NEET | JEE ESSENTIALS

Class XII

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Unit 1 THE SOLID STATE | SOLUTIONS

THE SOLID STATE

General Properties

- Solid is the state of matter in which constituent particles are firmly bound due to strong forces.
- Solids have a definite shape, mass and volume.
- Solids are almost incompressible, rigid and have high mechanical strength.
- Solids have high density and very slow diffusion rate.

Classification of Solids

Crystalline Solids	Amorphous Solids
• Definite geometry	• Constituents are not arranged in ordered manner.
• Sharp melting points and definite heat of fusion.	• Neither have sharp melting point nor definite heat of fusion.
• Generate plain and smooth surface on cutting.	• Have irregular surface.
• These show anisotropy.	• These show isotropy.
• True solid	• Pseudo solids or supercooled liquids

Classification of Crystalline Solids

S. No.	Characteristics	Molecular solids	Ionic solids	Metallic solids	Covalent solids
1.	Constituent particles present in lattice sites	molecules (polar or non-polar)	positive and negative ions	positive ions in a sea of delocalised electrons	non-metal atoms
2.	Bonding forces	weak van der Waals forces, hydrogen bonding, dispersion forces	electrostatic attraction between ions	electrostatic attraction between cations and sea of electrons (metallic bonds)	strong covalent bonds

3.	Hardness	very soft	hard	variable (hard or soft)	very hard, except graphite which is soft
4.	Brittleness	low	brittle	very low	medium
5.	Melting point	low	high	moderate to high	very high
6.	Electrical conductivity	bad conductors	insulator (in solid state) (conductors in molten state or in aqueous solutions)	good conductors	bad conductors except graphite
7.	Solubility	some are soluble and some are insoluble in both polar as well as non-polar solvents	soluble in polar and insoluble in non-polar solvents	insoluble in polar as well as non-polar solvents	insoluble in polar and usually soluble in non-polar solvents
8.	Examples	CH_4, H_2, solid CO_2, H_2O, sugar, etc.	NaCl, ZnS, KNO_3, CaO, $BaCl_2$, etc.	all metals and alloys	diamond, SiO_2 graphite, SiC fullerence, etc.

Crystal system/Unit cell : A unit cell is the smallest repeating structural unit of a crystalline solid. These are of seven types :

Crystal System	Axial lengths	Axial angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Pb, Cu, KCl, CsCl, Cu_2O, CaF_2, alum, diamond
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	SnO_2, TiO_2, $ZnSO_4$
Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	KNO_3, K_2SO_4, $BaSO_4$
Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$NaNO_3$, $CaCO_3$, As, Sb
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	ZnO, PbS, CdS, graphite, ice
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	$Na_2SO_4 \cdot 10H_2O$, monoclinic sulphur
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CaSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$, H_3BO_3

Crystal lattice :

Unit cell	No. of atoms and their contribution per unit cell			Total no. of atoms per unit cell
	at corners	at faces	in centre	
Simple cubic (Primitive unit cell)	$8 \times \frac{1}{8} = 1$	0	0	1
Body-centred cubic unit cell (*bcc*)	$8 \times \frac{1}{8} = 1$	0	1	1 + 1 = 2
Face-centred cubic unit cell (*fcc*)	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$	0	1 + 3 = 4

INFO SHOTS

Application of solid state !

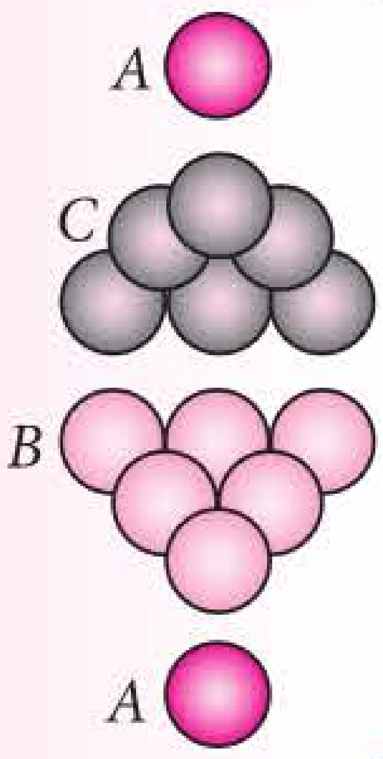
Recently, a new process used on the surface of TiO_2 films, is photoinduced superhydrophilicity. In photoinduced hydrophilicity, absorption of UV photons results in the generation of electrons in the conduction band and holes in the valence band. While electrons reduce Ti(IV) cations to Ti(III) , holes migrate to the TiO_2 surface where they oxidise the bridging O^{2-} anions. The latter reaction leads to the expulsion of an O atom followed by the adsorption of water molecules at the resulting vacancy site, thereby producing new OH groups and increasing the hydrophilicity of the surface.

Packing in Solids

Packing in Solid

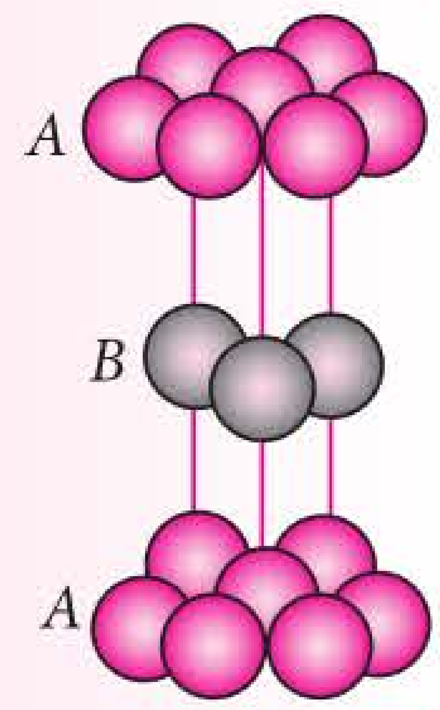
Cubic close packing (*ccp*) or *fcc*

ABCABC....type *i.e.*, spheres in every fourth layer are vertically aligned with the first larger spheres.



Hexagonal close packing (*hcp*)

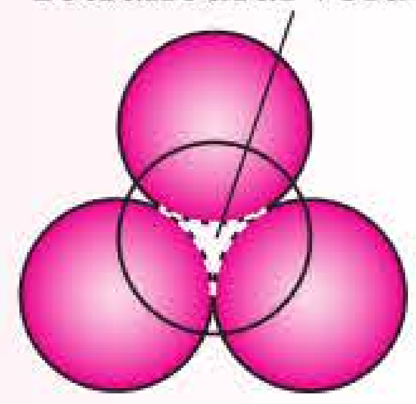
ABAB....type *i.e.*, spheres in every third layer are vertically aligned with the first layer spheres.



Voids

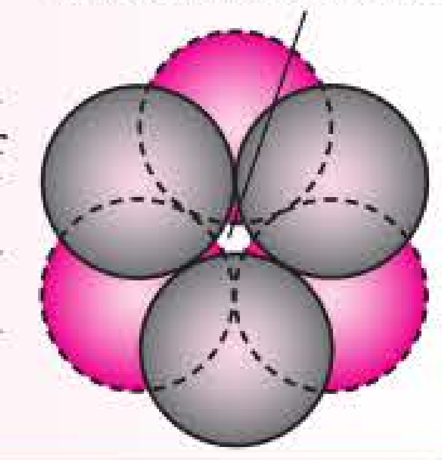
Tetrahedral void

It is simple triangular void in a crystal which is surrounded by four spheres. If N is the number of close packed spheres then number of tetrahedral voids = $2N$



Octahedral void

It is a double triangular void which is surrounded by six spheres. If N is the number of close packed spheres then number of octahedral voids = N



Dimensions of Unit Cells

Simple cubic unit cell	Face-centred cubic or cubic close packing unit cell	Body-centred cubic unit cell
$Z = 1$	$Z = 4$	$Z = 2$
$d = a = 2r,\ r = \frac{a}{2}$	$d = 2r = \frac{a}{\sqrt{2}},\ r = \frac{a}{2\sqrt{2}}$	$d = 2r = \frac{\sqrt{3}a}{2},\ r = \frac{\sqrt{3}a}{4}$
Packing efficiency = 52.4%	Packing efficiency = 74%	Packing efficiency = 68%
Coordination No. = 6	Coordination No. = 12	Coordination No. = 8

where, r = radius of the atom, a = edge length of the unit cell, d = nearest neighbouring distance

Density of Unit Cells

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

where, Z = Number of atoms per unit cell
M = Molar mass (kg/mol)
a = Edge length (metres)
ρ = Density of solid
N_A = Avogadro's number

It 'a' is taken in cm and 'M' in g/mol then

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

Radius Ratio and Coordination Number

Radius ratio	0.155 - 0.225	0.225 - 0.414	0.414 - 0.732	0.732 - 1
Coordination number	3	4	6	8
Structural arrangement	Planar triangular	Tetrahedral	Octahedral	Cubic
Example	B_2O_3	ZnS, HgS, CuI	NaCl (Rock salt)	CsCl, NH_4Br

Magnetic Properties of Solids

Solids

Paramagnetic substances
- Possess permanent dipoles and are attracted by magnetic field.
- They have unpaired electrons. *e.g.*, oxygen, Cu^{2+}, Fe^{3+}, Cr^{3+}, etc.

Diamagnetic substances
- Weakly repelled by magnetic field.
- These materials have all paired electrons (↑↓↑↓). *e.g.*, NaCl, water, benzene, etc.

Ferrimagnetic substances
- Substances having magnetic moment of domain in parallel and anti-parallel direction in unequal numbers *e.g.*, Fe_3O_4, etc.

Ferromagnetic substances
- Strongly attracted by magnetic field and show permanent magnetism even when magnetic field is removed.
- They have large number of unpaired electrons.
- Magnetic moment of domains in the same direction, ↑↑↑↑. *e.g.*, Fe, Co, Ni, Gd, CrO_2, etc.

Anti-ferromagnetic substances
- Substances having domain structure similar to ferromagnetic substances.
- Their domain are oppositely oriented and cancel each other's magnetic moment thus posses zero magnetic moment *e.g.*, MnO, etc.

SOLUTIONS

- Solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied within certain limits.

Types of Solutions

Solute	Solvent	Types of solution	Examples
		Solid solutions	
Solid	Solid	Solid in solid	All alloys like brass (Cu + Zn), bronze (Cu + Sn), German silver (Cu + Zn + Ni), etc.
Liquid	Solid	Liquid in solid	Amalgam of mercury with Na, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$
Gas	Solid	Gas in solid	Solution of H_2 in Pd, dissolved gases in minerals.
		Liquid solutions	
Solid	Liquid	Solid in liquid	Sugar solution, salt solution, I_2 in CCl_4.
Liquid	Liquid	Liquid in liquid	Benzene in toluene, alcohol in water
Gas	Liquid	Gas in liquid	CO_2 in water, NH_3 in water, aerated drinks, etc.
		Gaseous solutions	
Solid	Gas	Solid in gas	Iodine vapours in air, camphor vapours in N_2.
Liquid	Gas	Liquid in gas	Water vapours in air, $CHCl_3$ vapours in N_2.
Gas	Gas	Gas in gas	Air (O_2 + N_2)

INFO SHOTS

Purifying water !

A new way to recover almost 100 percent of the water from highly concentrated salt solutions has been developed. The system will alleviate water shortages in arid regions and reduce concerns surrounding high salinity brine disposal, such as hydraulic fracturing waste. It involves the development of a carbon nanotube-based heating element that will vastly improve the recovery of fresh water during membrane distillation processes.

DEFECTS IN SOLIDS

Any departure from perfectly ordered arrangement of constituent particles is called defect or imperfection.

Types of Defects

Stoichiometric Defect
(Intrinsic or Thermodynamic Defect)

Does not disturb the stoichiometry of solid.

Vacancy Defect
- It arises when some atoms are missing from the lattice sites.

Interstitial Defect
- It arises due to some extra atoms occupying the interstitial sites.

Schottky Defect
- It is due to equal number of cations and anions missing from lattice sites.
- It results in decrease in density of crystal.
- This is found in the highly ionic compounds having cation and anion of same size, *e.g.*, NaCl, CsCl, etc.

Frenkel Defect
- It is due to missing of ions (usually cations) from the lattice sites and these occupy interstitial sites.
- It has no effect on the density of crystal.
- This is found in crystal with low coordination number *e.g.*, AgI, ZnS, etc.

Non-stoichiometric Defect

Arises due to the presence of constituent particles in non-stoichiometric ratio, thus stoichiometry get disturbed.

Metal Excess Defect
- Arises due to anionic vacancies, leaving a hole which is occupied by an electron thus, maintaining electrical balance. The anionic sites, occupied by unpaired electrons, are called *F*-centres and these are responsible for imparting colour to the crystals.

Metal Deficiency Defect
- Arises when metal shows variable valency *i.e.*, in transition metals. The defect occurs due to missing of a cation from its lattice site and the presence of the cation having higher charge in the adjacent lattice site.

Impurity Defect
- Arises when foreign atoms are present at the lattice site in place of host atoms or at vacant interstitial sites.

Dislocation Defect
- Results from the improper orientation of planes with respect to one another in the crystal.

ELECTRICAL PROPERTIES OF SOLIDS

Solids

Conductors
Allow the passage of electric current.

Metallic conductors
Conducts electricity in solid as well as molten state. *e.g.*, metals like Cu, Ag, etc.

Electrolytic conductors
Conducts electricity only in molten state or aqueous solution. *e.g.*, NaCl, KCl, etc.

Semiconductors
Conduct electricity due to presence of impurities. *e.g.*, Si, Ge, etc.

Doping
Addion of impurities to a crystalline substance to change its electrical properties is called doping.

***p*-type semiconductors**
- By adding impurities of electron deficient elements like B, Al (group 13) to Si or Ge.
- Conductivity due to holes.

***n*-type semiconductors**
- By adding impurities of electron rich elements like P, As (group 15) to Si or Ge.
- Conductivity due to free electrons.

Insulators
Do not allow the passage of electric current. *e.g.*, glass, rubber, polythene, etc.