CLASS-XII

BRUSH UP for NEET/JEE 2021

Brush up your concepts 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

- The *solid state* represents the physical state of matter in which constituents have no translatory motion although vibratory or rotational motions are possible about their position in solid lattice.

CLASSIFICATION OF SOLIDS

Solids	
Crystalline solids	**Amorphous solids**
Ordered arrangement of particles	Irregular arrangement of particles
Long range order	Short range order
Anisotropic	Isotropic
Sharp melting point	Melt over a range of temperature

TYPES OF CRYSTALLINE SOLIDS

Ionic solids	**Constituent particles :** Ions of opposite charge	**Binding forces :** Electrostatic forces
Covalent solids	**Constituent particles :** Atoms	**Binding forces :** Covalent bonds
Molecular solids	**Constituent particles :** Molecules	**Binding forces :** van der Waals forces
Metallic solids	**Constituent particles :** Kernels and electrons	**Binding forces :** Metallic bonds

BRAGG'S LAW

- When a beam of X-rays of wavelength λ, strikes a crystal surface, the maximum intensity of reflected rays occur when

$$\sin\theta = \frac{n\lambda}{2d} \quad \text{or} \quad n\lambda = 2d\sin\theta \qquad \text{(Bragg's equation)}$$

It helps in the determination of crystal structure.

CRYSTAL SYSTEMS AND BRAVAIS LATTICES

- On the basis of primitives or axial distances and interfacial angles of a unit cell, there are seven crystal systems and fourteen Bravais lattices.

Crystal systems	Unit cell dimensions and angles	Bravais lattices	Examples
Cubic (most symmetrical)	$a = b = c; \alpha = \beta = \gamma = 90°$	Primitive, Body centred, Face centred	Cu, Zinc blende, KCl, NaCl
Orthorhombic	$a \neq b \neq c; \alpha = \beta = \gamma = 90°$	Primitive, Body centred, End centred, Face centred	Rhombic sulphur, KNO_3, $BaSO_4$
Tetragonal	$a = b \neq c; \alpha = \beta = \gamma = 90°$	Primitive, Body centred	Sn(White tin), SnO_2, TiO_2, $CaSO_4$
Monoclinic	$a \neq b \neq c; \alpha = \gamma = 90° \neq \beta$	Primitive, End centred	Monoclinic sulphur, $PbCrO_4$, $Na_2SO_4 . 10H_2O$
Rhombohedral	$a = b = c; \alpha = \beta = \gamma \neq 90°$	Primitive	$CaCO_3$ (Calcite), HgS (Cinnabar)
Triclinic (most unsymmetrical)	$a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90°$	Primitive	$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$, H_3BO_3
Hexagonal	$a = b \neq c; \alpha = \beta = 90°; \gamma = 120°$	Primitive	Graphite, ZnO, CdS

PACKING IN SOLIDS

Simple cubic packing

- No. of particles (Z) = 1
- *AAA* … type arrangement
- Packing efficiency = 52.4%
- C.No. = 6

Body centred cubic packing

- No. of particles (Z) = 2
- Slightly open square close packing in first layer. In second layer, spheres are on the top of hollows. Third layer is exactly over the first layer and so on.
- Packing efficiency = 68%
- C.No. = 8

Face centred cubic packing

- No. of particles (Z) = 4
- *ABCABC* … type arrangement
- Packing efficiency = 74%
- C.No. = 12

Hexagonal close packing

- No. of particles (Z) = 6
- *ABAB* … type arrangement
- Packing efficiency = 74%
- C.No. = 12

VOIDS

- If N is the number of close packed spheres, then
  - number of octahedral voids generated = N
  - number of tetrahedral voids generated = $2N$
- In *ccp* or *fcc*, total no. of voids per unit cell = 12
- In *hcp*, total no. of voids per unit cell = 18

CALCULATIONS INVOLVING UNIT CELL PARAMETERS

$$\text{Density of unit cell } (\rho) = \frac{Z \times M}{N_0 \times a^3}$$

LIMITING RADIUS RATIO, COORDINATION NUMBER AND GEOMETRY

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

IMPERFECTIONS 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 solids.
    - **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 sites *e.g.*, $SrCl_2$ in NaCl, $CdCl_2$ in 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 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.

ELECTRICAL PROPERTIES

Electrical Properties

- **Conductors**
  Conductivity range : 10^4 to 10^7 ohm^{-1} m^{-1}
- **Insulators**
  Conductivity range : 10^{-20} to 10^{-10} ohm^{-1} m^{-1}
- **Semiconductors**
  Conductivity range : 10^{-6} to 10^4 ohm^{-1} m^{-1}
  - ***n*-type semiconductors :** Group 14 element like Si or Ge doped with group 15 element like P or As etc., free electrons increase conductivity.
  - ***p*-type semiconductors :** Group 14 element like Si or Ge doped with group 13 element like B, Al or Ga, holes increase conductivity.

MAGNETIC PROPERTIES

Magnetic Properties

Paramagnetic	Diamagnetic	Ferromagnetic	Ferrimagnetic	Antiferromagnetic
Contains atleast one unpaired electron in the orbital thus, weakly attracted by the magnetic field *e.g.*, O_2, Cu^{2+}.	All electrons are paired and orbitals are completely filled thus, weakly repelled by the magnetic field. *e.g.*, NaCl, H_2O.	Unpaired electrons in same direction thus, strongly attracted by the magnetic fields and can be permanently magnetised. *e.g.*, Ni.	Unequal no. of parallel and anti-parallel arrangement of magnetic moments thus, have small net magnetic moment *e.g.*, Fe_3O_4.	Equal number of domains in opposite direction thus, no net magnetic moment. *e.g.*, MnO.

DIELECTRIC PROPERTIES

Dielectrical Properties

Piezoelectricity : The electricity produced when mechanical stress is applied on polar crystals *e.g.*, $PbZrO_3$, $NH_4H_2PO_4$ and quartz.

Pyroelectricity : The electricity produced when some polar crystals are heated. *e.g.*, Crystals of tartaric acid.

Ferroelectricity : In some piezoelectric crystals, the dipoles are permanently polarized even in the absence of electric field. However, on applying electric field, the direction of polarization changes. *e.g.*, $BaTiO_3$, KH_2PO_4, Rochelle salt.

Anti-ferroelectricity : In some piezoelectric crystals, the dipoles in alternate polyhedra point up and down so, that the crystal does not possess any net dipole moment. *e.g.*, $PbZrO_3$.

INFOSHOTS

Hardest amorphous substance that disappears on reducing pressure!

At high temperature of above 700 K and under extremely high pressure (10^5 - 10^6 atm) CO_2 forms a 'silica like solid' named, Carbonia (Greenhouse glass). Though it is hardest amorphous solid but interesting thing is that it disappears when pressure is reduced because CO_2 is not stable in solid state, under ordinary pressure.

Solutions

SOLUTION AND ITS TYPES

- *Solution* is a perfectly homogeneous mixture (having number of phases equal to one) of two or more components.
- **Different Types of Binary Solutions**

S.No.	Solute	Solvent	Example
1.	Solid	Solid	Alloy
2.	Solid	Liquid	Sugar solution in water
3.	Solid	Gas	Iodine vapours in air
4.	Liquid	Solid	Hydrated salt
5.	Liquid	Liquid	Ethanol in water
6.	Liquid	Gas	Water vapours in air
7.	Gas	Solid	Dissolved gases in minerals
8.	Gas	Liquid	Aerated drinks
9.	Gas	Gas	Air

- *Solubility* of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature.
- **Factors affecting solubility of a solid in a liquid :**
  - **Nature of solute and solvent :** Polar solutes dissolve in polar solvents and non-polar solutes in non-polar solvents. (*i.e.*, like dissolves like).
  - **Effect of temperature :**
    - If the dissolution process is endothermic ($\Delta_{sol}H > 0$), the solubility increases with rise in temperature.
    - If dissolution process is exothermic ($\Delta_{sol}H < 0$) the solubility decreases with rise in temperature.
  - **Effect of pressure** : Pressure does not have any significant effect on solubility of solids in liquids as these are highly incompressible.
- **Factors affecting solubility of a gas in a liquid :**
  - **Effect of pressure :** Henry's law states that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution" $p = K_H x$.

    Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.
  - **Effect of temperature :** As dissolution is an exothermic process, then according to Le Chatelier's Principle, the solubility should decrease with increase of temperature.

METHODS FOR EXPRESSING CONCENTRATION OF SOLUTIONS

Mass percentage, $\left(\frac{w}{W}\right)\% = \frac{w_2}{(w_1+w_2)}\times 100$

Volume percentage, $\left(\frac{v}{V}\right)\% = \frac{V_2}{(V_1+V_2)}\times 100$

Mass by volume percentage, $\left(\frac{w}{V}\right)\% = \frac{w_2}{V_{\text{solution}}\text{(in mL)}}\times 100$

Strength (g L^{-1}) $= \frac{w_2\text{(in g)}}{V_{\text{solution}}\text{ (in mL)}}\times 1000$

Mass fraction, $\left(\frac{w}{W_{\text{total}}}\right) \Rightarrow x_1 = \frac{w_1}{w_1+w_2}$ or $x_2 = \frac{w_2}{w_1+w_2}$

Parts per million (ppm) $= \frac{w_2}{(w_1+w_2)}\times 10^6$

Molarity, (M) (mol L^{-1}) $= \frac{w_2\times 1000}{M_2\times V_{\text{solution}}\text{(in mL)}}$

Molality, (m) (mol kg^{-1}) $= \frac{w_2\times 1000}{M_2\times w_1\text{(in g)}}$

Normality, (N) (g-eq L^{-1}) $= \frac{w_2\times 1000}{E_2\times V_{\text{solution}}\text{(in mL)}}$

Demal, (D) $= \frac{w_2\times 1000}{M_2\times V_{\text{solution}}\text{(in mL)}}$ (at 0°C)

Mole fraction, (x) $\Rightarrow x_1 = \frac{n_1}{n_1+n_2}$ or $x_2 = \frac{n_2}{n_1+n_2}$, and $x_1 + x_2 = 1$

Formality, (F) $= \frac{\text{No. of gram formula mass of solute}}{\text{Volume of solution (in L)}}$

VAPOUR PRESSURE

- *Vapour pressure* is the pressure exerted by the vapours over the solution when it is in equilibrium state at a given temperature.

$$\log\frac{P_2}{P_1} = \frac{\Delta_{vap}H}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \quad \text{(Clausius–Clapeyron equation)}$$

where P_1 and P_2 are the vapour pressures at temperatures T_1 and T_2 respectively.

Factors affecting Vapour Pressure

- Weaker cohesive forces, higher vapour pressure
- Higher boiling point, lesser vapour pressure
- Solution of non-volatile solute, vapour pressure of solution decreases
- Solution of volatile solute, vapour pressure of solutions depends on escaping tendency of solute molecules

- *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 in the solution.

For component 1, $p_1 = p_1^\circ x_1$

For component 2, $p_2 = p_2^\circ x_2$

$$P_{\text{total}} = p_1 + p_2 = x_1 p_1^\circ + x_2 p_2^\circ = p_1^\circ + (p_2^\circ - p_1^\circ)x_2$$

where p_1° and p_2° are the vapour pressures of pure components 1 and 2 respectively.

VAN'T HOFF FACTOR

- It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

$$i = \frac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$$

$$i = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$$

$$i = \frac{\begin{array}{c}\text{Total number of moles of particles}\\ \text{after association / dissociation}\end{array}}{\begin{array}{c}\text{Total number of moles of particles}\\ \text{before association / dissociation}\end{array}}$$

$$\alpha_{\text{dissociation}} = \frac{i-1}{n-1}$$

$$\alpha_{\text{association}} = \frac{1-i}{1-\frac{1}{n}}$$

- For substances undergoing association or dissociation in the solution, the various expressions for the colligative properties are modified as follows :

$$\frac{p_1^\circ - p_1}{p_1^\circ} = ix_2; \qquad \Delta T_b = iK_b\, m$$

$$\Delta T_f = iK_f\, m; \qquad \pi = iCRT$$

INFO SHOTS

Forward Osmosis - The future process of desalination!

Reverse osmosis (RO) process is generally employed in our domestic water purifiers for desalination of water but recently, scientists are interesting to employ forward osmosis (FO) process for desalination as it requires low energy and wastage of water is also less.

WRAP it up!

1. In the ionic compound AB the ratio $r_{A^+} : r_{B^-}$ is 0.414. Which of the following statements is correct ?
   (a) Cations form close packing and anions exactly fit into the octahedral voids.
   (b) Anions form close packing and cations occupy precisely half of the tetrahedral voids.
   (c) Anions form close packing and cations occupy precisely all the octahedral voids.
   (d) Anions form close packing and cations fit into the octahedral voids loosely.

2. Two solutions of KNO_3 and CH_3COOH are prepared separately. Molarity of both is 0.1 M and osmotic pressures are p_1 and p_2 respectively. The correct relationship between the osmotic pressures is
   (a) $p_1 = p_2$
   (b) $p_1 > p_2$
   (c) $p_2 > p_1$
   (d) $\frac{p_1}{p_1 + p_2} \neq \frac{p_2}{p_1 + p_2}$

3. Which method cannot be used to find out the molecular weight of non-volatile solute?
   (a) Victor Meyer's method
   (b) Osmotic pressure method
   (c) Cryoscopic method
   (d) Ebullioscopic method

4. A metal crystallizes in body-centred cubic structure. The correct statement amongst the following is
   (a) each atom touches 4 atoms in its own layer and 4 each in the layers immediately above and below it
   (b) each atom touches 6 atoms each in the layers immediately above and below it and none in its own layer
   (c) each atom touches 4 atoms each in the layers immediately above and below it and none in its own layer
   (d) each atom touches 8 atoms each in the layers immediately above and below it and none in its own layer.