

Chemistry Notes for class 12 Chapter 1 The Solid State

Solids

Solids are the chemical substances which are characterised 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.

Distinction Between Crystalline and Amorphous Solids

S.No Crystalline solid

- 1 These have definite and regular arrangement of the constituent particles in space.
- 2 These are true solids.
- 3 These have long order arrangement of the particles.
- 4 These are anisotropic in nature, i.e., their physical properties are different in different directions.
- 5 They have sharp melting points.
- 6 They undergo a clean cleavage when cut.

Amorphous solids

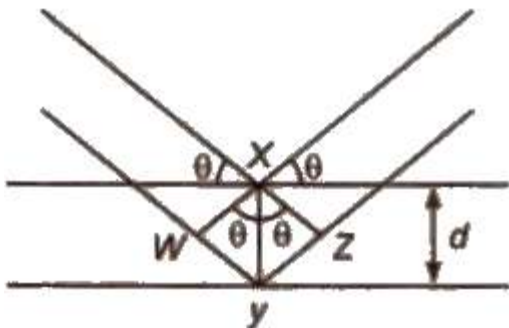
- These doesn't have any regular arrangement of the constituent particles in space.
- These are super cooled liquids or pseudo solids.
- These have short order arrangement of particles.
- These are isotropic in nature i.e., their physical properties are same in all the directions.
- They melt over a certain range of temperature.
- They undergo irregular cleavage when cut.

Types of Crystalline Solids

Character	Ionic solids	Covalent solids	Molecular solids	Metallic solids
Constituent particles	Positive and negative ions	Atoms	Molecules	Positive metal ions (kernels) and free electrons
Bonding forces	Electrostatic attraction	Covalent	van der Waals Dipole-dipole	Electrostatic attraction between positive ions and negative species
Melting point	High melting point	Very high melting point	Low melting point	Moderate to high melting point
Hard/soft	Hard and brittle	Very hard	Very soft	Hard and soft
Conductance	Conductor in aqueous solution or in molten state	Non-conductor	Insulator conductor	Good conductor
Examples	NaCl, CaF ₂	Diamond, Silica	H ₂ O, CO ₂	Cu, Fe

Structure Determination by X-ray Diffraction (Bragg's Equation)

When a beam of X-rays falls on a crystal plane composed of regularly arranged atoms or ions, the X-rays are diffracted. If the waves are in phase after reflection, the difference in distance travelled by the two rays (i.e., path difference) must be equal to an integral number of Wavelength, $n\lambda$ for constructive.



Thus, path difference = $WY + YZ$

$$= XY \sin \theta + xy \sin \theta$$

$$= 2 XY \sin \theta = 2d \sin \theta$$

$$\therefore n\lambda = 2d \sin \theta$$

This equation is called Bragg's equation.

Where, $n = 1, 2, 3 \dots$ (diffraction order)

λ = wavelength of X-rays incident on crystal

d = distance between atomic planes

θ = angle at which interference occurs.

Unit Cell

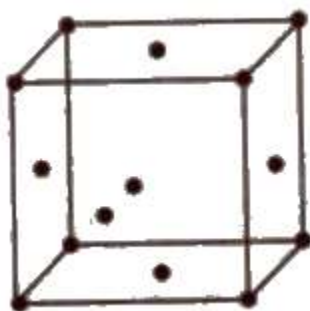
The smallest geometrical portion of the crystal lattice which can be used as repetitive unit to build up the whole crystal is called unit cell.

Types of Unit Cell

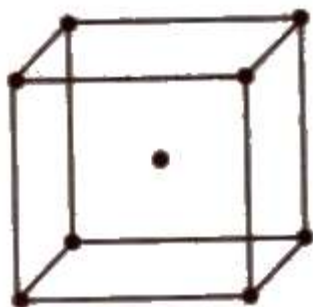
(i) **Simple or primitive Unit cell** In which the particles are present at the corners only.



(ii) **Face centred unit cell** In which the particles are present at the corners as well as at the centre of each of six faces



(iii) **Body centred unit cell** In which the particles are present at the corners as well as at the centre of the unit cell.



(iv) **End centred unit cell** In which the particles are present at the corners and at the centre of two opposite faces.



Number of Particles Per Unit Cell

Unit cell	No. of particles and their contribution			Total
	Corner	Face	Centre	
Simple cubic	$8 \times \frac{1}{8}$	—	—	1
Face centred	$8 \times \frac{1}{8}$	$6 \times \frac{1}{2}$	—	4
Body centred	$8 \times \frac{1}{8}$	—	1	2
End centred	$8 \times \frac{1}{8}$	$2 \times \frac{1}{2}$	—	2

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.

Seven Crystal Systems

	Crystal system	Parameters of unit cell	
		Intercepts/axes	Angles
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
3.	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
4.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
5.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
6.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

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.

(i) **Primitive cubic unit cell** Atoms touch each other along edges.

Hence, $d = a$ or $r = a / 2$

(r = radius of atom and a = edge length)

Therefore, $PF = 4 / 3 \pi r^3 / (2r)^3 = 0.524$ or 52.4%

(ii) **Face centred cubic unit cell** Atoms touch each other along the face diagonal.

Hence, $d = a / \sqrt{2}$

or $r = \sqrt{2}a / 4$

Therefore; $PF = 4 * 4 / 3 \pi r^3 / (4r / \sqrt{2})r^3 = 0.74$ or 74%

(iii) **Body centred cubic unit cell** Atoms touch each other along the body diagonal.

Hence, $\sqrt{3}a / 2$

or $r = \sqrt{3}a / 4$

Therefore; $PF = 2 * 4 / 3 \pi r^3 / (4r / \sqrt{3})r^3 = 0.68$ or 68%

Coordination Number

It is defined as the number of particles immediately adjacent to each particle in the crystal lattice.

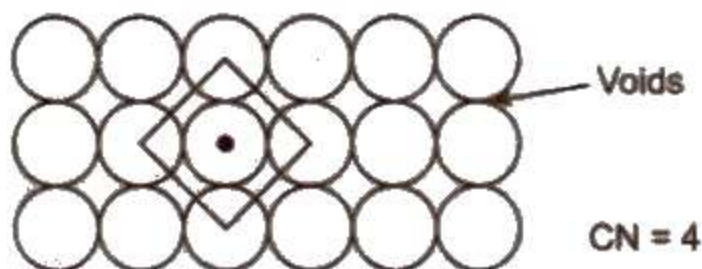
[In simple cubic lattice, CN is 6, in body centred lattice, CN is 8 and in face centred cubic lattice, CN is 12].

High pressure increases CN and high temperature decreases the CN.

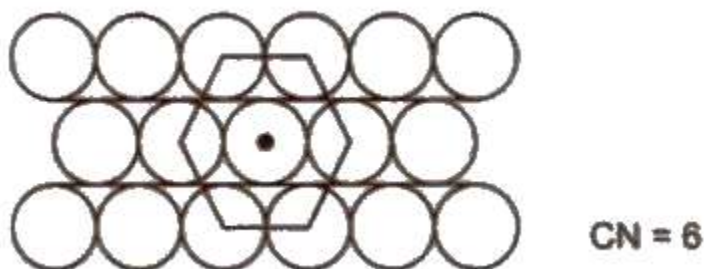
Close Packing in Crystals

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

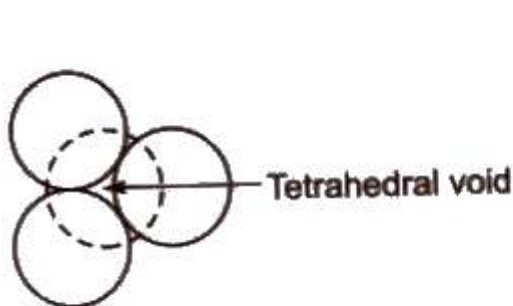
(i) ABAB arrangement gives hexagonal close packing (hcp).

(ii) ABCABC arrangement gives cubic close packing or face centred CUBIC packing (ccp or fcc).

- In both these arrangements 740/0 space is occupied
- Coordination number in hop 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).

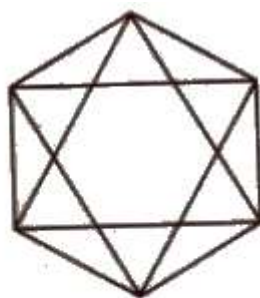
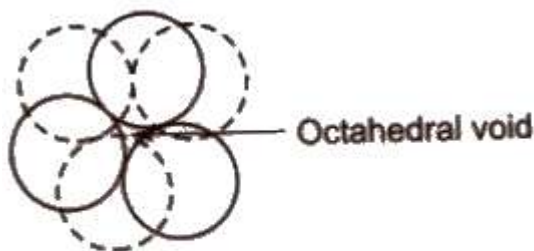
Void or Space or Holes

- 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** are holes or voids surrounded by four spheres Present at the corner of a tetrahedron. Coordination number of a tetrahedral void is 4.



$$r_{\text{void}} = 0.225 \times r_{\text{sphere}} \quad (\text{for tetrahedral voids})$$

- **Octahedral voids** are holes surrounded by six spheres located on a regular tetrahedron. Coordination number of octahedral void is 6.



$$r_{\text{void}} = 0.414 \times r_{\text{sphere}} \quad (\text{for octahedral voids})$$

[The number of octahedral voids present in a lattice is equal to the number of close packed particles. The number of tetrahedral voids present in a lattice is twice to the number of close packed particles.]

Density of Unit Cell (d)

Density of unit cell = mass of unit cell / volume of unit cell

$$d = Z * M / a^3 = ZM / a^3 * N_A$$

(The density of the unit cell is same as the density of the substance.)

where, d = density of unit cell

M = molecular weight

Z = no. of atoms per unit cell

N_A = Avogadro number

a = edge length of unit cell.

The Structure of Ionic Crystals

The ionic radius ratios of cation and anion, play a very important role in giving a clue to the nature of the crystal structure of ionic substances.

Radius Ratio and Crystal Structure

S. No.	Radius ratio (r^+ / r^-)	Coordination number	Shape	Crystal structure	Example
1.	< 0.225	2 or 3	Linear or triangular	Linear or triangular	B_2O_3
2.	0.225–0.414	4	Tetrahedral	ZnS type	CuCl, CuBr, HgS, BaS
3.	0.414–0.732	6	Octahedral	NaCl type	MgO, NaBr, CaS, KBr, CaO
4.	0.732 or more	8	Cube	CsCl type	CsI, CsBr, NH_4Br

Ionic crystals may be of two types

(i) AB type and

(ii) A_2B or AB_2

Structure of Ionic Crystals

Ionic crystal type	Cation occupy	Anion form	Coordination
NaCl (Rock salt structure) type	All octahedral voids	fcc unit cell	6 : 6
CsCl type	Body centre	simple cubic unit cell	8 : 8
ZnS (Sphalerite structure) type	Alternate tetrahedral voids	fcc unit cell	4 : 4
CaF ₂ (Fluorite structure) type	Alternate body centre	simple cubic unit cell	8 : 4
Na ₂ O (Antifluorite structure) type	All tetrahedral sites	fcc unit cell	4 : 8

On applying pressure NaCl structure (6 : 6 coordination) changes into CsCl structure (8 : 8 coordination) and reverse of this occur at high temperature (760 K).

Imperfections in Solids

- In a crystalline solid, the atoms, ions and molecules are arranged in a Definite repeating pattern, but some defects may occur in the pattern. derivations from perfect arrangement may occur due to rapid cooling or presence of additional particles.
- 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) psychometric 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

	Schottky defect	Frenkel defect
1.	It is due to equal number of cations and anions missing from the lattice sites.	It is due to the missing of ions (usually cations) from the lattice sites and they occupy the interstitial sites.
2.	This results in the decrease in density of crystal.	It has no effect on the density of crystal.
3.	This type of defect is found in highly ionic compounds with high coordination number, e.g., NaCl, CsCl, etc.	This types of defect is found in crystal, where the difference in the size of cations and anions is very large, e.g., AgCl, ZnS, etc.

AgBr has both Schottky and Frenkel defects. Frenkel defects are not found in pure alkali metal halides because cations are of large size.

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. When the impurity has the same charge as the host ion, it just substitutes some of the host ions.
- Impurity defects can also be introduced by adding impurity ions having different charge than host ions. e.g. molten NaCl containing a little amount of SrCl_2 is crystallised. In such cases,
- Cationic vacancies produced = [number of cations of higher valence * Difference in valence of the host cation and cation of higher valence]

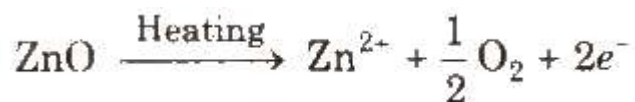
3. Non-Stoichiometric Defect

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:

(i) **Metal excess defect** Metal excess defect due to anionic vacancies: Alkali halides like NaCl and KCl show this type of defect. Centres are the sites from where anions are missing and the vacant sites are occupied by electrons. F-centres contribute colour and paramagnetic nature of the crystal [F stands for German word Farbe meaning colour].

Metal excess defect due to presence of extra cations at interstitial sites, e.g., zinc oxide is white in colour at room temperature. On heating, it loses oxygen and turns yellow.

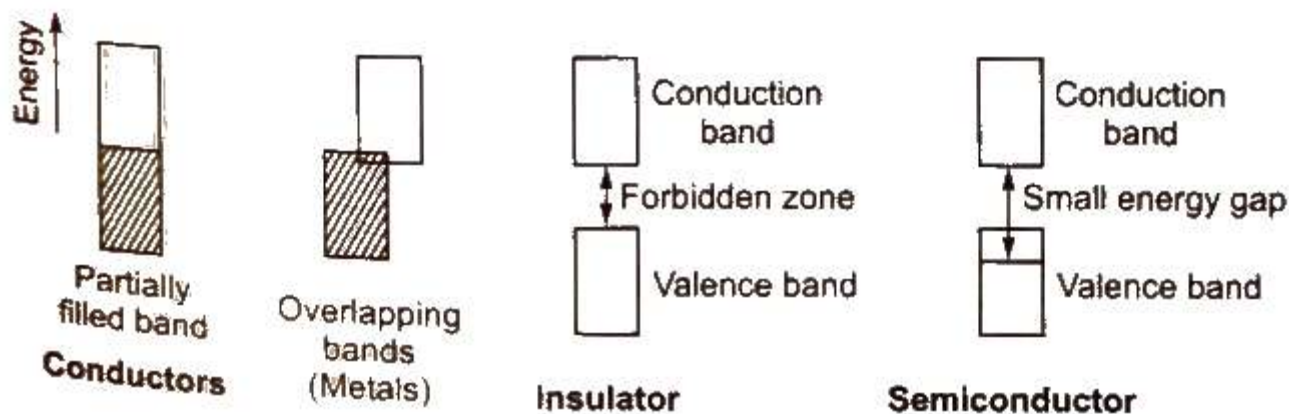


(ii) Metal deficiency defect due to cation vacancy It is due to the absence of a metal ion from its lattice site and charge is balanced by ion having higher positive charge. Transition metals exhibit this defect, e.g., FeO, which is found in the composition range from $\text{Fe}_{0.93}\text{O}$ to $\text{Fe}_{0.96}\text{O}$.

In crystal of FeO, some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

Classification of Solids on the Basis of Electrical Conductivity

Type of solid	Conductivity	Reason of conductivity	Examples
Conductors	$10^4 - 10^7$ (Very high)	Motion of electrons	Metals like Ag, Al
Insulators	10^{-20} to 10^{-10} (Very low)	Do not permit electricity to pass	Wood, rubber, bakelite
Semiconductors	$10^{-6} - 10^4$ (Moderate)	Motion of interstitial electrons or holes or both	Si, Ge, etc.



[The electricity produced on heating a polar crystal is called 'pyroelectricity'.]

When mechanical stress is applied on polar crystals, electricity produced due to displacement of ions is called 'piezoelectricity'.

Semiconductors

Electronic conductors having electrical conductivity in the range of $10^4 - 10^7 \Omega^{-1} \text{cm}^{-1}$ are known as semiconductors. Examples Si, Ge Sn (grey), Cu_2O , SiC and GaAs.

Intrinsic Semiconductors

Pure substances that are semiconductors are known as Intrinsic Semiconductors e.g., Si, Ge

Extrinsic Semiconductors

Their conductivity is due to the presence of impurities. They are formed by doping. It is defined as addition of impurities to a semiconductor to increase the conductivity. 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. The conductivity is due to the presence of negative charge (electrons),

(ii) **p-type semiconductors** Silicon doped with 13 group element like gallium is called p-type semiconductor. The conductivity is due to the presence of positive holes.

- Some typical 13-15 compounds are InSb, AlP and GaAs and Some typical 12-16 compounds are ZnS, CdS, CdSe and HgTe.
- These exhibit electrical and optical properties of great use in electronic industry.

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., TiO_2 , V_2O_5 , C_6H_6 , NaCl, 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., O_2 , Cu^{2+} , 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, MnO_2 , FeO, etc.

5. Ferrimagnetic Substances

These substances have a net dipole moment due to unequal parallel and anti-parallel alignment of magnetic moments, e.g., Fe_3O_4 , ferrites, etc.