Question Set 9

DERIVATIONS

Q. Answer the following : ***(2 or 3 marks each)***

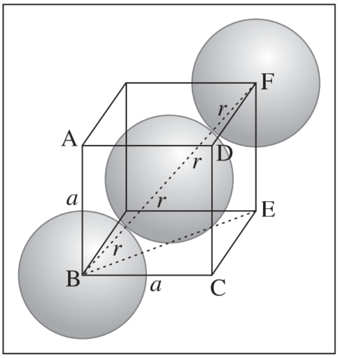
[**Note :** Derive the required equations involving various important steps. Explain briefly the terms involved.]

Chapter 1. Solid State

Q. 1. Obtain a relation between radius of an atom and edge length in the Body-centred cubic crystal.

Ans. Body-centred cubic (bcc) structure : In this unit cell, 8 atoms are present at 8 corners and 1 additional atom is present at the body centre.

The atoms are in contact along the body diagonal BF. Let a be the edge length and r the radius of an atom.



bcc structure

Consider a triangle BCE.

$BE^2 = BC^2 + CE^2 = a^2 + a^2 = 2a^2$

Consider triangle BEF.

$BF^2 = BE^2 + EF^2 = 2a^2 + a^2 = 3a^2$

$\therefore\ BF = \sqrt{3}a.$

From figure, $BF = 4r$

$\therefore\ 4r = \sqrt{3}a$

$\therefore\ r = \frac{\sqrt{3}}{4}a.$

Q. 2. Obtain the relationship between density of a substance and the edge length of unit cell.

Ans. (1) Consider a cubic unit cell of edge length *'a'*.

$\therefore$ the volume of unit cell $= a^3$

(2) If there are 'n' particles per unit cell and the mass of particle is 'm', then

Mass of unit cell $= m \times n$.

(3) If the density of the unit cell of the substance is ρ then,

$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$\therefore \ \rho = \frac{m \times n}{a^3}.$$

Chapter 2. Solutions

Q. 3. Using Raoult's law, how will you show that $\Delta P = P_1^0 x_2$ where x_2 is the mole fraction of solute in the solution and P_1^0 is vapour pressure of a pure solvent.

Ans. If x_1 and x_2 are the mole fractions of solvent and solute respectively, then

$x_1 + x_2$

By Raoult's law,

$P = x_1 \times P_0$

where P_0 is the vapour pressure of a pure solvent and P is the vapour pressure of the solution at given temperature.

$$\therefore \ \frac{P}{P_0} = x_1$$

$$1 - \frac{P}{P_0} = 1 - x_1$$

$$\therefore \ \frac{P_0 - P}{P_0} = x_2$$

If $P_0 - P = \Delta P$

then $\dfrac{\Delta P}{P_0} = x_2.$

Q. 4. Derive the relation between molar mass of the solute and boiling point elevation.

Ans. The boiling point elevation, ΔT_b of a solution is directly proportional to molality (m) of the solution.

$\therefore \ \Delta T_b \propto m$

$\therefore \ \Delta T_b = K_b \, m$

where K_b is a proportionality constant

If $m = 1$ molal, then $\Delta T_b = K_b$

where K_b is called molal elevation constant.

The molality of the solution is given by

$$m = \frac{\text{Number of moles of the solute}}{\text{Weight of the solvent in kg}}$$

Let W_1 = Weight (in gram) of a solvent

W_2 = Weight (in gram) of a solute

M_2 = Molecular weight of the solute

Then the molality (m) of the solution is given by

$$m = \frac{W_2 \times 1000}{W_1 M_2} = \frac{W_2}{W_1 \times M_2} \text{ mol kg}^{-1}$$

$$\therefore \Delta T_b = K_b \times \frac{W_2 \times 1000}{W_1 M_2}$$

$$\therefore M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

$$OR \; M_2 = \frac{K_b \times W_2}{\Delta T_b \times W_1}.$$

Q. 5. Obtain the relationship between freezing point depression of a solution containing nonvolatile nonelectrolyte and its molar mass.

Ans. The freezing point depression, ΔT_f of a solution is directly proportional to molality (m) of the solution.

$$\therefore \Delta T_f \propto m \qquad \therefore \Delta T_f = K_f m$$

where K_f is a molal depression constant.

The molality of a solution is given by

$$m = \frac{\text{Number of moles of the solute}}{\text{Weight of the solvent in kg}}$$

If W_1 grams of a solvent contain W_2 grams of a solute of the molar mass M_2, then the molality m of the solution is given by,

$$m = \frac{W_2 \times 1000}{W_1 M_2} = \frac{W_2}{W_1 \times M_2} \text{ mol kg}^{-1}$$

$$\therefore \Delta T_f = K_f \times \frac{W_2 \times 1000}{W_1 M_2}.$$

Chapter 3. Ionic Equilibria

Q. 6. Derive the relationship between degree of dissociation and dissociation constant for a weak electrolyte. *OR*

Derive the expression of Ostwald's dilution law in the case of a weak electrolyte.

Ans. Expression of Ostwald's dilution law in the case of a weak electrolyte : Consider the dissociation of a weak electrolyte BA. Let V dm^3 of a solution contain one mole of the electrolyte. Then the concentration of a solution is, $C=\frac{1}{V}$ mol dm^{-3}. Let α be the degree of dissociation of the electrolyte.

	BA	$\rightleftharpoons B^+$	$+ A^-$
Initial moles :	1	0	0
Moles at equilibrium :	$(1-\alpha)$	α	α
Concentration at equilibrium (mol dm^{-3}) :	$\frac{(1-\alpha)}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

Applying the law of mass action to this dissociation equilibrium, we have,

$$K=\frac{[B^+][A^-]}{[BA]}$$

$$\therefore\ K=\frac{\frac{\alpha}{V}\times\frac{\alpha}{V}}{\frac{(1-\alpha)}{V}}=\frac{\alpha^2}{(1-\alpha)V}$$

As the electrolyte is weak, α is very small as compared to unity

$\therefore\ (1-\alpha)\approx 1.$

$$\therefore\ K=\frac{\alpha^2}{V}\quad\therefore\ \alpha=\sqrt{KV}\quad\therefore\ \alpha\propto\sqrt{V}$$

$\frac{1}{V}=C$, where $C=$ concentration in mol dm^{-3}

$$\therefore\ K=\alpha^2 C\qquad\therefore\ \alpha=\sqrt{\frac{K}{C}}$$

$$\therefore\ \alpha=\sqrt{K\times V}$$

$$\because\ C=\frac{1}{V}\ \text{or}\ V=\frac{1}{C}$$

$$\alpha=\sqrt{\frac{K}{C}}$$

This is the expression of Ostwald's dilution law. Thus, the degree of dissociation of a weak electrolyte is directly proportional to the square root of the volume of the solution containing 1 mole of an electrolyte.

Q. 7. Derive Ostwald's dilution law for CH_3COOH.

Ans. Consider V dm^3 of a solution containing one mole of CH_3COOH. Then the concentration of acid is,

$C = \frac{1}{V}$ mol dm^3. Let α be the degree of dissociation of CH_3COOH.

	$CH_3COOH_{(aq)} \rightleftharpoons$	$CH_3COO^-_{(aq)}$	$+ H^+_{(aq)}$
Initial moles :	1	0	0
Moles at equilibrium :	$(1-\alpha)$	α	α
Concentration at equilibrium (mol dm^{-3}):	$\frac{(1-\alpha)}{V}$	$\frac{\alpha}{V}$	$\frac{\alpha}{V}$

If K_a is dissociation constant, then

$$K_a = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]} = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{(1-\alpha)}{V}} = \frac{\alpha^2}{(1-\alpha)V}$$

$\because\ C = \frac{1}{V}$ mol dm^3

$$\therefore\ K_a = \frac{C\alpha^2}{(1-\alpha)}$$

This is Ostwald's dilution law.

Q. 8. Derive the relationship between pH and pOH. *OR*

Derive the relation, pH + pOH = 14. ***(Sept. '21; March '22)***

Ans. The ionic product of water, K_w is given by

$K_w = [H_3O^+] \times [OH^-]$

At 298 K, $K_w = 1 \times 10^{-14}$

$\therefore\ pK_w = -\log_{10} K_w = -\log_{10} 1 \times 10^{-14} = 14$

$\because\ [H_3O^+] \times [OH^-] = 1 \times 10^{-14}$

Taking logarithm to base 10 of both sides

$\log_{10}[H_3O^+] + \log_{10}[OH^-] = \log_{10} 1 \times 10^{-14}$

Multiplying both the sides by -1

$-\log_{10}[H_3O^+] - \log_{10}[OH^-] = -\log_{10} 1 \times 10^{-14}$

$\because$ pH $= -\log_{10}[H_3O^+]$; pOH $= -\log_{10}[OH^-]$;

$pK_w = \log_{10} K_w$

$\therefore$ pH + pOH $= pK_w$

OR pH + pOH = 14.

Chapter 4. Chemical Thermodynamics

Q. 9. Derive the relation, $\Delta H = \Delta U + \Delta nRT$. *OR*

Obtain the relationship between ΔH and ΔU for gas phase reactions.

Ans. Consider a reaction in which n_1 moles of gaseous reactant in initial state change to n_2 moles of gaseous product in the final state.

Let H_1, U_1, P_1, V_1 and H_2, U_2, P_2, V_2 represent enthalpies, internal energies, pressures and volumes in the initial and final states respectively, then,

$$n_1 A_{(g)} \xrightarrow{T} n_2 B_{(g)}$$

H_1, U_1, P_1, V_1 $\qquad$ H_2, U_2, P_2, V_2

The heat of reaction is given by enthalpy change ΔH as

$\Delta H = H_2 - H_1$

By definition, $H = U + PV$

$\therefore H_1 = U_1 + P_1V_1$ and $H_2 = U_2 + P_2V_2$

$\because \Delta H = H_2 - H_1$

$\therefore \Delta H = (U_2 + P_2V_2) - (U_1 + P_1V_1) = (U_2 - U_1) + (P_2V_2 - P_1V_1)$

Now, $\Delta U = U_2 - U_1$

Since $PV = nRT$,

For initial state, $P_1V_1 = n_1RT$

For final state, $P_2V_2 = n_2RT$

$\therefore P_2V_2 - P_1V_1 = n_2RT - n_1RT = (n_2 - n_1)RT = \Delta nRT$

where $\Delta n = \begin{bmatrix} \text{Number of moles} \\ \text{of gaseous products} \end{bmatrix} - \begin{bmatrix} \text{Number of moles of} \\ \text{gaseous reactants} \end{bmatrix}$

$\therefore \Delta H = \Delta U + \Delta nRT.$

Q. 10. Derive the expression for maximum work.

Ans. Consider 'n' moles of an ideal gas enclosed in an ideal cylinder. Let V be the volume at temperature T and pressure P.

If in an infinitesimal change, pressure changes from P to $P-dP$ and volume increases from V to $V+dV$, then the work obtained is

$$dW = -(P-dP)\,dV = -PdV + dPdV$$

Since $dP \cdot dV$ is negligibly small relative to PdV,

$$dW = -PdV$$

Let the state of the system change from $A(P_1, V_1)$ to $B(P_2, V_2)$ isothermally and reversibly, at temperature T involving number of infinitesimal steps.

$$\underset{P_1,\ V_1}{A} \xrightarrow{T} \underset{P_2,\ V_2}{B}$$

Then the total work or maximum work in the process is obtained by integrating above equation.

$$W_{\max} = \int_A^B dW = \int_A^B -PdV$$

$$\because\ PV = nRT$$

$$\therefore\ P = \frac{nRT}{V}$$

$$W_{\max} = \int_{V_1}^{V_2} -nRT\ \frac{dV}{V} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= -nRT\,(\ln V_2 - \ln V_1) = -nRT \log_e \frac{V_2}{V_1}$$

$$\therefore\ W_{\max} = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$$

At constant temperature,

$$\because\ P_1 \times V_1 = P_2 \times V_2$$

$$\therefore\ \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\therefore\ W_{\max} = -2.303\ nRT \log_{10} \frac{P_1}{P_2}.$$

Q. 11. Obtain a relation between conductivity (κ) and molar conductivity ($\wedge_m$).

Ans. Conductivity or specific conductance (κ) is the conductance of 1 cm^3 of the solution in C.G.S. units, while molar conductivity is the conductance of a solution containing one mole of an electrolyte.

Consider C molar solution, i.e. C moles of an electrolyte present in 1 litre or 1000 cm^3 of the solution.

$\because$ C moles of an electrolyte are present in 1000 cm^3 solution.

$\therefore$ 1 mole of an electrolyte is present in $\frac{1000}{C}$ cm^3 solution,

Now

$\because$ conductance of 1 cm^3 of this solution is κ.

$\therefore$ conductance of $\frac{1000}{C}$ cm^3 of the solution is $\frac{\kappa \times 1000}{C}$.

This represents molar conductivity, $\wedge_m$.

$\therefore$ $\wedge_m = \frac{\kappa \times 1000}{C}\ \Omega^{-1}\ cm^2\ mol^{-1}$ (in C.G.S. units).

Q. 12. Obtain a relation between standard cell potential (or standard emf) and equilibrium constant of the cell reaction.

Ans. For any galvanic cell, the overall cell reaction at equilibrium can be represented as

Reactants $\rightleftharpoons$ Products.

[For example for Daniell cell

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}$]

The equilibrium constant, K for the reversible reaction will be

$$K = \frac{[\text{Products}]}{[\text{Reactants}]} \left(\text{E.g. for Daniell cell, } K = \frac{[Zn^{++}]}{[Cu^{++}]}\right)$$

The equilibrium constant is related to the standard free energy change $\Delta G°$, as follows :

$$\Delta G° = -RT\ln K$$

If E^0_{cell} is the standard cell potential (or emf) of the galvanic cell, then

$\Delta G^\circ = -nFE^0_{\text{cell}}$

By comparing above equations

$\Delta G^\circ = -nFE^0_{\text{cell}} = -RT\ln K$

$\therefore\ nFE^0_{\text{cell}} = RT\ln K$

$$\therefore\ E^0_{\text{cell}} = \frac{RT}{nF}\ln K$$

$$OR\quad E^0_{\text{cell}} = \frac{2.303\,RT}{nF}\log_{10} K$$

$$\text{At } 25^\circ\text{C},\quad E^0_{\text{cell}} = \frac{0.0592}{n}\log_{10} K$$

Chapter 6. Chemical Kinetics

Q. 13. Derive the expression for integrated rate law (equation) for the first order reaction. ***(Sept. '21)***

Ans. Consider the following first order reaction, $A \longrightarrow B$.

The rate of the chemical reaction is given by the rate law expression as

Rate, $R = k\,[A]$, where [A] is the concentration of the reactant A and k is the velocity constant or specific rate of the reaction.

The instantaneous rate is given by

$$R = k[A] = \frac{-d[A]}{dt}$$

$$\therefore\ \frac{-d[A]}{[A]} = k\cdot dt$$

If $[A_o]$ is the initial concentration of the reactant and $[A]_t$ at time t, then by integrating the above equation

$$-\int_{[A_0]}^{[A]_t} \frac{d[A]}{[A]} = k\int_0^t dt$$

$$\therefore\ -\log_e \frac{[A]_t}{[A_o]} = kt \qquad \therefore\ \log_e \frac{[A_o]}{[A]_t} = kt$$

$$\therefore\ k = \frac{1}{t}\log_e \frac{[A_o]}{[A]_t} \qquad \therefore\ k = \frac{2.303}{t}\log_{10}\frac{[A_o]}{[A]_t}.$$

This is the integrated rate equation for the first order reaction. This is also called integrated rate law.

Q. 14. Derive the expression for integrated rate law for zero order reaction A ⟶ Products.

Ans. Consider a zero order reaction A ⟶ Products

The rate of the reaction is

$$\text{Rate} = \frac{-d[\text{A}]}{dt}$$

By rate law,

$$\text{Rate} = k \times [\text{A}]^0 = k$$

$$\therefore \quad -d[\text{A}] = k \times dt$$

If $[\text{A}]_0$ is the initial concentration of the reactant A at $t = 0$ and $[\text{A}]_t$ is the concentration of A present after time t, then by integrating above equation

$$\int_{[\text{A}]_0}^{[\text{A}]_t} -d[\text{A}] = \int_{t=0}^{t=t} k\,dt$$

$$-\int_{[\text{A}]_0}^{[\text{A}]_t} d[\text{A}] = k\int_0^t dt$$

$$-[\text{A}]_{[\text{A}]_0}^{[\text{A}]_t} = k[t]_0^t$$

$$-\Big([\text{A}]_t - [\text{A}]_0\Big) = kt$$

$$\therefore \quad [\text{A}]_0 - [\text{A}]_t = kt$$

$$\therefore \quad k = \frac{[\text{A}]_0 - [\text{A}]_t}{t}$$

This is the integrated rate law expression for rate constant for zero order reaction.

Q. 15. Obtain an expression for half-life period of zero order reaction.

Ans. The rate law expression for zero order reaction is

$$[\text{A}]_t = -kt + [\text{A}]_0$$

where $[\mathrm{A}]_0$ and $[\mathrm{A}]_t$ are the concentrations of the reactant at time, $t = 0$ and after time t respectively.

Half-life period, $t_{1/2}$ is the time when the concentration reduces from $[\mathrm{A}]_0$ to $[\mathrm{A}]_0/2$, i.e. at $t = t_{1/2}$, $[\mathrm{A}]_t = [\mathrm{A}]_0/2$.

$$\therefore \frac{[\mathrm{A}]_0}{2} = -k t_{1/2} + [\mathrm{A}]_0$$

$$\therefore k t_{1/2} = [\mathrm{A}]_0 - \frac{[\mathrm{A}]_0}{2} = \frac{[\mathrm{A}]_0}{2}$$

$$\therefore t_{1/2} = \frac{[\mathrm{A}]_0}{2k}.$$

Hence for a zero order reaction, half-life period is directly proportional to the initial concentration of the reactant.

Q. 16. Derive the relation between the half-life period and rate constant of first order reaction. ***(March '22)***

Ans. Consider the following reaction

$$\mathrm{A} \longrightarrow \mathrm{B}$$

Concentration at time $t = 0$ — a — 0

Concentration at time $t = t$ — $(a - x)$ — x

If $[\mathrm{A}]_0$ and $[\mathrm{A}]_t$ are the concentrations of A at start and after time t, then $[\mathrm{A}]_0 = a$ and $[\mathrm{A}]_t = a - x$.

The velocity constant or the specific rate constant k for the first order reaction is represented as

$$k = \frac{2.303}{t} \log_{10} \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}$$

$$\therefore k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a - x} \right)$$

where, a is the initial concentration of the reactant A, x is the concentration of the product B after time t, so that $(a - x)$ is the concentration of the reactant A present after time t.

If $t_{1/2}$ is the half-life of a reaction, then at $t = t_{1/2}$, $x = a/2$, hence $a - x = a - a/2 = a/2$

$$\text{Now, } k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a - x} \right)$$

$$\therefore t = \frac{2.303}{k} \log_{10} \frac{a}{(a - x)}$$

Hence, $$t_{1/2} = \frac{2.303}{k} \log_{10} \frac{a}{a/2}$$

$$= \frac{2.303}{k} \log_{10} 2$$

$$= \frac{2.303 \times 0.3010}{k}$$

$$\therefore\ t_{1/2} = \frac{0.693}{k}.$$