2024

CHEMISTRY — HONOURS

Paper : DSCC-3

(Physical Chemistry - I)

Full Marks : 75

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question nos.*** **1, 2, 3 & 4** (compulsory) and ***any four*** from the rest (***question nos.*** **5** to **10**).

1. Answer ***any ten*** questions : 2×10

(a) Show that for an isothermal process undergone by an ideal gas, $\Delta G = \Delta A$.

(b) Define fugacity and fugacity coefficient.

(c) Derive the Nernst's distribution law.

(d) Draw graphs for conductometric titration mentioning proper axes, for the following dibasic acids, where in each case 0.1(N) acid is being titrated with 0.5(N) NaOH.

(i) Oxalic acid

(ii) Sulphuric acid.

(e) Find the condition for maximum value of buffer capacity.

(f) Draw T-S diagram of a Carnot cycle with proper labelling.

(g) Explain the concept of chemical potential as escaping tendency.

(h) Define advancement of a chemical reaction. Plot variation of free energy with advancement of the reaction indicating the state of equilibrium.

(i) State and explain the 'law of independent migration of ions'.

(j) "At high temperature the pH of pure water may deviate from 7.0." Justify or criticize.

(k) 'For any gas Cp is always greater than Cv.' — Explain qualitatively.

(l) Obtain the relation between molar conductance (Λ_m) and equivalent conductance (Λ_{eq}) for $Al_2(SO_4)_3$.

2. (a) Write short notes on the statements of 2nd law of thermodynamics covering the following points :

(i) Kelvin Planck and Clausius statements.

(ii) Equivalence of the two statements. 2+3

Or,

(b) Write short notes on Gibbs-Helmholtz equation covering the following points :

(i) Variation of G and $^{G}/_{T}$ with T (temperature)

(ii) Variation of $^{G}/_{T}$ with $^{1}/_{T}$. 3+2

3. (a) Write short notes on the effect of addition of an inert gas on the following equilibrium :

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) at constant pressure

(ii) at constant volume. 2½+2½

Or,

(b) Write short notes on change in Entropy(S) and Gibbs free energy (G) for mixing of two different ideal gases at a particular temperature. 3+2

4. (a) Write short notes on specific and equivalent conductance covering the following points.

(i) Definitions

(ii) Effect of dilution in case of strong electrolytes. 2+3

Or,

(b) Write short notes on buffer solutions covering the following points :

(i) Derivation of Henderson Equation

(ii) Explanation of buffer action in maintaining pH. 3+2

5. (a) Show that Joule-Thomson experiment is an isenthalpic process. Show that the inversion temperature for van der Waals gas is $T_i = {}^{2a}/_{Rb}$ (where a, b are van der Waals constants).

(b) For a reaction, K_p varies with T (temperature) as $\ln K_p = -1.04 - \frac{1088}{T} + \frac{1.51\times10^5}{T^2}$ (valid between 300K to 600K). Calculate ΔS° at 400K.

(c) The mean activity coefficient of a 1:2 type electrolyte (0.005M) is 0.75. Calculate Debye-Hückel constant using the limiting law. 4+3+3

6. (a) Derive an expression of pH for hydrolysis of a salt of weak acid and strong base.

(b) For partial molal properties, find the relation,

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}}.$$

(c) Find the ΔS (system) and ΔS (surr) for 3 moles of an ideal monoatomic gas expanding isothermally into vacuum at 298 K, expanding from a volume of 15L to 40L. 4+3+3

7. (a) At 25°C in a saturated solution of $BaSO_4$, Ba^{2+} and SO_4^{2-} ions take 151 and 121 seconds respectively to cover a distance of 1cm across which potential difference of 10 volts has been applied. The concentration solubility product of $BaSO_4$ at 25°C is 10^{-10} (concentration expressed in gm eqv./l). The conductance of the solution is 2.2×10^{-6}S in a cell in which the conductance of water is 0.8×10^{-6}S at 25°C. If at the same temperature and in the same cell, conductance of 0.01(N)KCl be 1.40×10^{-3}S, what would be the specific conductance of the KCl solution?

   (b) Does the equilibrium constant of a chemical reaction depend on :

   (i) Standard state chosen for the reactants and products?

   (ii) Stoichiometric representation of the reaction? Justify your answer.

   (c) State and prove Carnot's theorem. 4+3+3

8. (a) Starting from, Van't Hoff reaction isotherm, derive the Van't Hoff equation at constant pressure.

   (b) Define partial molal free energy (μ_i). Show that $\bar{V}_i = \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_{j\neq i}}$.

   (c) What should be the essential condition for a compound to be able to serve as an acid-base indicator? Find out the range of such an indicator. 4+3+3

9. (a) Show that for any reversible cycle (not necessarily a Carnot cycle), $\oint \frac{dQ_{rev}}{T} = 0$.

   (b) State four different thermodynamic criteria for equilibrium and spontaneity.

   (c) State Ostwald's dilution law. Find the relation $\frac{1}{\lambda} = \frac{1}{\lambda_o} + \frac{\lambda c}{k_a \lambda_o^{\,2}}$ for a dilute solution of weak acid (where all the terms have their usual significance). 4+3+3

10. (a) A Carnot engine works between 600K and 300K using 5 moles of an ideal gas as thermodynamic substance. Calculate :

   (i) Efficiency of the engine

   (ii) Work done by the gas during adiabatic reversible expansion

   (iii) Quantity of heat released to the sink when the engine absorbs 1000 kcal heat from the source [given $C_v = 5\text{cal K}^{-1}\text{mol}^{-1}$.]

   (b) How hydrolysis constant of a salt can be determined conductometrically?

   (c) Derive the working formula for determination of transport number of an ion using moving boundary method. 4+3+3
