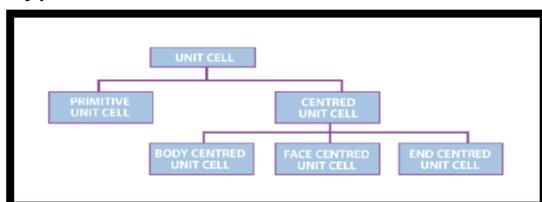


## The Gaseous State and Liquid State

- **Solids:** Solids are the chemical substances which are characterized by definite shape and volume, rigidity, high density, low compressibility. The constituent particles (atoms, molecules or ions) are closely packed and held together by strong interparticle forces.
- **Types of Solids:** The solids are of two types: Crystalline solids and amorphous solids.
- **Crystalline solids:** consist of atoms, ions and molecules arranged in definite and repeating three-dimensional patterns in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions. Ex. salt (sodium chloride), diamond, and sodium nitrate.
- **Amorphous solid,** any noncrystalline solid in which the atoms and molecules are not organized in a definite lattice pattern. Such solids include glass, plastic, and gel.
- **Structure Determination by X-ray Diffraction (Bragg's Equation):** The law states that when the x-ray is incident onto a crystal surface, its angle of incidence,  $\theta$ , will reflect back with a same angle of scattering,  $\theta$ . And, when the path difference,  $d$  is equal to a whole number,  $n$ , of wavelength, a constructive interference will occur.
- **Unit Cell:** The smallest geometrical portion of the crystal lattice which can be used as repetitive unit to build up the whole crystal is called unit cell.
- Types of unit cell:



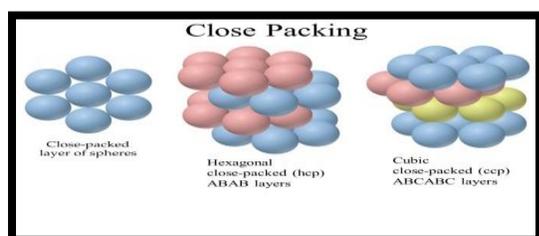
- **Seven Crystal Systems:** There are about 230 crystal forms, which have been grouped into 14 types of space lattices, called Bravais Lattices, on the basis of their symmetry and seven different crystal systems on the basis of interfacial angles and axes.

They are cubic, tetragonal, hexagonal (trigonal), orthorhombic, monoclinic, and triclinic.

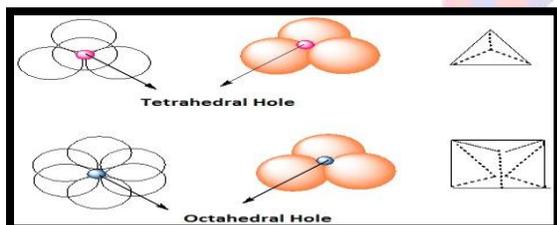
- **Packing Fraction:** It is defined as the ratio of the volume of the unit cell that is occupied by the spheres to the volume of the unit cell.
- **Packing fraction (P.F),** is calculated by volume occupied by the number of spheres in the unit cell divided by volume of a unit cell.

Unit Cell	n	APF
SC	1	0.52
BCC	2	0.68
FCC	4	0.74
HCP	6	0.74

- **Coordination Number:** It is defined as the number of particles immediately adjacent to each particle in the crystal lattice. [In simple cubic lattice, CN is 6, in body centered lattice, CN is 8 and in face centered cubic lattice, CN is 12]. High pressure increases CN and high temperature decreases the CN.
- **Close Packing in Crystals:** Two Dimensional Packing of Constituent Particles.
  - (i) **Square close packing** Space occupied by spheres is 52.4%.
  - (ii) **Hexagonal close packing** Space occupied by spheres is 60.4%. Hence. It is more efficient.
- **Three Dimensional Packing of Constituent Particles:**
  - (i) ABAB arrangement gives hexagonal close packing (hcp).
  - (ii) ABCABC arrangement gives cubic close packing or face centred CUBIC packing (ccp or fcc).
- In both these arrangements 74/0 space is occupied
- Coordination number in hcp and ccp arrangement is 12 while in bcc arrangement, it is 8.
- Close packing of atoms in cubic structure = fcc > bcc > sc. All noble gases have ccp structure except He (hcp structure).



- **Void or Space or Holes:** Empty or vacant space present between spheres of a unit cell, is called void or space or hole or interstitial void. When particles are closed packed resulting in either ccp or hcp structure, two types of voids are generated:
- **Tetrahedral voids:** These are holes or voids surrounded by four spheres Present at the corner of a tetrahedron. Coordination number of a tetrahedral void is 4
- **Octahedral voids** are holes surrounded by six spheres located on a regular tetrahedron. Coordination number of octahedral void is 6.



- **Density of Unit Cell (D):** Density of unit cell = mass of unit cell / volume of unit cell d.
- **Imperfections in Solids:** Any irregularity in the pattern of crystal arrangement in a solid lattice is called **imperfection in solids**. The occurrence of defects takes place when crystallization (the process of formation of crystals) occurs at a very fast or at an intermediate rate.
- The defects are of two types, namely point defects and line defects.
- **Point Defects:** Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance Point defects can be classified into three types : (1) stoichiometric defects (2) impurity defects (3) non-stoichiometric defects
- **1. Stoichiometric Defect:** These are point defects that do not disturb the stoichiometric of the solid. They are also called intrinsic or thermodynamic defects. In ionic solids, basically these are of two types, Frankel defect and Schottky defect

- **2. Impurity Defect:** It arises when foreign atoms or ions are present in the lattice. In case of ionic compounds, the impurity is also ionic in nature.
- **3. Non-Stoichiometric:** Defect Non-stoichiometric crystals are those which do not obey the law of constant proportions. The numbers of positive and negative ions present in such compounds are different from those expected from their ideal chemical formulae. However, the crystal as a whole is neutral. Types of non-stoichiometric defects are as follows:
- **Metal excess defect:** Metal excess defect due to anionic vacancies: Alkali halides like NaCl and KCl show this type of defect. Centers are the sites from where anions are missing and the vacant sites are occupied by electrons. F-centre contributes color and paramagnetic nature of the crystal.

- **Metal excess defect:** due to presence of extra cations at interstitial sites.



- **(ii) Metal deficiency defect:** It is due to the absence of a metal ion from its lattice site and charge is balanced by ion having higher positive charge. Transition metals exhibit this defect, e.g., FeO, which is found in the composition range from Fe<sub>0.93</sub>O to Fe<sub>0.96</sub>O.

- **Classification of Solids on the Basis of Electrical Conductivity:**

- **1. Intrinsic Semiconductors:** Pure substances that are semiconductors are known as Intrinsic Semiconductors e.g., Si, Ge
- **2. Extrinsic Semiconductors:** Their conductivity is due to the presence of impurities. They are formed by doping. Doping of Si or Ge is carried out with P, As, Sb, B, Al or Ga.

**(i) n-type semiconductors:** Silicon doped with 15 group elements like phosphorus is called n-type semiconductor.

**(ii) p-type semiconductors:** Silicon doped with 13 group element like gallium is called p-type semiconductor.

- **Magnetic Properties of Solids:** Solids can be divided into different classes depending on their response to magnetic field.

1. Diamagnetic Substances These are weakly repelled

by the magnetic field and do not have any unpaired electron, e.g.,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  etc.

**2. Paramagnetic Substances:** These are attracted by the magnetic field and have unpaired electrons. These lose magnetism in the absence of magnetic field, e.g.,  $\text{O}_2$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , etc.

**3. Ferromagnetic Substances:** These are attracted by the magnetic field and show permanent magnetism even in the absence of magnetic field, e.g., Fe, Co and Ni.

**4. Anti-ferromagnetic Substances:** These substances have net magnetic moment zero due to compensatory alignment of magnetic moments, e.g., MnO,  $\text{MnO}_2$ , FeO, etc.

**5. Ferromagnetic Substances:** These substances have a net dipole moment due to unequal parallel and anti-parallel alignment of magnetic moments, e.g.,  $\text{Fe}_3\text{O}_4$ , ferrites, etc.

HCP and CCP have equal efficiency i.e., 74% of space is occupied and coordination number is 12. CCP arrangement has FCC lattice.

#### Types of Crystalline Solid:

Type of Solid	Constituent Particles	Nature of interaction between the particles	Appearance	Melting Point	Examples
Ionic	Ions	Coulombic	Hard and brittle	High	Sodium chloride, zinc sulphide, etc
Molecular Non polar	Molecules	van der Waals Dipole-dipole	Soft brittle	low	Iodine, naphthalene, water, carbon dioxide.
Covalent	Atoms	Covalent bonding	Hard	Very high	Diamond, graphite, silica, etc.
Metallic	Atoms	Metallic bonding	Hard and malleable	Variable	Copper, silver, etc.

Unoccupied spaces in solids are called interstitial voids or interstitial sites.

N (where N is number of closed packed  $\times$  No. of tetrahedral voids = 2 particles)

No. of octahedral voids = N.

Valency defect lowers the density of a crystal.

Interstitial defect increases the density of a crystal.

**Calculation of number of particles/atoms/ions in a unit cell:**

#### Calculation of number of particles/atoms/ions in a unit cell :

Type of unit cell	Number of particles per unit cell	Relationship between edge length (a) and radius (r) of atom/ion
Simple cubic (SC)	1	$a = 2r$
Body centred cubic (BCC)	2	$a = \frac{4}{\sqrt{3}}r$
Face centred cubic (FCC)	4	$a = 2\sqrt{2}r$

#### Density of unit cell :

Here, M is molar mass, r is radius of atom, d is density and  $N_A$  is Avogadro's constant ( $6.022 \times 10^{23} \text{ mol}^{-1}$ )

$$\text{Packing density} = \frac{VZ}{V} = \frac{4}{3} \frac{\pi r^3 Z}{a^3}$$

The **limiting radius ratio** is the minimum allowable value for the **ratio** of ionic radii ( $\rho = r^+/r^-$ ) for this structure to be stable. Here,  $r^+$  is the **radius** of the cation and  $r^-$  is the **radius** of the surrounding anions. Note that the anions are usually larger than cations.

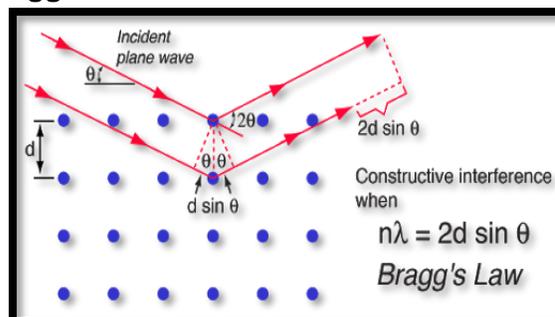
Radius Ratio	Coordination number	Type of void	Example
< 0.155	2	Linear	
0.155 - 0.225	3	Triangular Planar	$\text{B}_2\text{O}_3$
0.225 - 0.414	4	Tetrahedral	ZnS, CuCl
0.414 - 0.732	6	Octahedral	NaCl, MgO
0.732 - 1.000	8	Cubic	CsCl, $\text{NH}_4\text{Br}$
1	12	Close packing (ccp and hcp)	metals

Relationship between Radius Ratio and Coordination Number

#### Some Important terms:

S.No	Properties	Simple Cubic	Body Centered Cubic	Face Centered Cubic	Hexagonal Close Packed
1.	Unit Cell Volume	$a^3$	$a^3$	$a^3$	$3/2 \sqrt{3} a^3 c$
2.	Number of atoms per unit cell	1	2	4	6
3.	Coordination Number	6	8	12	12
4.	Atomic Radius	$\frac{a}{2}$	$\left( r = \frac{\sqrt{3}a}{4} \right)$	$\left( r = \frac{\sqrt{2}a}{4} \right)$	$\frac{a}{2}$
5.	Packing Factor	0.52	0.68	0.74	0.74
6.	Examples	Polonium	Iron, Barium, Chromium	Aluminum, Copper, Gold	Beryllium, Cadmium

#### Bragg's law of diffraction:



**Check Yourself**

- The coordination number of atoms in a cubic closed-packed is \_\_\_\_\_.  
(A) 2      (B) 8      (C) 12      (D) 6
- The type defect observed in ionic crystals which large difference in the size of ions is:  
(A) Interstitial defect  
(B) Frenkel defect  
(C) Scotty Defect  
(D) Stoichiometric Defect
- A mixed oxide has ccp arrangement in which the cations 'X' occupy  $\frac{1}{3}$ rd of octahedral voids and the cations 'Y' occupy  $\frac{1}{3}$ rd of tetrahedral voids. The formula of oxide is:  
(A)  $X_2Y_3O_2$     (B)  $XY_3O$   
(C)  $X_2YO_3$     (D)  $XY_2O_3$
- An element with molar mass  $64 \text{ g mol}^{-1}$  and density  $6.6 \text{ g cm}^{-3}$  forms a cubic unit cell. The edge length of unit cell is  $4 \times 10^{-8} \text{ cm}$ . The type of cubic unit cell formed is?  
(A) fcc    (B) ccp    (C) bcc    (D) hcp
- A solid is made up of 2 elements P and Q. Atoms Q are in ccp arrangement, while P atoms occupy all the tetrahedral sites. The formula of the compound is:  
(A)  $PQ_2$     (B)  $P_6Q_4$   
(C)  $P_2Q$     (D)  $PQ$

**Test Yourself**

**Question:** Classify the following as amorphous or crystalline solids: Polyurethane, naphthalene, benzoic acid, Teflon, potassium nitrate, cellophane, polyvinyl chloride, fiberglass, copper

**Answer:** Crystalline solids: Benzoic acid, potassium nitrate, copper  
amorphous solids: Polyurethane, Teflon, cellophane, polyvinyl chloride, fiberglass

**Stretch Yourself**

- The density of lead is  $11.35 \text{ g cm}^{-3}$  and the metal crystallizes with fcc unit cell. Estimate the radius of lead atom. (At Mass of lead =  $207 \text{ g mol}^{-1}$  and  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ )
- Aluminum crystallizes in a cubic close-packed structure. Radius of the atom in the metal is  $125 \text{ pm}$ .  
(i) What is the length of the side of the unit cell?  
(ii) How many unit cells are there in  $1 \text{ cm}^3$  of aluminium?
- Name the type of crystal defect which is produced when NaCl crystal is doped with MgCl.
- How are the following properties of crystals affected by Schottky and Frenkel defects?  
(i) Density    (ii) Electrical conductivity
- Write a feature which will distinguish a metallic solid from an ionic solid.



## Answers

### Check Yourself

Answer: 1(C); 2(B); 3(D); 4(A); 5(C)

### Stretch Yourself

#### 1. Hint:

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

- For the cubic close-packed structure Let  $a$  is the edge of the cube and  $r$  is the radius of atom Given that  $r = 125 \text{ pm}$ ,  $a = 2\sqrt{2} r$  Plug the value of  $r$  we get  
 $= 2 \times 1.414 \times 125 \text{ pm} = 354 \text{ pm}$  (approximately)  
 Volume of one unit cell =  $\text{side}^3 = (354 \text{ pm})^3$   
 $1 \text{ pm} = 10^{-10} \text{ cm} = (354 \times 10^{-10} \text{ cm})^3 = 4.4 \times 10^{-23} \text{ cm}^3$   
 Total number of unit cells in  $1.00 \text{ cm}^3 = \text{total volume} / \text{size of each cell}$   
 $= (1.00 \text{ cm}^3) / (4.4 \times 10^{-23} \text{ cm}^3)$   
 $= 2.27 \times 10^{22} \text{ unit cell}$
- A cation vacancy is formed, so impurity defect is produced. A substitution solid solution is formed (because  $2\text{Na}^+$  ions are replaced by one  $\text{Mg}^{2+}$  ion at the lattice site).
- In Schottky defect density slightly decreases and electrical conductivity slightly increases. In Frenkel defect density remains constant and conductivity slightly increases.
- Metals are malleable and ductile whereas ionic solids are hard and brittle.