ESSENTIAL CONCEPTS OF PHYSICAL CHEMISTRY

CONCEPT MAP

CLASS XII

Get well prepared for exams with quick revision of important concepts of physical chemistry.

Solid State

Packing efficiency

$$= \frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100$$

- Mass of the atoms of unit cell = Number of atoms in a unit cell (Z) × Mass of atom (M_{atom})
- Mass of one atom = $\frac{\text{Molar mass } (M)}{\text{Avogadro's constant } (N_A)}$
- Density (ρ) of unit cell of a cubic crystal = $\frac{ZM}{V \times N_A} = \frac{ZM}{a^3 N_A}$

- Bragg's equation : $2d \sin\theta = n\lambda$
- Number of octahedral voids = No. of particles present in the close packing
- Number of tetrahedral voids = 2 × No. of octahedral voids

Characteristics of Different Types of Unit Cells

Crystal	No. of atom(s)/ unit cell	Packing efficiency	C.No.	Relation in d, a and r
scc	1	52.4%	6	$r = d/2 = a/2$
bcc	2	68%	8	$r = d/2 = \sqrt{3}a/4$
fcc	4	74%	12	$r = d/2 = a/2\sqrt{2}$

Void	Radius Ratio
Triangular	$0.155 \le r^+/r^- < 0.225$
Tetrahedral	$0.225 \le r^+/r^- < 0.414$
Octahedral	$0.414 \le r^+/r^- < 0.732$
Body centred cubic	$0.732 \le r^+/r^- < 1$

Solids on the Basis of Electrical Properties

- **Conductors :** Electrical conductivity, 10^4 to 10^7 ohm^{-1} m^{-1}
- **Insulators :** Electrical conductivity, 10^{-20} to 10^{-10} ohm^{-1} m^{-1}
- **Semiconductors :** Electrical conductivity, 10^{-6} to 10^4 ohm^{-1} m^{-1}
  - ***n*-type semiconductors :** Group 14 elements doped with group 15 elements, free electrons increase conductivity.
  - ***p*-type semiconductors :** Group 14 elements doped with group 13 elements, holes increase conductivity.

Solutions

- Molality (m) = $\frac{M}{\rho - \frac{MM_2}{1000}}$
- Molarity (M) = $\frac{n_1}{(n_1M_1 + n_2M_2)/\rho}$

- **Henry's law :** $p_A = K_H x_A$; K_H increases with increase of temperature implying that solubility decreases with increase of temperature at the same pressure.
- **Raoult's law :** $p_1 = p_1^\circ x_1$, this law is applicable only if the two components form a homogeneous mixture.
- **Dalton's law of partial pressure :** $p_{total} = p_1 + p_2 + ... p_n$ and for two components system, $p_{total} = p_1^\circ + (p_2^\circ - p_1^\circ)x_2$

Ideal and Non-ideal Solutions

Ideal Solutions	Non-ideal Solutions
$p_1 = x_1p_1^\circ$; $p_2 = x_2p_2^\circ$ $\Delta H_{mix} = 0$, $\Delta V_{mix} = 0$ $A - B$ interactions = $A - A$ and $B - B$ interactions.	$p_1 \ne x_1p_1^\circ$; $p_2 \ne x_2p_2^\circ$ $\Delta H_{mix} \ne 0$, $\Delta V_{mix} \ne 0$ $A - B$ interactions ≠ $A - A$ and $B - B$ interactions.

Non-ideal Solutions Showing Positive and Negative Deviations from Raoult's Law

Solutions showing positive deviation	Solutions showing negative deviation
$A - B$ << $A - A$ or $B - B$ interactions. $\Delta H_{mix} > 0$, $\Delta V_{mix} > 0$ $p_1 > p_1^\circ x_1$	$A - B$ >> $A - A$ or $B - B$ interactions. $\Delta H_{mix} < 0$, $\Delta V_{mix} < 0$ $p_1 < p_1^\circ x_1$

Colligative Properties

- Relative lowering of vapour pressure : $(p_A^\circ - p_A)/p_A^\circ = x_B$
- Elevation in boiling point : $\Delta T_b = T_b - T_b^\circ = K_b m$
- Depression in freezing point : $\Delta T_f = T_f^\circ - T_f = K_f m$
- Osmotic pressure : $\pi = CRT = (n/V)RT$

van't Hoff Factor and Its Significance

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

- **For association of solute :** $nA \rightarrow (A)_n$
  Degree of association (α) = $(1 - i)\, n/(n - 1)$; $i < 1$
- **For dissociation of solute :** $(A)_n \rightarrow nA$
  Degree of dissociation (α) = $(i - 1)/(n - 1)$; $i > 1$
- **Modified colligative properties :**
  $(p_A^\circ - p_A)/p_A^\circ = i x_B$; $\Delta T_b = iK_b m$, $\Delta T_f = iK_f m$, $\pi = iCRT$