FOCUS

Class XII

NEET/JEE 2019

Focus more to get high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

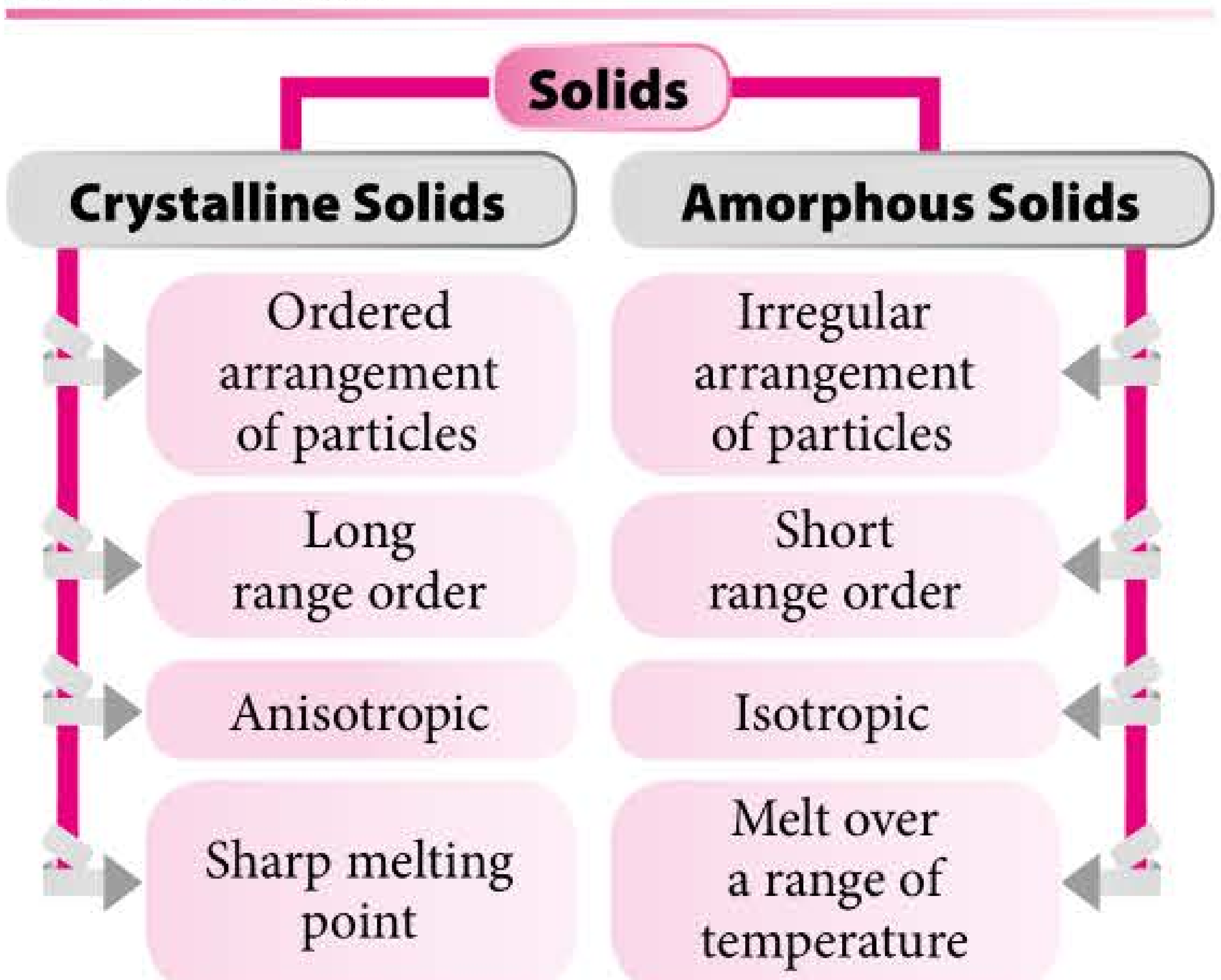
UNIT - 1 : The Solid State / Solutions

THE SOLID STATE

General characteristics

- Solids have definite mass, volume and shape due to the fixed positions of their constituent particles.
- Solids have short intermolecular distances and strong intermolecular forces.
- The constituent particles of solid (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.
- Solids are incompressible and rigid.

Classification



Crystal Lattice

The regular arrangement of an infinite set of points which describes the three-dimensional arrangement of constituent particles (atoms, ions or molecules) in space is called a crystal lattice or space lattice.

Unit Cell

- The smallest repeating unit of space lattice which when repeated over and over again in three-dimension, results into the whole of the space lattice of the crystal is called the unit cell.
- **Calculation of number of particles per unit cell :**
  Contribution of each atom present at the corner = 1/8
  Contribution of each atom present on the face = 1/2
  Contribution of each atom present on the edge centre = 1/4
  Contribution of each atom present at the body centre = 1

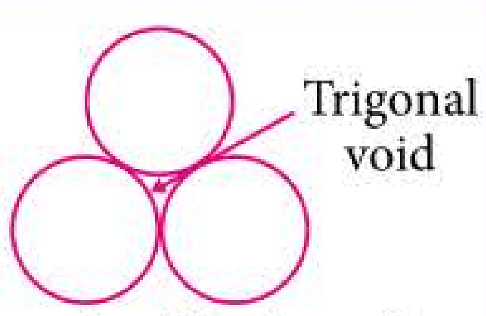
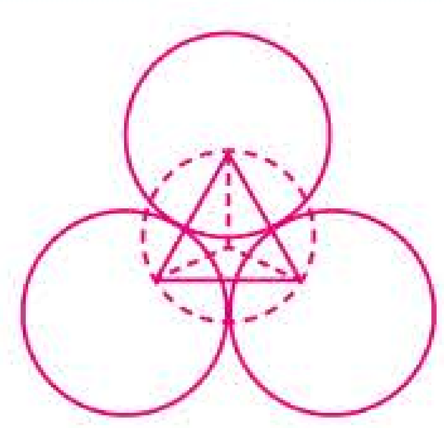
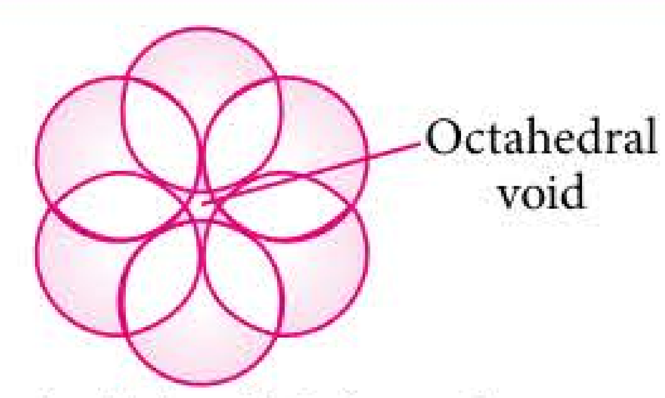
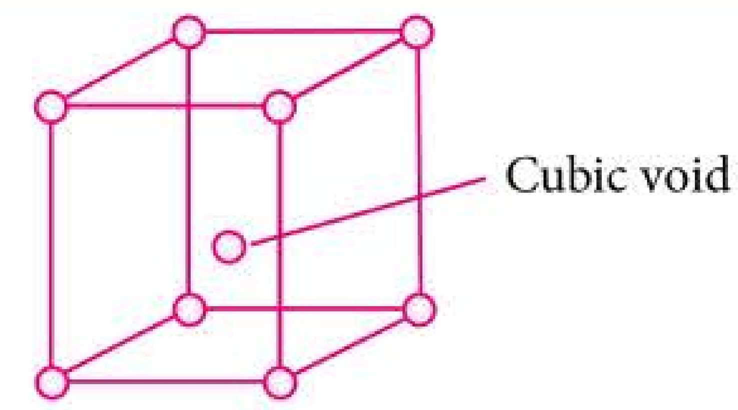
Characteristics of Different Types of Unit Cells

Characteristics	*sc*	*bcc*	*fcc*	*hcp*
Number of Atoms per unit cell	1	2	4	6
Coordination number	6	8	12	12
Packing efficiency	52%	68%	74%	74%
Radius (r)	$\frac{a}{2}$	$\frac{\sqrt{3}}{4}a$	$\frac{a}{2\sqrt{2}}$	$\frac{a}{2}$

SEVEN TYPES OF CRYSTAL SYSTEMS

Crystal systems	Axial distances or edge lengths	Axial angles	Examples
Cubic (most symmetrical)	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Cu, Zinc blende, KCl, NaCl
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Sn(White tin), SnO_2, TiO_2, $CaSO_4$
Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°; \beta \neq 90°$	Monoclinic sulphur, $Na_2SO_4 \cdot 10H_2O$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°; \gamma = 120°$	Graphite, ZnO, CdS
Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$CaCO_3$ (Calcite), HgS (Cinnabar)
Triclinic (most unsymmetrical)	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, H_3BO_3

INTERSTITIAL SITES IN CLOSED PACKED STRUCTURES

Trigonal Void	Tetrahedral Void	Octahedral Void	Cubic Void
 Trigonal void is formed at the centre of three spheres	 Tetrahedral void is formed by covering trigonal voids	 Octahedral void is formed at the centre of six spheres	
$r = 0.155\ R$	$r = 0.225\ R$	$r = 0.414\ R$	$r = 0.732\ R$
where r = radius of void, R = Radius of closely packed spheres			

CALCULATION INVOLVING UNIT CELL DIMENSIONS

Radius Ratio

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}} = \frac{r_+}{r_-}$$

Packing Fraction

$$f = \frac{\text{Number of spheres/unit cell } (Z) \times \text{Volume of one spheres in the unit cell}}{\text{Volume of the unit cell } (V)} = \frac{Z \times \frac{4}{3}\pi r^3}{a^3}$$

Density

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

where, Z = no. of atoms/unit cell,
M = atomic mass of the element,
a = edge length of the unit cell,
N_A = Avogadro's number

Limiting Radius Ratio, Coordination Number and Geometry

r_+/r_-	C. No.	Geometry
< 0.155	2	Linear
0.155 - 0.225	3	Plane triangular
0.225 - 0.414	4	Tetrahedral
0.414 - 0.732	6	Octahedral
0.732 - 1.000	8	Cubic (body centred)

Defects in Solids

Imperfections/Defects in Solids

- **Point defects**
  Deviations from ideal arrangement around a point or an atom.
  - **Stoichiometric/Intrinsic/Thermodynamic defects**
    Do not disturb stoichiometry of solid.
    - **Vacancy defect :** Arises when lattice sites are vacant. Decreases density, shown by non-ionic solids.
    - **Interstitial defect :** Arises when constituent particles occupy interstitial site. Increases density, shown by non-ionic solids.
    - **Frenkel defect :** Smaller ion (usually cation) dislocates from its normal site to an interstitial site. Does not change density, shown by ionic solids, *e.g.*, ZnS, AgCl, AgBr, AgI, etc.
    - **Schottky defect :** Arises when equal number of cations and anions are missing. Decreases density, shown by ionic solids, *e.g.*, NaCl, KCl, CsCl, AgBr, etc.
  - **Impurity defects**
    Arise when foreign atoms are present at lattice site *e.g.*, $SrCl_2$, $CdCl_2$, AgCl etc.
  - **Non-stoichiometric defects**
    Disturb stoichiometry of solids.
    - **Metal excess defect**
      - **Due to anionic vacancies**
        A negative ion is missing from its lattice site, leaving a 'hole' which is occupied by an electron to maintain electrical neutrality, *e.g.*, LiCl, NaCl.
      - **Due to the presence of extra cations**
        Usually arises when metal oxides are heated, *e.g.*, ZnO.
    - **Metal deficiency defect**
      Arises when metal shows variable valency *e.g.*, Fe^{2+}, Fe^{3+}.
- **Line defects**
  Deviations from ideal arrangement in entire rows of lattice points.

SOLUTIONS

- Solutions are homogeneous mixtures of two or more than two components.
- Homogeneous mixture means all the components are uniformly distributed throughout the solution.
- A binary solution is composed of two components. Solution may also be known as ternary and quaternary when it is made up of three and four components respectively.

Different Types of Binary Solutions

Solute	Solvent	Solution	Example
Solid	Solid	Solid	Certain alloys
Liquid	Solid	Solid	Hg in Ag
Gas	Solid	Solid	H_2/Pd
Solid	Liquid	Liquid	Sugar in water
Liquid	Liquid	Liquid	Benzene + Toluene
Gas	Liquid	Liquid	O_2 in water
Solid	Gas	Gas	Carbon in air (smoke)
Liquid	Gas	Gas	Fog
Gas	Gas	Gas	Air

Concentration Terms

Name	Symbol	Formula
Mass percentage	%(*w*/*w*)	$\frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100$
Mass by volume percentage	% (*w*/*v*)	$\frac{\text{Mass of solute}}{\text{Total volume of solution (mL)}} \times 100$
Volume percentage	%(*v*/*v*)	$\frac{\text{Volume of solute}}{\text{Total volume of solution}} \times 100$

Parts per million	ppm	$\frac{\text{No. of parts of solute}}{\text{Total no. of parts of all components of solution}} \times 10^6$
Mole fraction	x	$x_A = \frac{n_A}{n_A + n_B}$
Molarity	M	$\frac{\text{Moles of solute}}{\text{Volume of solution in L } (dm^3)}$
Molality	m	$\frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$

Solubility

The maximum amount of solute that can be dissolved in a specified amount of solvent at a specified temperature.

Solubility of a gas in liquid (Henry's law): The mass of a gas dissolved in a given volume of the liquid at constant temperature is directly proportional to the pressure of the gas present in equilibrium with the liquid.

$m = K_H P$

Factors affecting solubility of a solid in liquid

- **Nature of solute and solvent**
  Polar solutes dissolve in polar solvents and non-polar solutes in non-polar solvents.
- **Temperature**
  If the dissolution process is endothermic, solubility increases with rise in temperature. If dissolution process is exothermic, solubility decreases with rise in temperature.
- **Pressure**
  Pressure does not have any significant effect on solubility of solids in liquids as these are highly incompressible.

Ideal Solutions

The solutions which obey Raoult's law at all temperatures and concentrations are called ideal solutions.

Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution *i.e.*, $p_1 = p_1^\circ x_1$ and $p_2 = p^\circ_2 x_2$, where p_1° and p_2° are vapour pressures of pure components 1 and 2 respectively, at the same temperature.

In ideal solution, for a binary solution of components A and B, $A—B$ interactions are equal to $A—A$ and $B—B$ interactions.

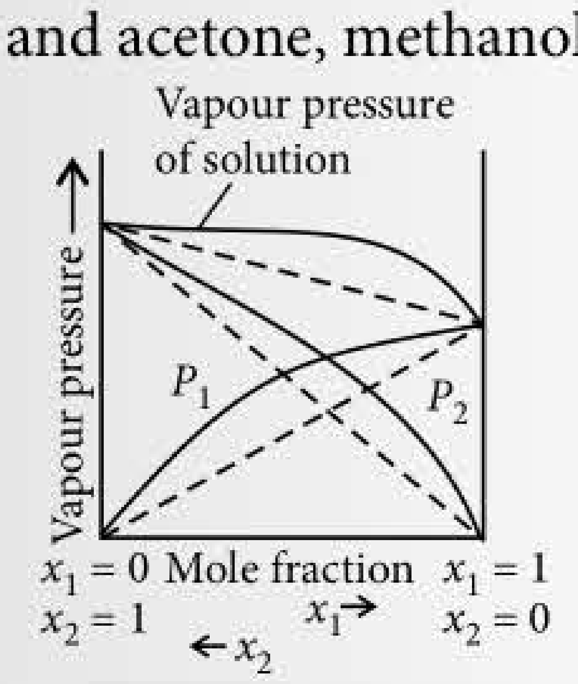
$\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$

Non-ideal Solutions

- Do not obey Raoult's law at all temperatures and concentrations.
- $p_1 \neq x_1 p_1^\circ$; $p_2 \neq x_2 p_2^\circ$; $\Delta H_{mix} \neq 0$ and $\Delta V_{mix} \neq 0$
- $A - B$ interactions $\neq A - A$ and $B - B$ interactions.
- Form azeotropes.

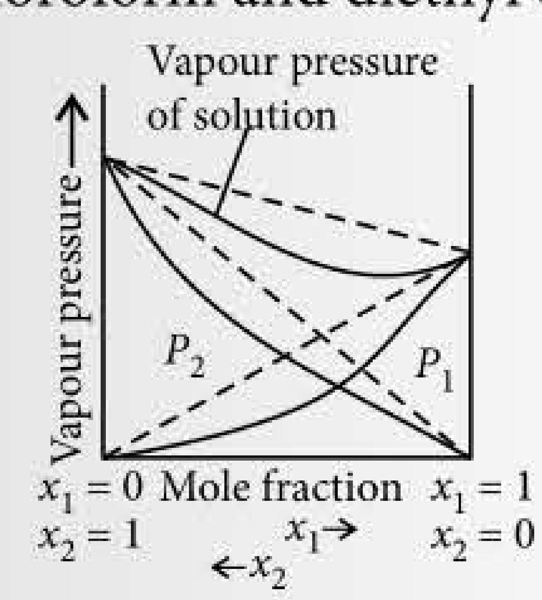
Solutions Showing Positive Deviation

- $A - B << A - A$ or $B - B$ interactions
- $\Delta H_{mix} > 0$, $\Delta V_{mix} > 0$; $p_i > p_i^\circ x_i$
- Form minimum boiling azeotropes
- Examples : Ethanol and acetone, carbon disulphide and acetone, methanol and water, etc.



Solutions Showing Negative Deviation

- $A - B >> A - A$ or $B - B$ interactions
- $\Delta H_{mix} < 0$, $\Delta V_{mix} < 0$; $p_i < p_i^\circ x_i$
- Form maximum boiling azeotropes
- Examples : Phenol and aniline, chloroform and acetone, chloroform and diethyl ether, etc.



Colligative Properties

The properties which depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution.

Elevation in Boiling Point :

$\Delta T_b = T_b - T_b^\circ \propto m = K_b m$

$\Delta T_b = K_b\left(\dfrac{W_B \times 1000}{M_B \times W_A}\right) \Rightarrow M_B = \dfrac{1000 \times W_B \times K_b}{\Delta T_b \times W_A}$

K_b is called boiling point elevation constant or molal elevation constant or Ebullioscopic constant, having unit K kg mol^{-1}.

Relative lowering of Vapour Pressure :

$\dfrac{p_A^\circ - p_A}{p_A^\circ} = x_B = \dfrac{n_B}{n_A + n_B} = \dfrac{n_B}{n_A} = \dfrac{W_B \times M_A}{M_B \times W_A}$

($\because$ for dilute solutions, $n_B << n_A$)

Depression in Freezing Point :

$\Delta T_f = T_f^\circ - T_f \propto m = K_f m$

$\Delta T_f = K_f\left(\dfrac{W_B \times 1000}{M_B \times W_A}\right)$

$\Rightarrow M_B = \dfrac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$

K_f is known as freezing point depression constant or molal depression constant or Cryoscopic constant, having unit K kg mol^{-1}.

Osmosis and Osmotic Pressure :

$\pi = CRT = \left(\dfrac{n_B}{V}\right)RT$,

$\pi V = \dfrac{W_B RT}{M_B}$ or $M_B = \dfrac{W_B RT}{\pi V}$

van't Hoff Factor

- $i = \dfrac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$
- $= \dfrac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$
- $i = \dfrac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$

  For association, $i < 1$; For dissociation, $i > 1$

- **Relation between van't Hoff factor and degree of dissociation :** $\alpha = \dfrac{i-1}{n-1}$
- **Relation between van't Hoff factor and degree of association :** $\alpha = \dfrac{1-i}{1-1/n}$
- **Modified equations for colligative properties :**

  $\dfrac{p_A^\circ - p_A}{p_A^\circ} = i \cdot \dfrac{n_B}{n_A}$,

  $\Delta T_b = iK_b\, m$, $\Delta T_f = iK_f m$, $\pi = i\, n_B RT/V$

SPEED PRACTICE

1. A hard, crystalline solid with a high melting point does not conduct electricity in any phase. This solid is most likely
   (a) an ionic solid
   (b) a metallic solid
   (c) a molecular solid
   (d) a network covalent solid.

2. Which of the following options does not represent concentration of semi-molal aqueous solution of NaOH having $d_{\text{solution}} = 1.02$ g/mL?
   (a) Molarity $= \dfrac{1}{2}$ M (b) $X_{\text{NaOH}} = \dfrac{9}{1009}$
   (c) % w/w = 10% (d) % w/v = 2%

3. The crystal system of a compound with unit cell dimensions a = 0.387 nm, b= 0.387 nm and c = 0.504 nm and $\alpha = \beta = 90°$ and $\gamma = 120°$ is
   (a) cubic (b) hexagonal
   (c) orthorhombic (d) rhombohedral.