centred	$a \neq b \neq c$	$\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
12.	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, H_3BO_3
13.	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	ZnO , BeO , CoS , SnS .
14.	Rhombohedral	Primitive	$a = b = c$	$\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$	Calcite, NaNO_3 , FeCO_3

Q.24. Distinguish between hexagonal and monoclinic unit cells. (NCERT)

Ans: For hexagonal unit cell, $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

For monoclinic unit cell, $a \neq b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma \neq 90^\circ$

Q.25. 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.26. 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. More the coordination number, more tightly the particles are packed in the crystal lattice.
- iii. Coordination number is also the measure of hardness of the crystal.

***Q.27. Explain how to deduce coordination number of cation.**

- 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. If particular sphere is shared, then its contribution to a given cation is accounted accordingly.
- iii. In case of ionic crystals, coordination number of an ion in the crystal is the number of oppositely charged ions surrounding that ion.

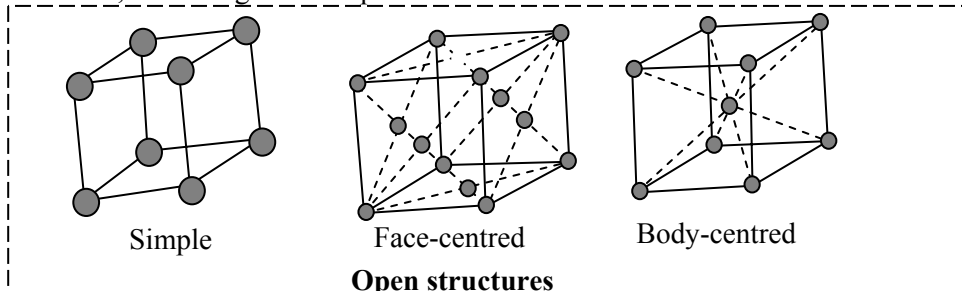
Q.28. Explain the following:

- i. **Open structure** ii. **Space filling structure**

Ans: i. Open structure:

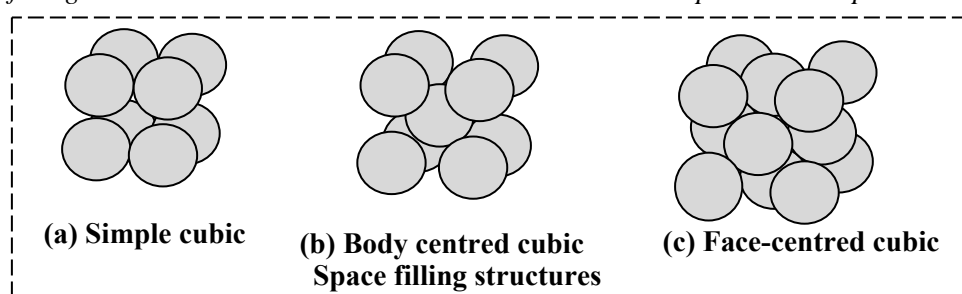
Open structures are those structures where each small sphere represents only the centre of the particle occupying that position and not the actual size of the particle.

In this structure, the arrangement of particles is easier to follow as shown in the following figures.



ii. **Space filling structures:**

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

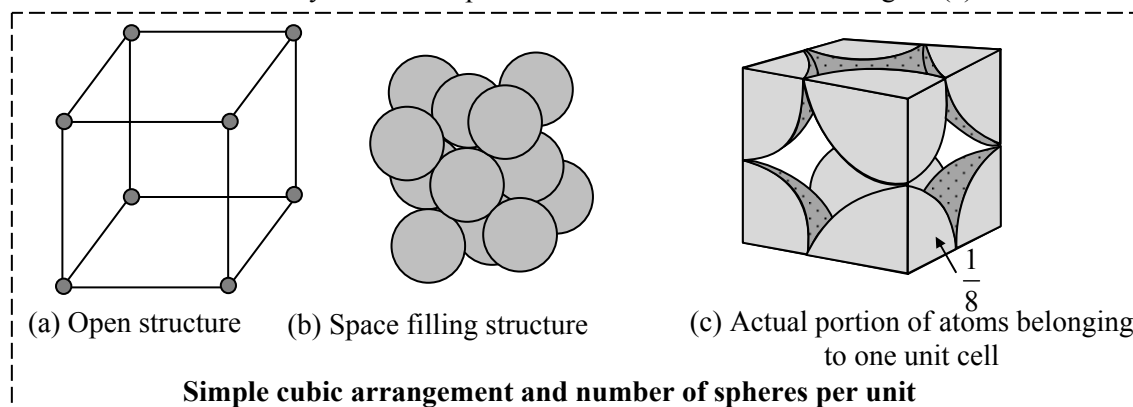


Q.29. Calculate the number of atoms present per unit cell in:

- i. **Simple or primitive cubic lattice** ii. **Body-centred cubic lattice**
 iii. **Face-centred cubic lattice**

Ans: i. Simple or primitive cubic lattice:

- It is evident from figure (a) that in case of simple cubic unit cell there are eight particles (spheres) at eight corners of unit cell.
- The complete crystal is formed by repetition of unit cells in all three directions and the particles at the corners are shared between neighbouring unit cells.
- Every particle at the corner of unit cell is shared by eight neighbouring unit cells. Hence each unit cell contains only $1/8^{\text{th}}$ of the particle at its corners as shown in figure (c).



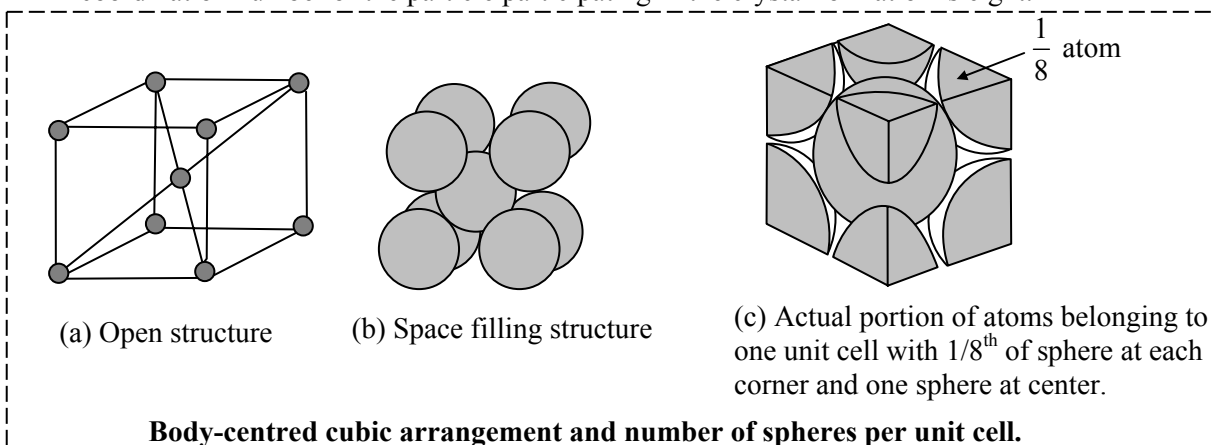
- d. There are eight corners of the unit cell and $1/8^{\text{th}}$ of the particle is present at each corner.

$$\therefore \text{The number of atoms present in each unit cell} = 8 \text{ corner atoms} \times \frac{1}{8} \text{ atom per unit cell} = 1$$

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

ii. Body-centred cubic lattice (bcc):

- a. Body centred cubic unit cell (bcc type) is a modification of simple cubic unit cell. Like simple cubic unit cell, it has one particle at every corner of cubic cell. In addition it has one more particle at the centre of the body of unit cell as shown in the figure (a) and (b).
- b. Like simple cubic unit cell at every corner of the cube, there are $\frac{1}{8}$ th of sphere as there are eight corners. In addition to this there is one sphere at the centre of the cube as shown in figure (c). Hence total number of spheres in body centred cubic unit cell = $\frac{1}{8} \times 8 + 1 = 2$ spheres (atoms, ions or molecules).
- c. A simple cubic structure is formed by superimposing layers of atoms on one another. A body centred cubic structure is formed by fitting second layer of spheres into depression of the first layer and the third layer spheres in the depression of the second layer and so on. Each sphere is surrounded by eight spheres, four in the layer above and four in the layer below. Hence the coordination number of the particle participating in the crystal formation is eight.



- d. Thus, the number of atoms present at the corners per unit cell

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

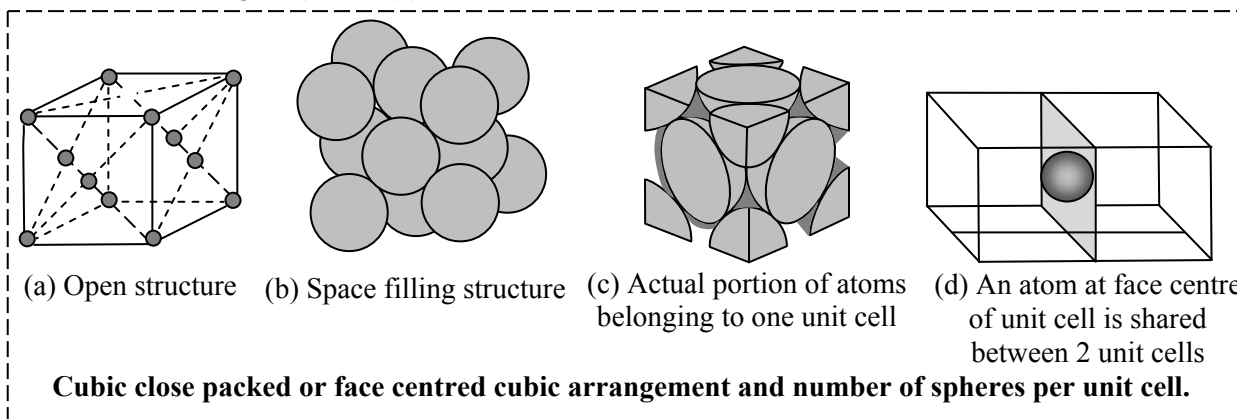
\therefore The number of atoms present at the centre of the cube = 1

\therefore The number of atoms present in the cell = $1 + 1 = 2$

Thus, body centred cubic has 2 atoms per unit cell.

iii. Face-centred cubic lattice (fcc):

- a. Face centred cubic unit cell is also modification of simple cubic unit cell. There are eight spheres at eight corners of the cube. In addition there is one sphere at the centre of each face as shown in figure (a) and (b).



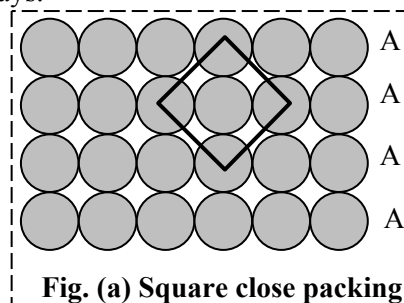
- b. The number of atoms situated at eight corners of unit cell of fcc type are also $\frac{1}{8} \times 8 = 1$.

Q.32. Explain two dimensional close packing in solid.

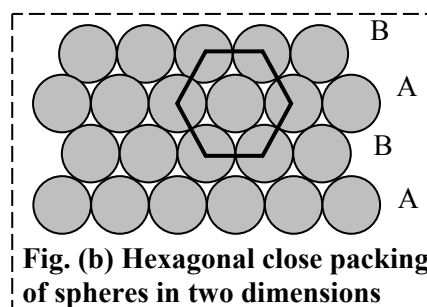
Ans: Two dimensional close packed structures can be generated by stacking (placing) the rows of one dimensional close packed spheres. This can be done in two different ways.

i. Square close packing (AAAA type arrangement):

- 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.
- Thus all the spheres of different rows are aligned horizontally as well as vertically.
- 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.
- The planar two dimensional arrangement is called **AAAA type of arrangement** as shown in figure (a).
- In this arrangement, each sphere is in contact with four of its neighbours. Thus, the **coordination number of the sphere is four**.
- Also 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 dimension.

**Fig. (a) Square close packing****ii. Hexagonal close packing (ABAB type arrangement):**

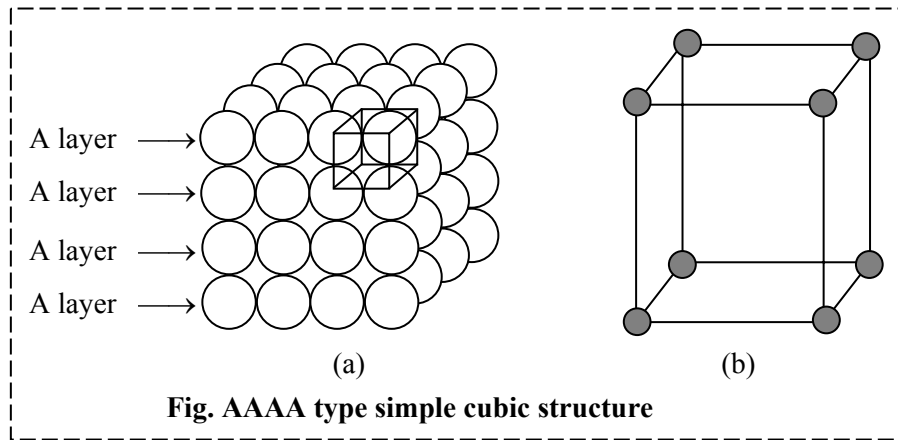
- The second row may be placed above the first one in staggered manner such that its spheres fit in the depressions of the first row.
- If the arrangement of spheres in the first row is called 'A' type, the one in the second row is different and may be called 'B' type.
- When the third row is placed 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).
- Hence, this arrangement is of **ABAB type**. In this arrangement there is less free space and this packing is more efficient than the square close packing.
- Each sphere is in contact with six of its neighbours and the two dimensional **coordination number is six**.
- The centres of these six spheres are at the corners of a regular hexagon as shown in the figure (b). Hence this packing is called **two dimensional hexagonal close packing**.

**Fig. (b) Hexagonal close packing of spheres in two dimensions****Note:**

The number of these two types of voids depends upon the number of close packed spheres.

Q.33. Explain with the help of neat diagram AAAA and ABAB and ABCABC type of three dimensional packings.*Ans: i. AAAA type of three dimensional packing:**

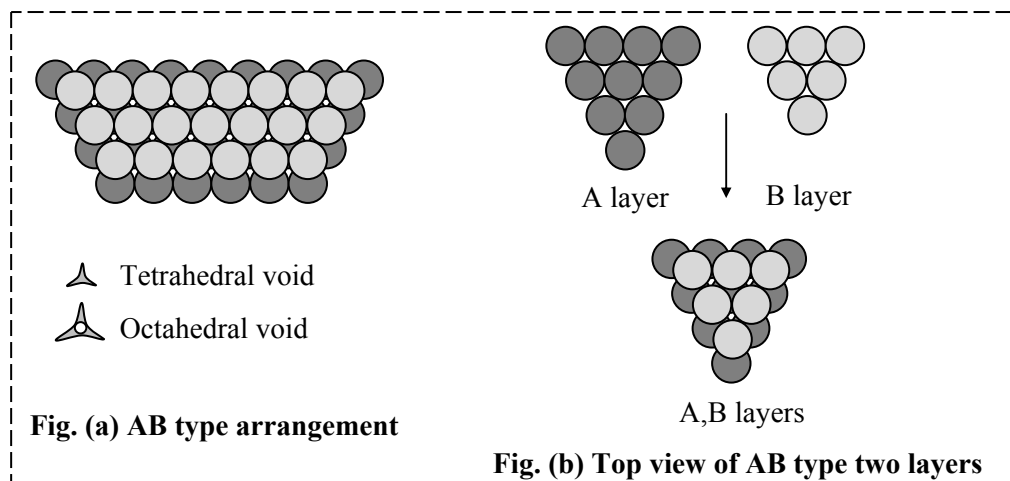
- AAAA type of two dimensional crystal layers are placed one over the other such that all the spheres of the successive layers are exactly above the spheres of the lower layers.
- All spheres of different layers of the crystal structures are perfectly aligned horizontally and also vertically so that any unit cell of the crystal has simple cubic structure as shown in figure (a).
- It is evident from the figure that each sphere is surrounded by six spheres, 4 in the layer of sphere and one in layer above and one below the layer. Hence coordination number of the sphere participating in formation of simple cubic structure is six.
- There is more empty space in the simple cubic structure.



ii. ABAB type of three dimensional packing:

In this type (ABAB) of crystal structure packing is more efficient than simple cubic structure.

- a. Consider two ABAB type planar two dimensional crystal structure as shown in figure. In both the structure, the central spheres are surrounded by six spheres in each layer.
- b. Now consider that the spheres of second layer are packed into depressions between the spheres of the first layer.
- c. This first layer is of ABAB type, but, for convenience it is called A type.
- d. The second ABAB layer spheres are fitted in the depressions of A type layer and conveniently called B type layer. This arrangement of two layers is called AB type. This AB type of arrangement of two layers when viewed from top may appear as shown in the figure (b).

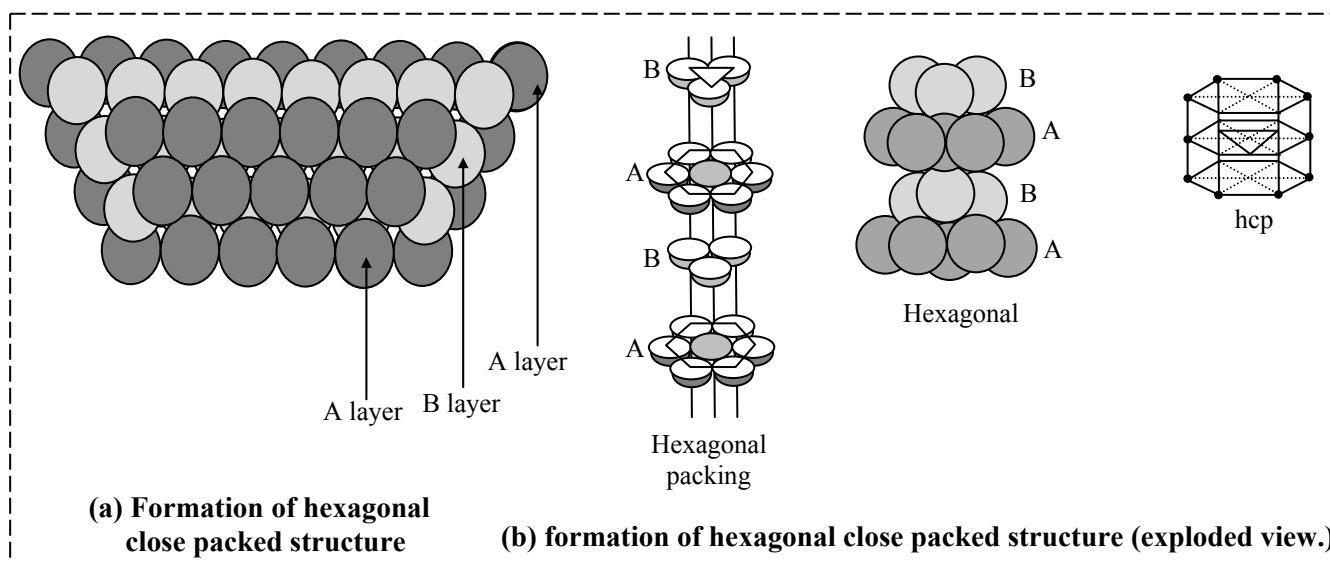


- e. It is evident from figure (b) that,
 1. only half the number of triangular open spaces of lower A are completely covered by spheres of upper layer B leading to the formation of tetrahedral voids formed by four spheres, three in the lower layer A and one in the upper layer B.
 2. Simultaneously new tetrahedral voids are also created by three neighbouring spheres of top layer and one sphere of the lower layer.
 3. The remaining half of the tetrahedral voids of the lower layer are partially covered by three neighbouring spheres of upper layer leading to the formation of octahedral voids, formed by total six spheres.
- f. In the case of tetrahedral voids four spheres are involved in its formation. If the centres of these four spheres are connected, a tetrahedron is formed.
- g. Similarly in case of octahedral voids six spheres are involved and when centres of six spheres are connected, octahedron is formed.

- h. The number of the two types of voids depends upon the total number of close packed spheres. If the number of close packed spheres are N , the number of octahedral voids are N and the number of tetrahedral voids are $2N$.
- i. In short there are two types of depressions formed at the end of fixing B layer over A layer, the octahedral voids and the tetrahedral voids. Hence, third layer can be fitted into the second layer in the following two ways.
1. Placing the spheres of the third layer into the tetrahedral voids (ABAB type).
 2. Placing the spheres of the third layer into the octahedral voids (ABCABC type).

Placing the spheres of the third layer into the tetrahedral voids:

- If the tetrahedral voids of the second layer are covered by the spheres of the third layer, then it is evident that all spheres of the third layer are exactly over the spheres of the first layer and the fourth layer has to be fitted like second layer i.e. the overall arrangement becomes ABAB type.
- The generated crystal structure is called hexagonal close packed (hcp) structure.
- The three layer crystal structure of ABAB type is shown in figure (a) and the exploded view is shown in figure (b).

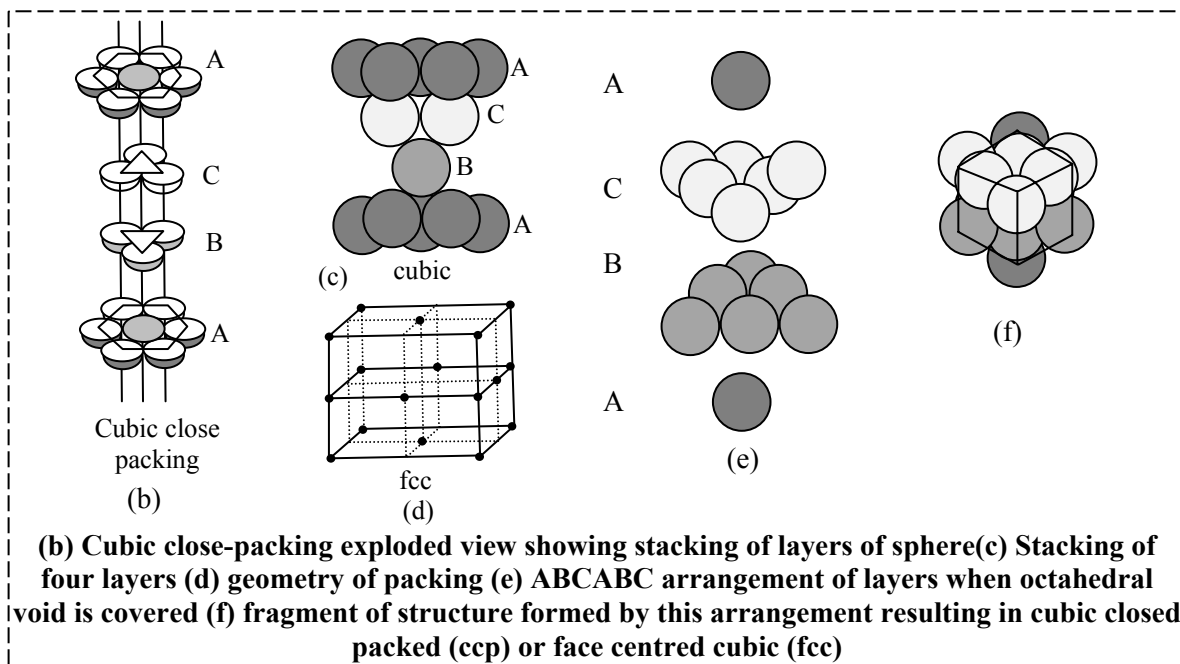
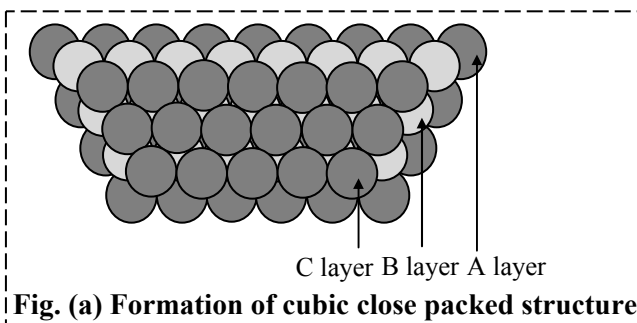


iii. ABCABC type of three dimensional packing

OR

Placing the spheres of the third layer into octahedral voids:

- The third layer may be placed over the second layer such that all the spheres of the third layer fit in octahedral voids.
- This arrangement of the third layer is different than arrangements of layer A and layer B. The different arrangement is called C type and the structure is called ABC type.
- If the stacking of layers is continued then it is found that every fourth layer is aligned with the first layer spheres. Hence the complete arrangement is called ABCABC type. This is shown in figure (a).
- The ABC type arrangement is called cubic close packed (ccp) structure. This structure is the same as face-centered cubic structure.
- The exploded view of ABCABC type of arrangement is shown in figure (b) and (c).
- In the hcp and ccp structures, each sphere has 6 neighbouring spheres in its own layer, 3 spheres in the layer above and 3 spheres in the layer below it.
- Thus a single sphere is surrounded by twelve spheres. Therefore, co-ordination number of sphere in ABAB type or ABCABC type is same i.e. 12.
- The packing cannot be made more efficient as it is not possible to increase coordination number beyond 12.



***Q.34. Distinguish between the following**

- i. Crystal lattice and unit cell.
- ii. Hexagonal close packing and cubic close packing.
- iii. Tetrahedral void and octahedral void.

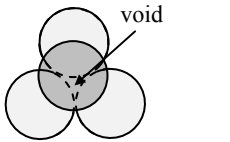
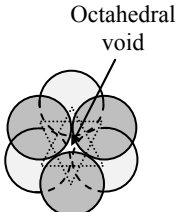
Ans: i. Crystal lattice and unit cell

	Crystal lattice	Unit cell
i.	The three dimensional arrangement of constituent particles of a substance (atoms, ions or molecules) is called crystal lattice.	Unit cell is the smallest portion of a crystal lattice which when repeated in different directions, generates the entire space lattice.
ii.	It has a repeating pattern.	It does not have a repeating pattern.
iii.	Crystal lattice is symmetrical with respect to rotations and reflections.	Unit cell may not necessarily be symmetrical with respect to rotations and reflections.

ii. Hexagonal close packing and cubic close packing

	Hexagonal close packing (hcp)	Cubic close packing (ccp)
i.	In hcp, the spheres of the third layer are exactly aligned with those of the first layer.	In ccp, the spheres of the third layer are not aligned with those of the first layer or second layer. The spheres of fourth layer are aligned with those of the first layer.
ii.	This arrangement is represented as ABAB type.	This arrangement is represented as ABCABC type.
iii.	In hcp, the tetrahedral voids of the second layer may be covered by the spheres of the third layer.	In ccp, the third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids.

iii. Tetrahedral voids and octahedral voids:

	Tetrahedral voids	Octahedral voids
i.	Tetrahedral void is much smaller than the size of the spheres in the packing.	The size of the octahedral void is smaller than that of the spheres in the packing but larger than the tetrahedral voids.
ii.	Each tetrahedral void is surrounded by 4 spheres. Hence, its coordination number is 4.	Each octahedral void is surrounded by 6 spheres. Hence, its coordination number is 6.
iii.	In the hcp or ccp packing, each sphere is in contact with three spheres in the layer above it and three spheres in the layer below it, thus forming one tetrahedral void above and one tetrahedral void below. Hence, there are two tetrahedral voids per sphere, i.e. number of tetrahedral voids is double the number of spheres in the packing.	As octahedral void is a combination of two voids of the two layers, number of octahedral voids is equal to half the number of tetrahedral voids and hence equal to the number of spheres in the packing.
iv.	Figure: 	Figure: 

1.6 Density of unit cells

***Q.35. Derive density formula for unit cell of a simple cubic cell.**

Ans: i. Consider a unit cell of cubic crystal of length 'a' units and radius 'r' of each constituent sphere then $a = 2r$

$$\therefore \text{Volume of unit cell (V)} = a^3 = 8r^3$$

ii. Each corner of unit cell is shared by eight unit cells i.e. each corner of unit cell effectively contain only $\frac{1}{8}$ th of the atom. There are eight corners of the simple cubic unit cell. Hence total number of

atoms contained by a unit cell is equal to $\frac{1}{8} \times 8 = 1$ atom.

iii. The total volume of unit cell contains only one atom of radius r.

Hence actual volume occupied by one atom of radius r is equal to $\frac{4}{3}\pi r^3$.

iv. Hence, empty space in a unit cell = Total volume – volume of one sphere.

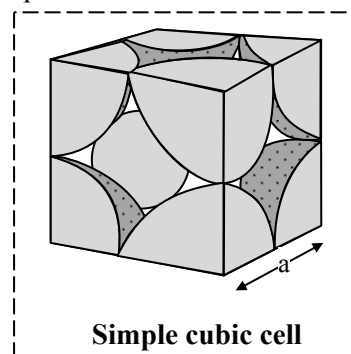
$$= 8r^3 - \frac{4}{3}\pi r^3 = \left(8 - \frac{4}{3}\pi\right)r^3$$

v. Total volume of unit cell is equal to $8r^3$.

\therefore entire volume occupied by $8r^3$ is 100%.

But the volume occupied is $\frac{4}{3}\pi r^3$

i.e. the volume occupied is $\frac{4\pi r^3}{3 \times 8r^3} \times 100 = 52.4\%$



- vi. \therefore volume unoccupied i.e. empty space or void is 47.6%
Hence, almost half the space is empty and thus the simple cubic crystalline solid is loosely bounded.
- vii. If atomic mass is known, the mass of unit cell is equal to,

$$\frac{\text{atomic mass}}{\text{Avogadro number}} = \frac{\text{atomic mass}}{6.022 \times 10^{23}} \text{ g.}$$

- viii. The volume of the unit cell is $8r^3$.

$$\text{Hence, density of unit cell} = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

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

If density of the crystalline solid is known, the radius of the constituent atom can be determined.

***Q.36. Calculate the percentage efficiency of packing in case of the following crystals**

- Simple cubic
- Body centred cubic
- Face centred cubic with all atoms touching one another.

Ans: i. Simple cubic:

- 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. Thus, the edge length or side of the cube 'a', and the radius of each particle, r are related as $a = 2r$

$$\text{The volume of the cubic unit cell} = a^3 = (2r)^3 = 8r^3$$

- b. Since a simple cubic unit cell contains only 1 atom

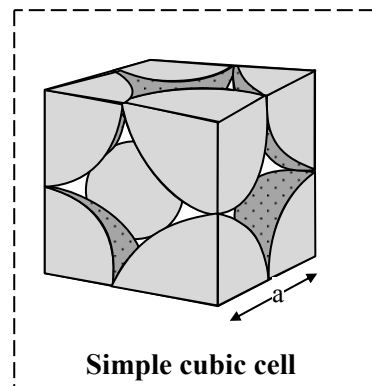
$$\text{The volume of the occupied space} = \frac{4}{3} \pi r^3$$

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

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

$$= 52.36\% = \mathbf{52.4\%}$$

- d. The packing efficiency of simple cubic metal crystal is 52.4%. Thus, we can conclude that simple cubic has minimum packing efficiency. Hence almost half the space is empty and thus the simple cubic crystalline solid is loosely bonded.



ii. Body centred cubic:

- a. In a body centered crystal lattice one atom is at the centre of the body and $1/8^{\text{th}}$ of the atom is at eight corners of the cube as shown in figure

- b. AB is the diagonal of length b of a side, of the cube. AD is the diagonal of length c of the cube.

- c. In right angled triangle ABC, $b^2 = a^2 + a^2 = 2a^2$.

$$\text{Similarly in right angled triangle ABD, } c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2.$$

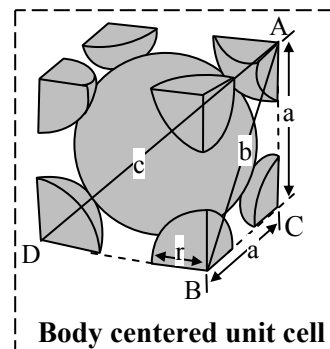
$$\text{Hence } c^2 = 3a^2 \text{ or } c = \sqrt{3} a$$

$$\text{But } c = 4r$$

$$\text{Therefore, } c = \sqrt{3} a = 4r \text{ and } a = \frac{4r}{\sqrt{3}}$$

- d. The total volume of the cube = $a^3 = \frac{64r^3}{3\sqrt{3}}$

- e. Each unit cell of bcc type contains total of two atoms
i.e. eight corners of unit cell containing $8 \times 1/8 = 1$
atom and one atom at the centre of body.



Therefore, the volume occupied by the atoms in bcc type unit cell = $2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3$

- f. Now, if the volume of unit cell $\frac{64r^3}{3\sqrt{3}}$ is completely occupied the volume occupied is 100%.

However, volume occupied is $\frac{8}{3} \pi r^3$.

Hence actual volume occupied by two atoms in unit cell or packing efficiency is, $\frac{8}{3} \pi r^3 \times \frac{3\sqrt{3}}{64r^3} \times 100 = 68.04\%$ and the empty volume or unoccupied volume or void is about 32%.

iii. Face centred cubic:

- a. Consider the view of face centred cubic structure shown in the figure.

Consider triangle ABC of a side of a face centred cubic unit cell,

The hypotenuse BA = b = 4r

Similarly, $b^2 = a^2 + a^2 = 2a^2 = 16r^2$

Hence, $a = \sqrt{8} r$

- b. Volume of unit cell = $a^3 = 8\sqrt{8} r^3$

Face centred unit cell contains $\frac{1}{8}$ atoms at eight corners and therefore,

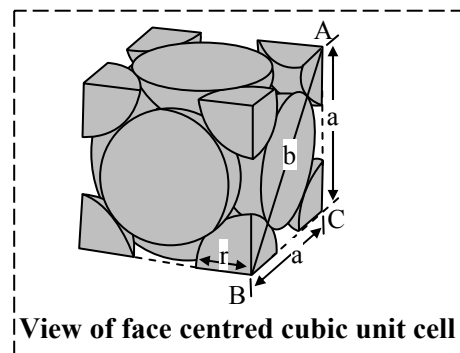
Total atoms in a fcc unit cell = $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 1 + 3 = 4$ atoms

- c. Actual volume occupied by a cube of a fcc unit cell = $4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3$

Hence the volume unoccupied = $8\sqrt{8} r^3 - \frac{16}{3} \pi r^3 = \left(8\sqrt{8} - \frac{16}{3} \pi \right) r^3 = 5.87 r^3$

- d. Now the total volume of unit cell $8\sqrt{8} r^3$ is completely occupied, the packing efficiency is 100%. However volume occupied is $\frac{16}{3} \pi r^3$. Hence, packing efficiency is $\frac{16}{3} \pi r^3 \times \frac{1}{8\sqrt{8} r^3} \times 100 = 74.0\%$.

The empty space or unoccupied volume or void is $(100 - 74.0)$ equal to 26%. This is the most efficient packing efficiency.



Q.37. 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)

Ans: Since, $d = \frac{z \cdot M}{a^3 \cdot N_A}$

On rearranging, we get

Atomic mass, $M = \frac{d \cdot a^3 \cdot N_A}{z}$

On substituting the values of density (d), dimension (a), Avogadro number (N_A) and number of atoms per unit cell (z), we get atomic mass of an unknown metal.

Note:

i. If a is taken in cm and M is molar mass in g mol^{-1} , the above expression becomes

$$d = \frac{z \times M}{a^3 \times N_A} \text{ g / cm}^3$$

ii. In terms of SI units, M is in kg mol^{-1} , a is in meters, then

$$d = \frac{z \times M}{a^3 \times N_A} \text{ kg m}^{-3}$$

iii. 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**Q.38. How can we calculate the formula of a compound from number of voids filled?**

- Ans:**
- 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.
 - 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 = $2N$
 - 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, if it is bigger then octahedral voids are occupied.
 - 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 = \mathbf{XY}

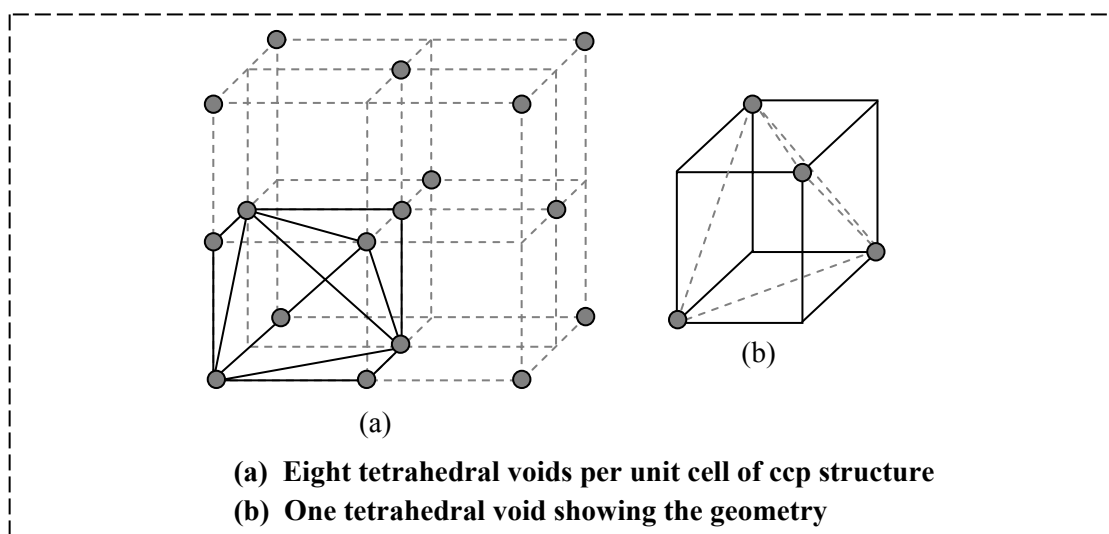
Q.39. Explain how voids are located in an ionic solid.

Ans: Locating voids in a crystal:

In the cubic close packing (ccp) or face-centred cubic (fcc) unit cell, there are 4 atoms or ions per unit cell. Therefore, there are 4 octahedral voids and 8 tetrahedral voids. These are located at different positions as explained below:

i. Locating tetrahedral voids:

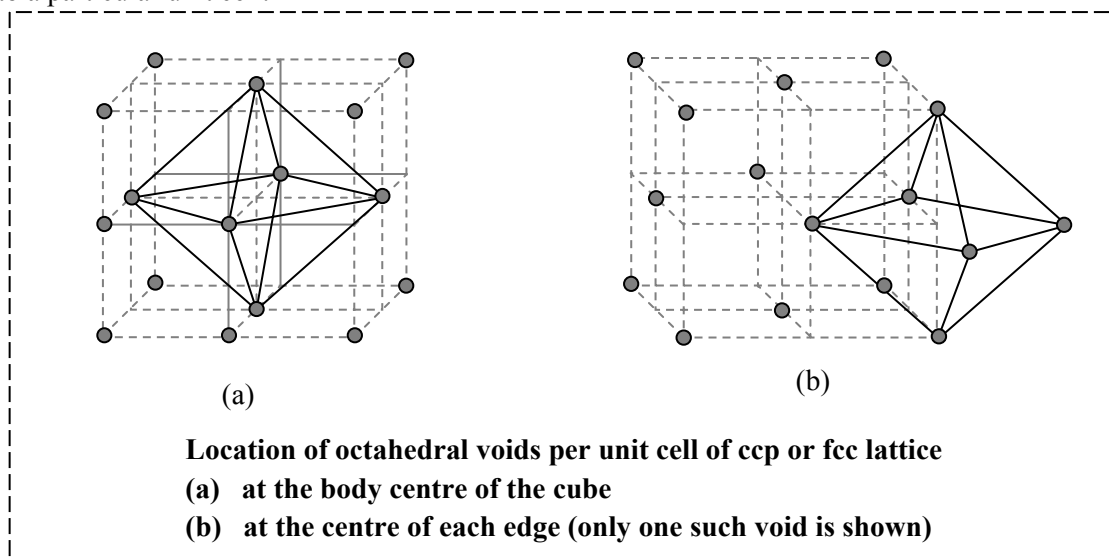
Consider a unit cell of ccp or fcc lattice. The unit cell is divided into eight small cubes. Each small cube has atoms at alternate corners as shown in figure (a). In all, each small cube has 4 atoms. When joined to each other, they make a regular tetrahedron. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total. Each of the eight small cubes have one void in one unit cell of ccp structure. We know that ccp structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.



ii. **Locating octahedral voids:**

Consider a unit cell of ccp or fcc lattice as shown in figure (a). The body centre of the cube, is not occupied but it is surrounded by six atoms on face centres. If these face centres are joined, an octahedron is generated. Thus, this unit cell has one octahedral void at the body centre of the cube.

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges as shown in figure (b). It is surrounded by six atoms, four belonging to the same unit cell (2 on the corners and 2 on face centre) and two belonging to two adjacent unit cells. Since each edge of the cube is shared between four adjacent unit cells, the octahedral void is located on it. Only $\frac{1}{4}$ th of each void belongs to a particular unit cell.



Thus in cubic close packed structure:

Octahedral void at the body centre of the cube = 1

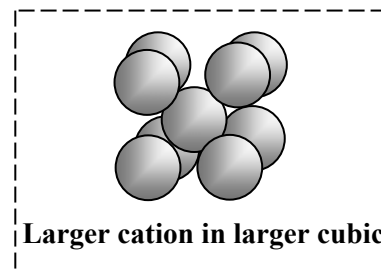
12 octahedral voids located at each edge and shared between four unit cells = $12 \times \frac{1}{4} = 3$

\therefore Total number of octahedral voids = $3 + 1 = 4$

We know that in ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

***Q.40. Explain the packing and voids in ionic solids.**

- Ans:**
- Ionic solids consists of the + vely charged cations and – vely charged anions.
 - The number of oppositely charged ions are appropriately adjusted such that the charges are balanced and the compound formed is electrically neutral.
 - Depending on relative sizes of the cations and anions of the ionic compound, the relatively smaller ion, the cation occupies either tetrahedral or octahedral hole of the crystal lattice.
 - If the cation is relatively small then it occupies tetrahedral hole. Bigger cations occupy octahedral holes.
 - In case if the size of the cation is too large to be accommodated in the small space of octahedral hole, the packing of the anions are modified, anions are appropriately separated from one another and larger cations are accommodated in larger cubic hole as shown in the adjacent figure.

***Q.41. Write a note on radius ratio rule of ionic compounds.**

- Ans:**
- The structure of any ionic compound depends upon stoichiometry and the sizes of the ions.
 - Bigger cations can be accommodated in cubic or in octahedral holes whereas smaller cations can be accommodated in tetrahedral holes.
 - The geometry of unit cell also depends upon the coordination number of the ion in the crystal structure.
 - There is a limiting value of ratio of the radius of cation to that of the anion i.e. r^+/r^- for a given coordination number.
 - If the value of ratio r^+/r^- is less than the expected value then the ionic structure becomes unstable.
 - The limiting values of r^+/r^- for the coordination number and the hole occupied by the cation are given in the following table.

Coordination number of cation	Limiting value of r^+/r^-	Type of hole occupied	Example
3	0.155 to 0.225	Planar triangular	B_2O_3
4	0.225 to 0.414	Tetrahedral	ZnS
6	0.414 to 0.732	Octahedral	NaCl
8	> 0.732	Cubic	CsCl

- The radius ratio rule is applicable only to ionic compounds.
- The rule is not obeyed if the bonds are covalent.
- The rule is useful for predicting structures of many ionic solids.

1.8 Defects in Crystal Structure**Q.42. Define crystal defect.**

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

Q.43. 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. The defects are more if the process of crystallisation occurs at faster rate. The crystal defect changes the original physical and chemical properties of a crystalline solid.

Q.44. Define Line defects.

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

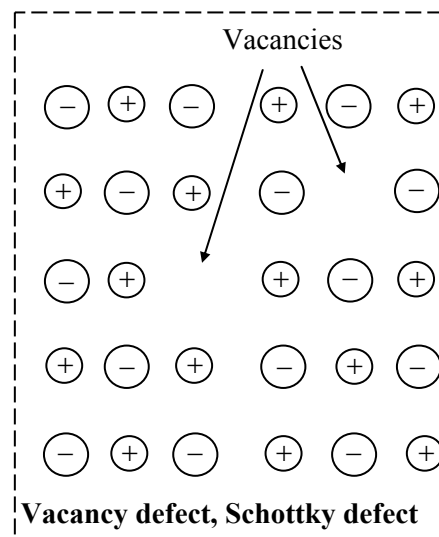
***Q.45. What are point defects?**

Ans: The defect is 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.

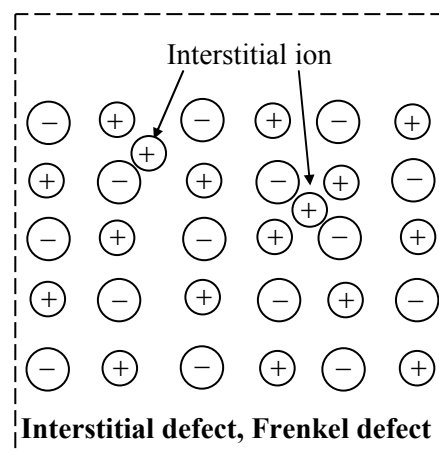
The point defects are classified into three types;

i. Vacancy defect or Schottky defect:

- Sometimes during crystallisation some of the places of the constituent particles remain unoccupied and the defect generated is called vacancy defect.
- The unoccupied positions are called vacancies.
- It results in the decrease in density of the substance.
- In case of ionic solids, cations and anions in stoichiometric proportions remain absent from their position to maintain electrical neutrality.
- In Ionic compounds this defect is known as Schottky defect.
- The defects are observed in solids with cations and anions having almost equal size like NaCl, KCl, CsCl etc.

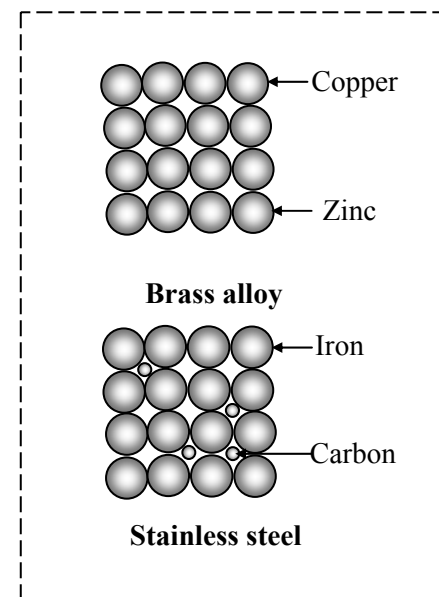
**ii. Interstitial defect (Frenkel defect):**

- 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.
- The presence of this defect does not alter the density of the solid.
- This defect is common when the difference in ionic radii of cations and anions is large.
- This defect is observed in AgCl solid because of Ag^+ ions or ZnS solid because of Zn^{++} ions.

**iii. Impurity defect:**

- The impurity defect occurs when a regular cation of the crystal is replaced by some different cation.
- If the impurity cation is substituted in place of regular cation, it is called substitution impurity defect.
- If the impurity is present in the interstitial positions, it is called interstitial impurity defect.
- Alloys are formed by substitution defects. Brass is a substitution alloy formed by substituting copper metal by zinc metal in 3 : 1 ratio.
- Stainless steel is an interstitial alloy formed by introducing carbon atom as impurity.
- The original properties of crystalline solid are almost completely changed due to impurity defect.

Eg. Pure iron is soft malleable and ductile while stainless steel is hard, stronger, less ductile, shiny and bright in appearance.



*Q.46. Explain interstitial defects and impurity defects.

Ans: Refer Q.45 ii. and iii.

*Q.47. Explain the terms

- i. Schottky defect ii. Frenkel defect

Ans: Refer Q 45. i and ii

Q.48. What type of stoichiometric defect is shown by: (NCERT)

- i. ZnS ii. KCl

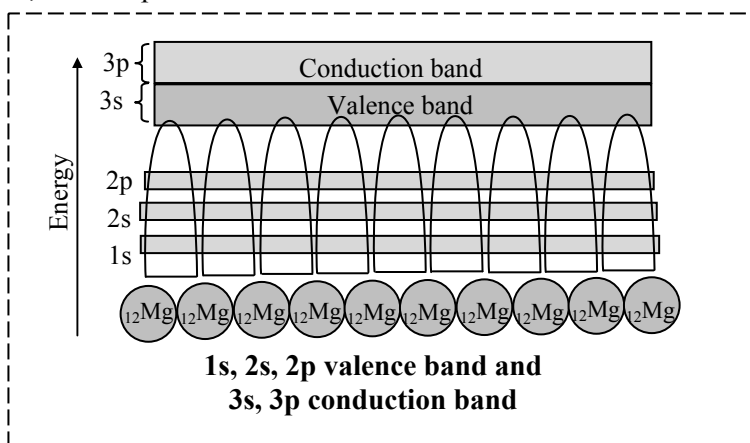
Ans: i. ZnS shows Frenkel defect because its ions have a large difference in size.

ii. KCl shows Schottky defects, as its cations and anions have almost equal size.

1.9 Electrical Properties

*Q.49. Explain band theory.

- Ans: i. The variation in the property of ability to conduct electricity of metals, non metals and semi conductors can be explained with the help of band theory.
- ii. The theory assumes that the atomic orbitals of the atoms in the crystal combine to form molecular orbitals which are spread over the complete crystal structure. With increase in number of atoms participating in crystal formation, the number of molecular orbitals containing electrons is greatly increased.
- iii. A small plate of about 1g of metal may contain very large number of about 10^{20} electrons. With increase in participating atoms of the crystal the number of molecular orbitals containing electrons increases enormously.
- iv. As the number of molecular orbitals increases the energy difference between the adjacent orbitals i.e. energy levels decreases. Until finally the energy gap becomes very small and molecular discrete energy levels merge into one another to form continuous band of molecular orbitals which extends over the entire length of the crystal.
- v. Each atomic orbital of the crystal corresponds to one energy level in the band which contains two electrons. The electrons in the higher energy level of a band are free and mobile and are responsible for electrical conductivity.
- vi. Better understanding of band energy may be obtained by considering the example of magnesium metal with atomic number 12, with electronic configuration $1s^2, 2s^2, 2p^6, 3s^2$.
- vii. Each magnesium atom has two valence electrons in the outermost orbital 3s. One gram of magnesium strip contains $6.022 \times 10^{23}/24 \approx 2.5 \times 10^{22}$ closely packed atoms and there are 10^{22} valence shells.
- viii. The interaction between these large number of orbitals leads to the formation of bonding and anti-bonding molecular orbitals.
- ix. All the molecular orbitals are very close to each other and can not be distinguished from one another and therefore, these orbitals are collectively called a band.
- x. The upper parts of the energy levels are formed by overlap of filled 3s orbitals and empty 3p orbitals and are called conduction bands. The lower part of the energy levels are formed by overlap of filled 1s, 2s and 2p orbitals are called valence band.



- xi. In metallic crystals, the valence bands and conduction bands are very close to each other and a very little energy is required to excite electrons from valence band into the conduction band. In conduction band the electrons are delocalised and are free to move from one end to the other end of the metal piece. This migration of electrons makes the metal good conductor of heat and electricity.
- xii. The substances like glass, rubber, polythene, plastic, wood and diamond are bad conductors of heat and electricity because the spacing between the valence band and conduction band is relatively more so that more energy is required to promote electrons from valence band to conduction band. This relatively more amount of energy is not available. Hence electrons remain in valence band and thus cannot move freely, and therefore do not conduct heat and electricity but act as insulators.

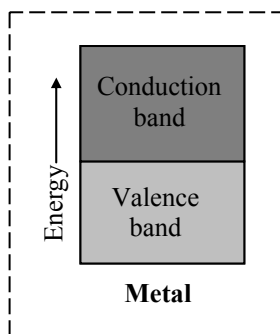
***Q.50. Explain the origin of electrical properties in solids.**

- Ans:** i. Electrical properties of solids can be explained on the basis of electrical conductivities possessed by solids.
- ii. Depending upon the difference in electrical conductivities, the solids are classified into the following three types;

a. Conductors:

In metals, the conduction band is very close to the valence band. Hence, under the influence of electric field the electrons can easily go into the conduction band. Therefore, metals are good conductors.

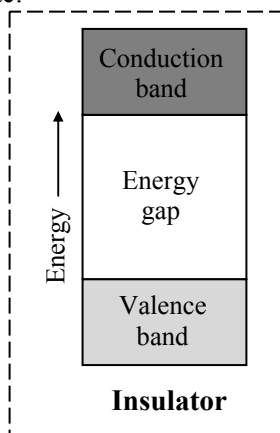
Eg. Copper, Aluminium



b. Insulators:

In insulator, 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. Thus, the insulators have extremely low conductivity.

Eg. Rubber, wood, plastics etc.

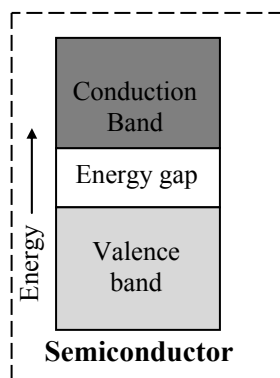


c. Semiconductors:

1. Several solids have properties intermediate between metals and insulators. These are called semi-metals or semiconductors.
2. 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.

3. Conductivity of semiconductor increases with increase in temperature, because with increase in temperature large no. of electrons jump from valence band to conduction band.

Eg. silicon, germanium.



*Q.51. Distinguish between conductor, insulator and semiconductor.

OR

In terms of band theory, what is the difference between: (NCERT)

- a conductor and an insulator?
- a conductor and a semiconductor?

Ans:

	Conductors	Insulators	Semiconductors
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 substances which has poor electrical conductance at low temperature but higher conductance at higher temperature is called semi-conductor.
Band theory	The energy gap is either very small or there is overlapping between valence band and conduction band	The energy gap between the valence band and the conduction band is very large	The energy gap between valence band and conduction band is small.
Electric conductivity	Under an applied electric field, the electrons can jump from valence band to conduction band and the substance shows conductivity. Eg. Cu, Zn, Al, etc.	Under an applied electric field, the electrons cannot jump from valence band to conduction band and hence, such a substance has very small conductivity and behaves as an insulator. Eg. Rubber, Plastic	The electrons from valence band can be excited to conduction band on slight heating. The number of electrons available for conducting electricity is relatively less in semiconductor as compared to the number of electrons in any metal. Eg. Silicon, germanium

Note:

Doping:

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

***Q.52. What is semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism. (NCERT)**

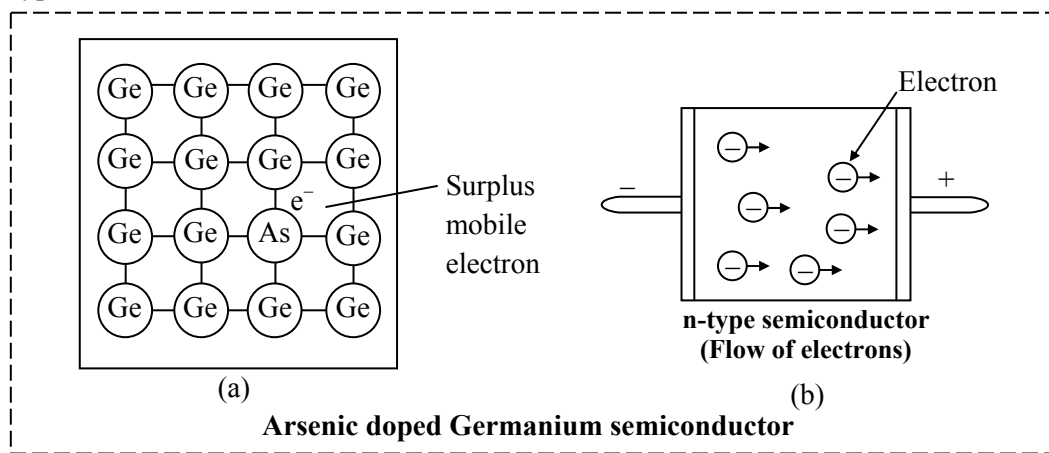
Ans: A substance which has poor electrical conductance at low temperature but higher conductance at higher temperature is called semiconductor.

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.

- Silicon and germanium belong to group 14 of the periodic table and have four valence electrons. In their crystals, each atom forms four covalent bonds with its neighbours.
- 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 with five electrons in their outermost shell.
- 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).
- Hence, an extra electron, over and above 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 can serve to conduct electricity and therefore, germanium containing traces of arsenic (or arsenic doped germanium) exhibit high electrical conductivity.
- This type of conduction is known as n-type semiconduction where 'n' stands for negative because electrons are responsible for semi conducting behaviour. This is shown in figure (b). Doping of a germanium or silicon with other group-15 elements such as P, Sb or Bi also give n-type semiconductors.

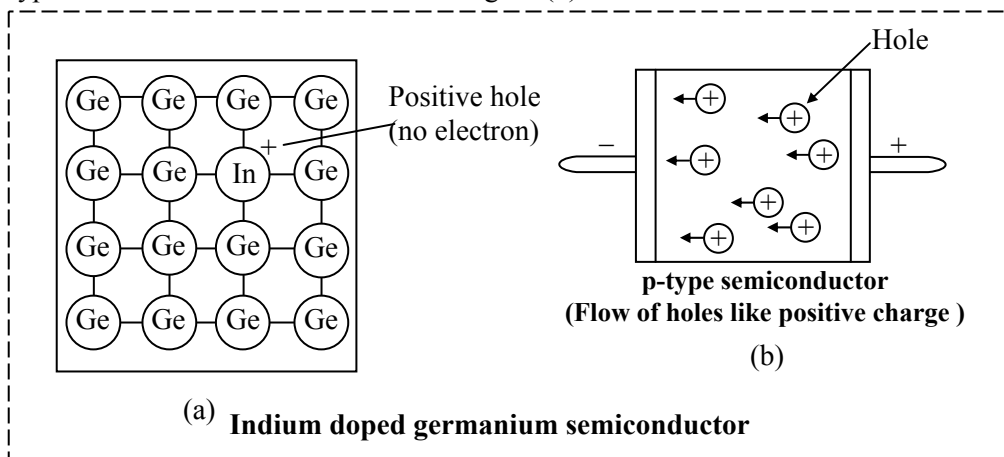


ii. p-type semiconductor (Electron deficient or acceptor impurity):

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

- Some atoms of germanium are doped with acceptor atoms having only three outer shell electrons such as Indium (of Group 13).
- 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.
- 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.
- 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.

- g. 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.
- h. Doping of silicon or germanium with other group-13 elements such as B, Al or Ga also give p-type semiconductors. This is shown in figure (b).



Q.53. Write a short note on:

- i. n-type semiconductor
- ii. p-type semiconductor

Ans: Refer Q.52.

*Q.54. Classify each of the following as being either p-type or n-type semiconductor: (NCERT)

- i. Ge doped with In ii. Si doped with B
- iii. Si doped with As iv. Si doped with P

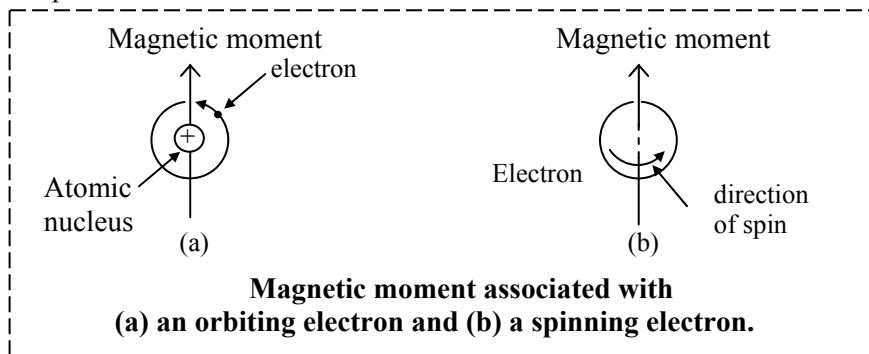
- Ans:
- i. Ge doped with In : p-type
 - ii. Si doped with B : p-type
 - iii. Si doped with As : n-type
 - iv. Si doped with P : n-type

1.10 Magnetic properties

*Q.55. Explain the origin of magnetic properties in solids.

Ans: Magnetic property of substance:

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



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

***Q.56. Explain**

- i. **Paramagnetism**
- ii. **Diamagnetism**
- iii. **Ferromagnetism**

Ans: i. Paramagnetism:

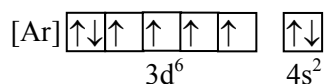
- a. *The substances which have permanent magnetic dipoles and are attracted by the magnetic field are known as paramagnetic substances. The property thus exhibited is called paramagnetism.*
- b. If an atom or a molecule contains more unpaired electrons revolving in their orbitals, the magnetic moments do not cancel each other.
- c. There is a net magnetic moment associated with the species and the species experience net force of attraction when placed in magnetic field.
- d. This property of a substance due to presence of unpaired electrons, due to which substance experiences pull in magnetic field, is called paramagnetism.
- e. The extent of paramagnetism present in the substance depends upon number of unpaired electrons present in the substance. More the number of unpaired electrons in the substance the stronger is the pull due to paramagnetism of the substance.
- f. **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. If an atom or a molecule contains all electronic orbitals completely filled i.e. there are two electrons in each orbital, then their spins are $+\frac{1}{2}$ and $-\frac{1}{2}$ i.e. the two electrons spinning in opposite direction one clockwise and other anticlockwise. The spins are paired and magnetic field will be repelled. This phenomenon is called diamagnetism.
Eg. Water, sodium chloride, benzene are some diamagnetic substances.

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 ferromagnetic substances. The property thus exhibited is called ferromagnetism.*
- b. Substances like iron, cobalt, nickel, CrO_2 , etc. exhibit very strong magnetic property. These substances can be permanently magnetised. They contain large number of unpaired electrons.
- c. **Eg.** Iron with electronic configuration $[\text{Ar}] 3d^6 4s^2$ i.e.,



There are four unpaired electrons. Hence, iron is strongly ferromagnetic.

#Q.57. Identify the following substances as paramagnetic, diamagnetic or ferromagnetic.

- i. Sodium $_{11}\text{Na}$
- ii. Magnesium $_{12}\text{Mg}$
- iii. $_{20}\text{Ca}^{2+}$ cation
- iv. $_{17}\text{Cl}^-$ anion
- v. Iron $_{26}\text{Fe}$
- vi. $_{27}\text{Co}$ atom
- vii. $_{28}\text{Ni}$ atom

Ans: Paramagnetic: Sodium $_{11}\text{Na}$,

Diamagnetic: $_{17}\text{Cl}^-$ anion, Magnesium $_{12}\text{Mg}$, $_{20}\text{Ca}^{2+}$ cation

Ferromagnetic: Iron $_{26}\text{Fe}$, $_{27}\text{Co}$ atom, $_{28}\text{Ni}$ atom

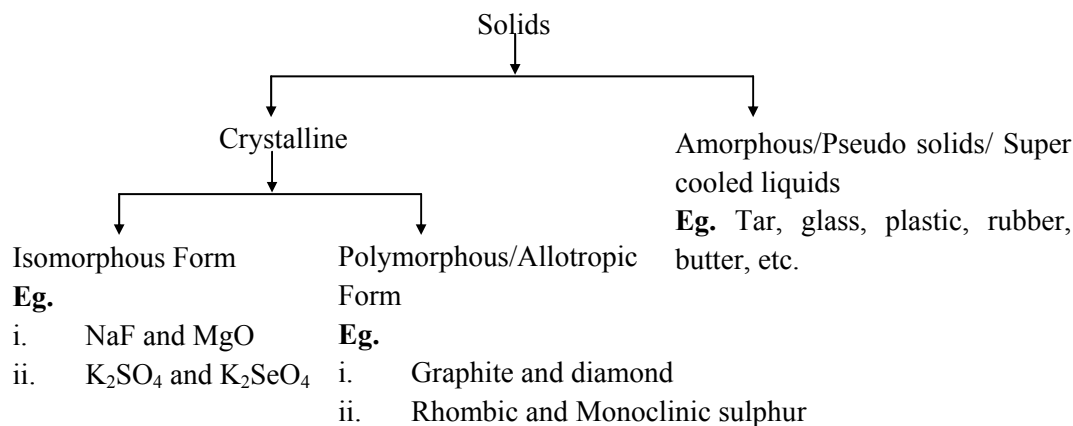
Points To Remember

- Solid state is stable at low temperature, the thermal energy is so low that intermolecular forces hold the molecules at their fixed positions. Molecules can only oscillate about their mean positions and are very close to one another.
- Solids have definite shape and volume, are rigid and incompressible. They have high density and diffuse very slowly.
- Based upon the arrangement of their constituent particles solids are classified as crystalline and amorphous.
- In crystalline solids, the particles are arranged in a definite ordered pattern.
- In amorphous solids, there is no well defined ordered structure.
- Based upon the nature of inter-particle interactions, crystalline solids can be classified as molecular solids, ionic solids, covalent or network solids and metallic solids.
- A lattice is an infinite array of points in a space in which each point has identical surroundings in the same orientation.
- A regular three dimensional arrangement of points in space is called space lattice or crystal lattice in which each lattice point represents the location of one constituent particle in space.
- A unit cell is the smallest portion of a crystal lattice which when represented in different directions generates the entire lattice.
- A unit cell is characterised by its dimensions in different directions and the angles between its sides.
- Crystals are classified as cubic, tetragonal, orthorhombic, hexagonal, trigonal or rhombohedral, monoclinic and triclinic based on the shape of their unit cell.
- Unit cells are classified on the basis of location of particles at positions in addition to corner positions are primitive with particles only at corner positions and non-primitive (centred) with particles at other positions as well.
- There are three types of non-primitive unit cells:
 - i. body-centred with one particle at the body centre of the unit cell.
 - ii. face-centred, with one particle at each face of the unit cell.
 - iii. end-centred with one particle at the centre of any two opposite faces.
 Not all variations are possible in each of the seven types of unit cells.
- There are total 14 types of primitive and centred unit cells which form 14 Bravais lattices.
- A simple cubic unit cell contains only 1 atom (or any other constituent particle) per unit cell, a body-centred cubic unit cell has 2 and a face-centred cubic unit cell has 4 atoms per unit cell.
- Density of a substance can be related to its unit cell properties as $d = \frac{z \cdot M}{a^3 \cdot N_A}$

where d is the density, a is the edge length of cubic unit cell, z the number of atoms per unit cell, M the molar mass of the substance and N_A the Avogadro constant.
- The two dimensional hexagonal close packing results in two different but equally efficient lattices- hexagonal close packed (hcp) structure and cubic close packed (ccp) structure which is also called face-centred cubic lattice (fcc).
- Two types of voids are generated in hcp and ccp lattices : Tetrahedral voids and Octahedral voids.
- Tetrahedral voids are smaller in size and twice the number of close packed spheres (particles).
- Octahedral voids are bigger in size and same in number of close packed spheres.
- Formula of a compound can be deduced from the information about the nature and fraction of voids occupied in its structure.
- Imperfections or defects in crystals are deviations from the ideal structures.

- Defect in crystals are broadly of two types-point defects (irregularities around a point) and line or plane defects (irregularities present in entire row or layer of the particles).
- Point defects are of three types-vacancy defect, interstitial defect and impurity defect.
- Vacancy defect arises, due to the vacancy of lattice sites. This is also known as Schottky defect.
- Interstitial defect or Frenkel defect takes place as cation or anion migrate to interstitial position leaving the lattice site.
- Impurity defect arises when foreign atoms are present at the lattice site.
- On the basis of conductivity, substances can be classified as conductors, insulators and semiconductors.
- Electrical conductivity of semiconductors can be increased by doping them with electron-rich or electron-deficit impurities.
- On the basis of magnetic properties, substances can be classified as paramagnetic, diamagnetic and ferromagnetic.

Quick Review



Formula

1. Density of unit cell:

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

where, a is edge of unit cell

N_A = Avogadro number (6.023×10^{23})

M = Molar mass

z = number of atoms per unit cell

For fcc, z = 4

for bcc, z = 2

for simple cubic, z = 1

Solved Example

Type I: Problems based on density of unit cell.

Example 1

A compound 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 = 290×10^{-10} cm
Atomic mass (M) = 50

To find: density (d) = ?

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

Calculation: Since it is bcc arrangement
Number of atoms per unit cell $z = 2$

\therefore From the formula,

$$d = \frac{2 \times 50}{(290 \times 10^{-10})^3 \times 6.023 \times 10^{23}}$$

$$d = \frac{100}{24.39 \times 10^{-24} \times 6.023 \times 10^{23}}$$

$$d = 6.81 \text{ g cm}^{-3}$$

Ans: The density of unit cell is **6.81 g cm⁻³**

Example 2

An element crystallized in a structure has fcc unit cell of an edge 200 pm. Calculate its density if 200 g of this element contain 24×10^{23} atoms.

Solution:

Given: Edge length (a) = 200 pm = 200×10^{-10} cm
Mass = 200 g

No. of atoms = 24×10^{23} atoms

To find: density = ?

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

Calculation Since the element has fcc arrangement, the number of atoms per unit cell = 4
From the formula,

$$\therefore d = \frac{4 \times 200}{(200 \times 10^{-10})^3 \times 24 \times 10^{23}} = \frac{800}{8 \times 10^{-24} \times 24 \times 10^{23}} = 41.67 \text{ g cm}^{-3}$$

Ans: The density of given element = **41.67 g cm⁻³**

Example 3

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:

Given: density (d) = 7.29 g cm^{-3}
Edge length (a) = 289 pm = 289×10^{-10} cm

To find: Type of unit cell = ?

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

Calculation: From the formula,

$$\begin{aligned} \therefore z &= \frac{d \cdot a^3 \cdot N_A}{M} \\ &= \frac{7.29 \times (289 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{52} \\ &= \frac{7.29 \times 24.14 \times 10^{-24} \times 6.023 \times 10^{23}}{52} \\ &= 2.0 \\ z &\cong 2 \end{aligned}$$

Ans: Since the unit cell contain **2** atoms, hence it is body centred cubic (bcc).

Example 4

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 = 288×10^{-10} cm.

Density (d) = 7.2 g cm^{-3}

To find: atomic mass = M = ?

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

Calculation: Since it is bcc arrangement,
Number of atoms per unit cell, $z = 2$
From the formula,

$$\begin{aligned} \therefore M &= \frac{d \cdot a^3 \cdot N_A}{z} \\ &= \frac{7.2 \times (288 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{2} \\ &= 3.6 \times 23.89 \times 10^{-24} \times 6.023 \times 10^{23} \\ &= 51.8 \text{ a.m.u.} \end{aligned}$$

Ans: The atomic mass of element is **51.8 a.m.u.**

Example 5

Calculate the value of Avogadro number from the following data:

Density of NaCl = 2.165 g cm^{-3} ,

distance between Na^+ and Cl^- ions in NaCl crystal = 281 pm

Solution:

Given: density (d) = 2.165 g cm^{-3}

Distance between Na^+ and Cl^- = 281 pm.

To find: Avogadro number (N_A) = ?

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

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

Calculation: Sodium chloride has fcc structure.

\therefore Number of molecules per unit cell, $z = 4$

Molar mass of NaCl (M) = 23 + 35.5 = 58.5

Edge length is double the distance between Na^+ and Cl^- ions.

\therefore Edge length (a) = $2 \times 281 = 562 \text{ pm} = 562 \times 10^{-10} \text{ cm}$.

From formula,

$$N_A = \frac{4 \times 58.5}{(562 \times 10^{-10})^3 \times 2.165}$$

$$= \frac{234}{(562 \times 10^{-10})^3 \times 2.165}$$

$$= \frac{234}{17.75 \times 10^{-23} \times 2.165}$$

$\therefore N_A = 6.089 \times 10^{23}$

Ans: The Avogadro number is 6.089×10^{23}

Example 6

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: Edge length (a) = $288 \text{ pm} = 288 \times 10^{-10} \text{ cm}$

Density (d) = 7.2 g cm^{-3}

M = 208 g

To find: Number of atoms ?

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

Calculation: z = 2 for bcc structure

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

$$= \frac{7.2 \times (288 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{2} = 51.79 \text{ g}$$

According to definition of Avogadro number 51.79 g of element contains 6.023×10^{23} atoms

$$\therefore 208 \text{ g of element will contain } \frac{208 \times 6.023 \times 10^{23}}{51.79} = 24.19 \times 10^{23} \text{ atoms}$$

Ans: Number of atoms present in 208 g of element is 24.19×10^{23}

Example 7

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:

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

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

Density of gold = 19.3 g cm^{-3}

Density = $\frac{\text{mass of unit cell}}{\text{volume of unit cell}}$

Volume of unit cell,

$$V = \frac{130.83 \times 10^{-23}}{19.3 \text{ g cm}^{-3}} = 6.78 \times 10^{-23} \text{ cm}^3$$

$$V = a^3 = 6.78 \times 10^{-23} \text{ cm}^3$$

$$\therefore a = \sqrt[3]{6.78 \times 10^{-23}} = 4.08 \times 10^{-8} \text{ cm}$$

Where a is the edge of unit cell

$$a = \sqrt{8} r$$

$$\begin{aligned} \text{Hence } r &= \frac{a}{\sqrt{8}} = \frac{4.08 \times 10^{-8} \text{ cm}}{\sqrt{8}} \\ &= 1.44 \times 10^{-8} \text{ cm} \\ &= 144 \text{ pm.} \end{aligned}$$

Example 8

X-ray diffraction studies show that copper crystallise in an fcc unit cell edge of $3.608 \times 10^{-8} \text{ cm}$. 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) = $3.608 \times 10^{-8} \text{ cm}$
Density (d) = 8.92 g cm^{-3}

To find: Atomic mass M = ?

$$\text{Formula: } d = \frac{z \cdot M}{a^3 \cdot N_A}$$

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

Calculation: Since it is fcc lattice,

\therefore Number of atoms per unit cell, $z = 4$

From the formula,

$$M = \frac{8.92 \times (3.608 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{4} = 13.43 \times 46.97 \times 10^{-24} \times 10^{23}$$

$$M = 63.08 \text{ a.m.u.}$$

Ans: The atomic mass of copper is **63.08 a.m.u.**

Example 9

Silver forms ccp lattice and x-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver. (atomic mass = 107.94) (NCERT)

Solution:

Given: Edge length (a) = 408.6 pm = $408.6 \times 10^{-10} \text{ cm}$
Atomic mass (M) = 107.94

To find: Density (d) = ?

$$\text{Formula: } d = \frac{z \cdot M}{a^3 \cdot N_A}$$

Calculation: Since the lattice is ccp,

The number of atoms per unit cell, $z = 4$

From the formula,

$$d = \frac{4 \times 107.94}{(408.6 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = \frac{431.76}{68.21 \times 10^{-24} \times 6.023 \times 10^{23}}$$

\therefore $d = 10.51 \text{ g cm}^{-3}$

Ans: The density of silver is **10.51 g cm⁻³**

Example 10

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

Solution:

Given: Molar mass (M) = $2.7 \times 10^{-2} \text{ kg mol}^{-1}$
 Edge length (a) = 405 pm = $405 \times 10^{-12} \text{ m}$
 Density (d) = $2.7 \times 10^3 \text{ kg m}^{-3}$

To find: Nature of cubic unit cell = ?

$$\text{Formula: } d = \frac{z \cdot M}{a^3 \cdot N_A}$$

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

Calculation: From the formula,

$$z = \frac{2.7 \times 10^3 \times (405 \times 10^{-12})^3 \times 6.023 \times 10^{23}}{2.7 \times 10^{-2}}$$

$$z = \frac{66.43 \times 10^3 \times 10^{-30} \times 6.023 \times 10^{23}}{10^{-2}} = 4.00$$

Thus, there are 4 atoms of the element present per unit cell.

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

***Example 11**

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

Solution:

Given: Edge length (a) = $4.07 \times 10^{-8} \text{ cm}$
 Density (d) = 10.5 g cm^{-3}

To find: Molecular mass (M) = ?

$$\text{Formula: } d = \frac{z \cdot M}{a^3 \cdot N_A}$$

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

Calculation: Since it is fcc lattice, the number of atoms per unit cell = 4
 From the formula,

$$\therefore M = \frac{10.5 \times (4.07 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{4} = \frac{10.5 \times 6.74 \times 10^{-23} \times 6.023 \times 10^{23}}{4}$$

$$\therefore M = 106.56 \text{ g mol}^{-1}$$

Ans: The molecular mass of silver is **106.56 g mol⁻¹**

***Example 12**

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

Solution:

Given: Edge length (a) = $3.61 \times 10^{-8} \text{ cm}$
 Molecular mass (M) = 63.5 g mol^{-1}

To find: density (d) = ?

$$\text{Formula: } d = \frac{z \cdot M}{a^3 \cdot N_A}$$

Calculation: Since it is fcc lattice
Number of atoms present per unit cell, $z = 4$
From the formula,

$$d = \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times 6.023 \times 10^{23}} = \frac{254}{47.05 \times 10^{-24} \times 6.023 \times 10^{23}}$$

$$d = 8.96 \text{ g cm}^{-3}$$

Ans: The density of copper is **8.96 g cm⁻³**

Example 13

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:

$$\begin{aligned} \text{Number of atoms in the close packing} &= 0.5 \text{ mol} \\ &= 0.5 \times 6.023 \times 10^{23} \\ &= 3.011 \times 10^{23} \text{ atoms} \\ \therefore \text{Number of octahedral voids} &= \text{number of atoms in the packing} = 3.011 \times 10^{23} \\ \therefore \text{Number of tetrahedral voids} &= 2 \times \text{number of atoms in the packing} \\ &= 2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23} \\ \therefore \text{Total number of voids} &= 3.011 \times 10^{23} + 6.022 \times 10^{23} \\ &= 9.033 \times 10^{23} \end{aligned}$$

Ans: The total number of voids in 0.5 mol is **9.033 × 10²³**

*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:

Given:

$$\begin{aligned} \text{Edge length (a)} &= 412.1 \text{ pm} \\ &= 4.12 \times 10^{-8} \text{ cm} \\ \text{Molecular mass (M)} &= 133 + 35.5 \\ &= 168.5 \text{ g mol}^{-1} \end{aligned}$$

To find: Density (d) = ?

Formula:

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

Calculation: In the unit cell of CsCl, there is one Cs ion at the body centre and 8 Cl⁻ ions are at 8 corners.

$$\therefore \text{Number of Cs}^+ \text{ in unit cell} = 1$$

$$\text{Number of Cl}^- \text{ ions} = \frac{1}{8} \times 8 = 1$$

\therefore The unit cell contains one CsCl molecule
Hence, $z = 1$

$$\begin{aligned} d &= \frac{1 \times 168.5 \text{ g mol}^{-1}}{(4.12 \times 10^{-8} \text{ cm})^3 \times 6.023 \times 10^{23} \text{ mol}^{-1}} \\ &= \frac{1 \times 168.5 \text{ g mol}^{-1}}{6.9934 \times 10^{-23} \text{ cm}^3 \times 6.023 \times 10^{23} \text{ mol}^{-1}} \\ &= \frac{168.59}{42.12 \text{ cm}^3} \end{aligned}$$

$$\therefore d = 4.0 \text{ g cm}^{-3}$$

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

***Example 15**

Unit cell of iron crystal has edge length of 288 pm and density of 7.86 g cm^{-3} . Determine the type of crystal lattice (Fe = 56).

Solution:

Given: Density (d) = 7.86 g cm^{-3}
 Edge length (a) = $288 \text{ pm} = 288 \times 10^{-10} \text{ cm}$.
 Molecular mass (M) = 56.

To find: Number of atoms in unit cell (z) = ?

Formula: $d = \frac{z.M}{a^3 N_A}$
 i.e. $z = \frac{a^3 d N_A}{M}$

Calculation: $z = \frac{(288 \times 10^{-10} \text{ cm})^3 \times 7.86 \text{ g cm}^{-3} \times 6.023 \times 10^{23} \text{ mol}^{-1}}{56 \text{ g mol}^{-1}}$
 $= \frac{18.7696 \times 6.023}{56}$
 $= \frac{113.045}{56}$

$\therefore z = 2.01 \approx 2$

Ans: As the number of atoms in unit cell is 2, hence it is a bcc type.

***Example 16**

Niobium is found to crystallise with bcc structure and found to have density of 8.55 g cm^{-3} . Determine the atomic radius of niobium if its atomic mass is 93 a.m.u. (14.29 nm). (NCERT)

Solution:

Given: Atomic mass (M) = 93 a.m.u.
 Density (d) = 8.55 g cm^{-3}

To find: Atomic radius (r) = ?

Formula: $d = \frac{z.M}{a^3 N_A}$
 i.e. $a^3 = \frac{z.M}{d.N_A}$

Calculation: Since it is a bcc arrangement.
 Number of atoms per unit cell, $z = 2$.

$$a^3 = \frac{2 \times 93 \text{ g mol}^{-1}}{8.55 \times 6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$a^3 = \frac{186 \text{ g}}{51.50 \times 10^{23}}$$

$$= 3.61 \times 10^{-23}$$

$$= 36.1 \times 10^{-24} \text{ cm}^3$$

$\therefore a = (36.1 \times 10^{-24})^{1/3}$
 $= 3.304 \times 10^{-8} \text{ cm}$
 $= 330.4 \times 10^{-10} \text{ cm}$
 $= 330 \text{ pm}$

$$[x = (36)^{1/3}, \log x = \frac{1}{3} \log 36$$

$$= \frac{1}{3} \times 1.5575$$

$$= 0.519$$

$$\text{Or } x = \text{antilog } 0.519 = 3.304]$$

For body-centred cubic,

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

$$= 0.433 a$$

$$= 0.433 \times 330.4 \text{ pm} = \mathbf{143.1 \text{ pm.}}$$

Ans: Atomic radius of niobium is **143.1 pm.**

***Example 17**

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:

Given: Density (d) = 10 g cm^{-3}
 Edge length (a) = $100 \text{ pm} = 100 \times 10^{-10} \text{ cm}$.
 $z = 4$ \because it is fcc crystal lattice.

To find: Number of atoms = ?

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

Calculation:
$$\therefore M = \frac{d \cdot a^3 \cdot N_A}{z} = \frac{10 \times (100 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{4} = 1.506 \text{ g}$$

According to definition of Avogadro number 1.506 g of element contains 6.023×10^{23} no. of atoms

$$\therefore 1 \text{ g of element will contain } \frac{1 \times 6.023 \times 10^{23}}{1.506} = 3.99 \times 10^{23} \text{ atoms} \approx 4 \times 10^{23} \text{ atoms}$$

Ans: Number of atoms in the crystal is **4×10^{23} atoms**

Type II: Problems based on formula of compound.

Example 18

A compound formed by the elements A and B crystallises in the cubic arrangement in which A atoms are at the corners of a cube and B atoms are at the face centres. What is the formula of the compound?

Solution:

In a cube, A atoms are at the 8 corners each shared by 8 cubes.

$$\therefore \text{Number of A atoms in the unit cell} = 8 \times \frac{1}{8} = 1$$

B atoms are at the centres of 6 faces and each face is shared by two cubes.

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

$$\therefore \text{The formula of compound} = \mathbf{AB_3}$$

Example 19

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:

Let the atoms N in ccp be 'n'

$$\therefore \text{number of tetrahedral voids} = 2n$$

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

$$\therefore \text{number of atoms M} = 2n \times \frac{1}{3} = \frac{2n}{3}$$

$$\begin{aligned} \therefore \text{Ratio of M : N} &= \frac{2n}{3} : n \\ &= 2 : 3 \end{aligned}$$

Hence, the formula is M_2N_3 .

Example 20

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:

Let the number of oxide ions (O^{2-}) in the packing = n

$$\therefore \text{number of octahedral voids} = n$$

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

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

$$\text{Ratio of } Fe^{3+} : O_2 = \frac{2n}{3} : n$$

$$\therefore \text{Hence the formula of ferric oxide is } Fe_2O_3.$$

Example 21

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:

The number of tetrahedral voids formed is equal to twice the number of atoms of element B and only 2/3rd of these are occupied by the atoms of element A. Hence the ratio of the number of atoms of A and B is $2 \times (2/3) : 1$ or 4:3 and the formula of the compound is A_4B_3 .

***Example 22**

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: C is fcc 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, therefore, 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, therefore, 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: Hence, the formula of the compound is **CD₃**.

*Example 23

An element A and B constitute bcc type crystalline structure. Element A occupies body centre position and B is at the corner of cube. What is the formula of the compound? What are the coordination numbers of A and B?

Solution:

Given: A is bcc.

B is at the corner.

To find: Formula of the compound

Co-ordination numbers.

Calculation: As atoms B are present at the 8 corners of the cube, therefore, number of atoms of B in the unit cell

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

As atoms A are present at the body centre, therefore, number of atoms of A in the unit cell = 1

\therefore Ratio of A : B = 1 : 1

Ans: Hence, the formula of the compound is **AB**.
Co-ordination number of each A and B = **8**.

Practice Problems

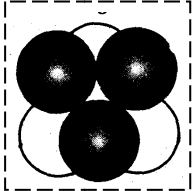
- The edge length of NaCl unit cell is 564 pm. What is the density of NaCl in g cm^3 . ($N_A = 6.023 \times 10^{23}$ and atomic masses of Na = 23, Cl = 35.5)
- An element occurs in bcc structure. It has a cell edge of 250 pm. Calculate its atomic mass if its density is 8.0 g cm^3
- Tungsten has body 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 50g of the element.
- An element density 6.8 g cm^{-3} occurs in bcc structure with cell edge of 290 pm. Calculate the number of atoms present in 200g of the element.
- Lead (II) sulphide crystal has NaCl structure. What is its density? The edge length of the unit cell of PbS crystal is 500 pm.
(atomic masses : Pb = 207, S = 32)

- If three elements P, Q and R crystallizes in a cubic solid lattice with P atoms at the corners, Q atoms at the cube centre and R atoms at the centre of edges, then write the formula of compound.
- 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

- 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) AuCu₃ (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 the three
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. Which of the following is/are pseudo solids?
 i. KCl
 ii. Barium chloride dihydrate
 iii. Rubber
 iv. Solid cake left after distillation of coal tar
 (A) i, iii (B) ii, iii
 (C) iii, iv (D) only iii
7. A solid having no definite shape is called
 (A) Amorphous solid
 (B) Crystalline solid
 (C) Anisotropic solid
 (D) Allotropic solids
8. Which is/are amorphous solids
 (A) Rubber (B) Plastics
 (C) Glass (D) All of the three
9. Amorphous substances show
 (i) short and long range order
 (ii) short range order
 (iii) long range order
 (iv) no sharp melting point
 (A) (i) and (iii) are correct
 (B) (ii) and (iii) are correct
 (C) (iii) and (iv) are correct
 (D) (ii) and (iv) are correct
10. Most crystals show good cleavage because their atoms, ions or molecules are
 (A) Weakly bonded together
 (B) Strongly bonded together
 (C) Spherically symmetrical
 (D) Arranged in planes
11. Which one of the following is a good conductor of electricity?
 (A) Diamond
 (B) Graphite
 (C) Silicon
 (D) Amorphous carbon
12. To get a *n*-type semiconductor, the impurity to be added to silicon should have which of the following number of valence electrons
 (A) 1 (B) 2
 (C) 3 (D) 5
13. The number of atoms present in a simple cubic unit cell are
 (A) 4 (B) 3
 (C) 2 (D) 1
14. The number of atoms in a face-centred cubic unit cell are
 (A) 4 (B) 5
 (C) 6 (D) 2
15. The number of unit cells in 58.5 g of NaCl is nearly
 (A) 6×10^{20} (B) 3×10^{22}
 (C) 1.5×10^{23} (D) 0.5×10^{24}
16. The number of octahedral sites per sphere in a fcc structure is
 (A) 8 (B) 4
 (C) 2 (D) 1
17. Body centred cubic lattice has a coordination number of
 (A) 4 (B) 8
 (C) 12 (D) 6
18. In body centred cubic structure the space occupied is about **[Mar 2013]**
 (A) 68% (B) 53%
 (C) 38% (D) 32%
19. The number of atoms in 100 g of an fcc crystal with density $d = 10 \text{ g / cm}^3$ and cell edge equal to 100 pm is equal to
 (A) 4×10^{25} (B) 3×10^{25}
 (C) 2×10^{25} (D) 1×10^{25}

20. Crystals can be classified into ____ basic crystal lattices
 (A) 3 (B) 7
 (C) 14 (D) 4
21. In cubic closest packing (ccp) structure of NaCl, the coordination number of Na^+ ion is
 (A) 2 (B) 4
 (C) 6 (D) 8
22. 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
 (A) 24.16×10^{23} (B) 36.18×10^{23}
 (C) 6.04×10^{23} (D) 12.08×10^{23}
23. 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) $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
 (D) $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$
24. The arrangement ABCABCABC is referred as
 (A) Octahedral close packing
 (B) Hexagonal close packing
 (C) Tetragonal close packing
 (D) Cubic close packing
25. Close packing is maximum in the crystal lattice of
 (A) Simple cubic
 (B) Face centred
 (C) Body centred
 (D) None
26. ABAB type represents an arrangement of layers called
 (A) hexagonal closed packing
 (B) cubic closed packing
 (C) body centred cubic packing
 (D) fluorite close packing
27. The coordination number of a metal crystallizing in a hexagonal close packed structure is
 (A) 4 (B) 12
 (C) 8 (D) 6
28. 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
 (A) 4 and 2 (B) 9 and 14
 (C) 14 and 9 (D) 2 and 4
29. The empty space between the shared balls and hollow balls as shown in the diagram is called
 (A) hexagonal void
 (B) octahedral void
 (C) tetrahedral void
 (D) double triangular void
- 
30. In a closed packed lattice containing n-particles, the number of tetrahedral and octahedral voids respectively are
 (A) n, 2n (B) n, n
 (C) 2n, n (D) 2n, n/2
31. 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
 (A) AB (B) A_2B
 (C) AB_2 (D) AB_4
32. 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) $\text{X}_2\text{Y}_4\text{Z}$ (B) XY_2Z_4
 (C) $\text{X}_4\text{Y}_2\text{Z}$ (D) X_4YZ_2
33. In octahedral holes (voids)
 (A) A simple triangular void is surrounded by four spheres
 (B) A bi-triangular void is surrounded by four spheres
 (C) A bi-triangular void is surrounded by six spheres
 (D) A bi-triangular void is surrounded by eight spheres
34. An fcc unit cell of aluminium contains the equivalent of how many atoms?
 (A) 1 (B) 2
 (C) 3 (D) 4

35. The formula for determination of density of unit cell is

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

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

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

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

36. Schottky defect defines imperfection in the lattice structure of a

- (A) Solid (B) Liquid
(C) Gas (D) Plasma

37. Frenkel and Schottky defects are

- (A) Nucleus defects
(B) Non-crystal defects
(C) Crystal defects
(D) None of these

38. Which of the following defect, if present, lowers the density of the crystal?

- (A) Frenkel
(B) Schottky
(C) Edge dislocation
(D) Constitution of F-centres

39. Doping of silicon (Si) with boron (B) leads to

- (A) n-type semiconductor
(B) p-type semiconductor
(C) Metal
(D) Insulator

40. Which one of the following has Frenkel defect?

- (A) Sodium chloride
(B) Graphite
(C) Silver chloride
(D) Diamond

Answers to Multiple Choice Question

1. (C) 2. (A) 3. (D) 4. (C)
5. (B) 6. (C) 7. (A) 8. (D)
9. (D) 10. (D) 11. (B) 12. (D)
13. (D) 14. (A) 15. (C) 16. (D)
17. (B) 18. (A) 19. (A) 20. (B)
21. (C) 22. (A) 23. (A) 24. (D)
25. (B) 26. (A) 27. (B) 28. (D)
29. (B) 30. (C) 31. (C) 32. (A)
33. (C) 34. (D) 35. (B) 36. (A)
37. (C) 38. (B) 39. (B) 40. (C)

Answers to Practice Problems

1. 2.16 g cm^3
2. 37.64
3. 1.63×10^{23} atoms.
4. 2.4×10^{24} atoms.
5. 12.7 g cm^{-3}
6. PQR_3
7. XY_2