

2025

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) Can an engine operate by absorbing heat from only one reservoir and converting it entirely into work? Explain.
- (b) How can you differentiate between reversible and irreversible processes using Clausius inequality?
- (c) Show that, at constant temperature, the maximum work obtainable from a system is equal to the decrease in Helmholtz free energy, i.e., $W_{max} = -(\Delta A)_T$.
- (d) Explain the abnormal transport number of Cd^{2+} ion in concentrated cadmium iodide solution.
- (e) Write Walden's rule and explain what it indicates about ionic mobility.
- (f) For $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, by what factor would the value of K_p change if the standard state were taken to be 0.5 bar instead of 1.0 bar?
- (g) Chemical potential of a gas is expressed as $\mu = \mu^0 + RT \ln f$. Comment on pressure and temperature dependence of μ and μ^0 (Terms have their usual significance).
- (h) Using the Debye-Hückel limiting law, compare the effect of ionic charge on the activity coefficients of electrolytes such as NaCl, CaCl_2 and MgSO_4 in dilute aqueous solutions of same ionic strength.
 - (i) Explain why ionic conductance of Lithium ion is less than that of the Potassium ion.
 - (j) Express activity of ZnCl_2 in terms of molality and mean ionic activity coefficient.
- (k) "An endothermic process with $\Delta S = -ve$ is thermodynamically impossible."— Justify or criticize.
- (l) The ionic strength of 0.1(N) CH_3COOH solution is 0.001 at 20°C. Calculate the pH of the solution.

Please Turn Over

(4851)

2. (a) Write short notes on Gibbs-Duhem equation covering the following points :

(i) Derivation of the equation

(ii) Significance of it.

3+2

Or

(b) Write short notes on Entropy change for an adiabatic process covering the following points :

(i) Reversible adiabatic process

(ii) Irreversible adiabatic process with calculation and entropy change of the universe.

1+4

3. (a) Write short notes on Le Chatelier principle covering the following points :

(i) Statement

(ii) Thermodynamic explanation with appropriate example.

1+4

Or

(b) Write short notes on the conditions for spontaneity and equilibrium starting from the Clausius inequality covering the following points :

(i) Conditions in terms of Gibb's free energy (with derivation)

(ii) Conditions in terms of Helmholtz free energy (with derivation)

(iii) Suitability of the above two conditions in case of laboratory chemical reactions with explanation.

2+2+1

4. (a) Write short notes on determination of transport number of ions using Hittorf's method covering the following points :

(i) Principle of the method

(ii) Working formula.

3+2

Or

(b) Write short notes on Debye-Hückel theory of ion-atmosphere covering the following points :

(i) Asymmetric effect

(ii) Relaxation effect

(iii) Electrophoretic effect.

1½+1½+2

5. (a) For n moles of an ideal gas expanding isothermally from V_1 to V_2 at temperature T , evaluate ΔS_{system} , $\Delta S_{\text{surrounding}}$ and ΔS_{Total} for (i) free expansion and (ii) reversible expansion.

(b) Consider the dissociation equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$. Now assuming that we start with 1 mole of $\text{N}_2\text{O}_4(\text{g})$ and no $\text{NO}_2(\text{g})$, show that the degree of dissociation of $\text{N}_2\text{O}_4(\text{g})$ may be written

$$\text{as } \alpha = \left(\frac{K_p}{K_p + 4P} \right)^{1/2}, \text{ where 'P' is total pressure at equilibrium.}$$

Check whether your result is in accord with Le Chatelier's principle.

- (c) The specific conductance for pure water is $38.4 \times 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 18°C . The equivalent conductance at infinite dilution of H^+ and OH^- ions are 315.2 and $173.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ respectively. Calculate the ionic product of water at 18°C . Is this water alkaline with respect to water at 25°C ($\text{pH} = 7$)? 4+3+3

6. (a) Derive an expression of pH for hydrolysis of a salt of weak acid and weak base.
 (b) Define fugacity. Starting from the condition of chemical potential, derive an expression relating fugacity and pressure for a real gas. Show that fugacity approaches pressure in the limit of low pressure.
 (c) Show that for a van der Waals' gas,

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0. \quad \text{4+3+3}$$

7. (a) For the gas-phase reaction at 298 K , $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g})$, the standard Gibbs free energy change is $\Delta G^\circ = +8.0 \text{ kJ mol}^{-1}$. (i) Using the reaction isotherm, $\Delta G = \Delta G^\circ + RT \ln Q$, derive an expression for the maximum value of the reaction quotient (Q_{max}) for which the reaction will be spontaneous in the forward direction at 298 K . (ii) Comment briefly on how a reaction with a positive ΔG° can still proceed to a considerable extent.
 (b) Sketch the plot of conductometric titration of acetic acid with NaOH and explain it.
 (c) Evaluate ΔA for the reversible isothermal expansion of one mole of the gas having an equation of state $P\bar{V} = RT \left(1 + \frac{B}{\bar{V}}\right)$ from an initial volume \bar{V}_1 to final volume \bar{V}_2 , where 'B' is constant.

(2+2)+(1+2)+3

8. (a) Thermodynamic equation of state, given by $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$ may be derived from a Maxwell relation. Derive that particular Maxwell relation and hence derive the given thermodynamic equation of state.
 (b) Hydrogen and Helium gases are different from all other gases with respect to Joule-Thomson expansion. Explain.
 (c) State Kohlrausch's law of independent migration of ions. Why is Kohlrausch's law applicable only at infinite dilution? Can the limiting equivalent conductance (Λ^0) of a weak electrolyte be determined from its equivalent conductance values measured at different concentrations? Explain using Λ_{equiv} vs Concentration graph. (2+2)+3+(1+1+1)

9. (a) For the heterogeneous equilibrium $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$, the equilibrium constant K_p is found to be 0.05 (pressures in atm) at 20°C . In a 2.4 litre of evacuated flask maintained at 20°C , a total of 0.06 mol of solid NH_4HS is introduced.
 (i) Calculate the percentage of solid NH_4HS decomposed at equilibrium.
 (ii) Calculate the number of moles of NH_3 that must be added to the flask so that the decomposition of NH_4HS is reduced to 1.0% . (Assume all gases behave ideally.)

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(4851)

- (b) Ice requires 6000 J mol^{-1} of heat to transform to water at 0°C . Find ΔS_{system} . If surrounding is at $+1^\circ\text{C}$, find ΔS_{uni} . Comment on the spontaneity of the process.
- (c) Calculate the solubility of PbI_2 at 25°C in a mixed electrolyte solution of KNO_3 (0.01m) and KI (0.08 m), applying the Debye-Hückel limiting law. [$K_{\text{sp}} = 2.5 \times 10^{-12}$] (2+2)+(1+1+1)+3
10. (a) Equivalent conductance at infinite dilution of HCl , NaCl and CH_3COONa are 426.2, 126.5 and $91.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ gmeqv}^{-1}$ respectively at 25°C . A conductivity cell filled with 0.01 M KCl has a resistance of 257.3 ohm at 25°C . The same cell filled with 0.2N acetic acid has a resistance of 508.6 ohm. Calculate the dissociation constant of the acetic acid.
(Given specific conductance of the 0.01 M KCl at 25°C is $1.41 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$.)
- (b) A solute is dissolved in a mixture of two immiscible solvents A and B . If in B , the solute gets dimerised, then from thermodynamic consideration, show that the ratio $\frac{C_A}{\sqrt{C_B}}$ will be constant at a particular temperature. [C_A and C_B denotes concentrations of solute in respective solvent.]
- (c) How can you determine the solubility product of a sparingly soluble salt from conductance measurement? 4+3+3