2023

CHEMISTRY — HONOURS

Paper : CC-5

(Physical Chemistry - 2)

Full Marks : 50

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 no.*** **1** and ***any eight*** questions from the rest.

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

(a) Why does C_P exceed C_V for an ideal gas? Give a molecular explanation.

(b) In a given change of state, 44 J of work are destroyed and the internal energy increases by 170 J. If the temperature of the system rises by 10 K, what is the heat capacity of the system?

(c) What is the connection between Hess's law and the fact that enthalpy is a state function?

(d) Plot the value of $(\mu - \mu_0)/RT$ for an ideal gas as a function of pressure.

(e) At 298 K, calculate the value of ΔA for an isothermal expansion of one mole of an ideal gas from 10 L to 40 L.

(f) Suggest a physical interpretation of the dependence of the Gibbs energy on the temperature.

(g) Ice is melted at 273 K and 1 atm.— State which of ΔU, ΔH, ΔS, ΔS_{univ}, ΔA and ΔG must be zero for the process.

(h) Define ionic mobility and mention its unit.

(i) Define standard electrode potential.

(j) Define equivalent conductance of an electrolyte solution (without using its relation with specific conductance). What is its C.G.S. unit?

(k) 'Joule's Experiment is an isenthalpic process.'— Comment on the statement.

(l) Why is a dilute solution of ammonium acetate itself a buffer?

2. (a) Evaluate the value of $\left(\frac{\partial C_V}{\partial V}\right)_T$ for a van der Waals gas.

(b) The coefficient of thermal expansion α of copper at 298 K is 5.00×10^{-5} K^{-1} and its isothermal compressibility β is 7.85×10^{-7} atm^{-1}. Given that the density of copper is 8.92 gm cm^{-3} at 298 K. Calculate the value of $\bar{C}_P - \bar{C}_V$ for copper. [Given molar mass of Cu = 63.54 gm mol^{-1}] 2+3

3. (a) Derive the equation that shows temperature dependence of enthalpy change of a reaction.

(b) Distinguish between 'Bond energy' and 'Bond dissociation energy'. 3+2

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

(b) One mole of CO is transformed from 298 K and 5 atm. to 398 K and 2 atm. If $\bar{C}_P / R = (3.1916 + 0.9241 \times 10^{-3} T - 1.410 \times 10^{-7} T^2)$, calculate ΔS assuming the gas to be ideal. 3+2

5. (a) Show that for a gas obeying equation $P\bar{V} = RT(1 + bP)$, where 'b' is constant, the following relations held good : (i) $\left(\frac{\partial U}{\partial V}\right)_T = bP^2$ (ii) $\mu_{J,T} = 0$. Comment on the value of $\mu_{J,T}$.

(b) Comment on the validity of the relation, $\Delta H = q$, for the process in which pressure is not constant throughout, but the initial and the final pressures are same. 3+2

6. (a) Using Maxwell's relation, show that

$$Tds = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$= C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

(b) Show that for a multi-component open system, where G is a function of pressure, temperature and composition of different components, $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}}$. 3+2

7. (a) A gas 'A' isomerizes to 'B' according to the reaction, $A \rightarrow B$ and forms an ideal gas mixture with equilibrium constant, K_P. Starting with 1 mole of pure 'A' at 1 atm., the gas is allowed to isomerise at constant T and P until it reaches equilibrium.

(i) Express the free energy change (ΔG) as a function of x, where x is the number of moles of 'B' at any time during the course of reaction.

(ii) Show the equilibrium, $\Delta G^\circ = \mu_B^\circ - \mu_A^\circ$

$$= -RT \ln K_P$$

$$= -RT \ln \frac{x_e}{1 - x_e},$$

where x_e is the number of moles of 'B' at equilibrium.

(b) Nitrogen trioxide dissociates according to the equation $N_2O_3(g) \rightleftharpoons NO_2(g) + NO(g)$.

At 298 K and 1 atm. total pressure, the degree of dissociation is 0.30. Calculate ΔG° for this reaction at 298 K. 3+2

8. (a) Discuss the relaxation effect and electrophoretic effect in the light of the Debye-Hückel theory.

(b) At 291 K, the mobility at infinite dilution of the ammonium ion is 6.6×10^{-4} $cm^2\ V^{-1}S^{-1}$, while that of the chlorate ion is 5.7×10^{-4} $cm^2\ V^{-1}S^{-1}$. Calculate Λ°_{eq} of ammonium chlorate and the transport number of the two ions. 3+2

9. (a) Consider the hydrolysis of a salt (BCl) formed from a strong acid and weak base. Show that,

$$[H_3O^+]^3 K_b + [H_3O^+]^2 K_w - (K_b + C)K_w\left[H_3\overset{+}{O}\right] - K_w^2 = 0,$$

where C is the concentration of the salt in water, K_b is the dissociation constant of the weak base.

Simplifying the above expression, show that; $pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log C$.

(b) Calculate the ionic strength of a solution obtained by mixing aqueous solution of 25 ml of 0.02 M K_2SO_4 and 0.02 M urea. 3+2

10. (a) How can you determine the degree of hydrolysis and the hydrolytic constant from the conductance measurement of the solution of a salt from a weak acid? (e.g., aniline hydrochloride)

(b) $\Delta_f G^\circ_{298}$ values for $K^+(aq)$, Cl^- (aq) and KCl(s) are -283.3 KJ mol^{-1}, -131.2 KJ mol^{-1} and -409.2 KJ mol^{-1}, respectively. Find K_{sp} for KCl in water at 25°C. 3+2

11. (a) How can you determine the ionic product of water (K_w) from e.m.f. measurement?

(b) Calculate the E.M.F. of the electrode-concentration cell :

$$Hg - Zn(C_1)|\ Zn^{2+}(aq)\ |Hg - Zn(C_2) \text{ at } 25°C,$$

if the concentrations of the zinc amalgam are :

$C_1 = 2$ gm of Zn/100 gm of Hg and $C_2 = 1$ gm of Zn/100 gm of Hg. 3+2

12. (a) Show that pressure of an ideal gas is a state function.

(b) Calculate the entropy change when,

(i) one mole of He and one mole of H_2 are mixed at constant temperature (298 K).

(ii) one mole of He is mixed with one mole of He at constant temperature (298 K). 2+3

13. (a) Derive the equations showing the temperature dependence of G and G/T at a constant pressure.

(b) One mole of oxygen expands adiabatically against a constant external pressure of 1 atm. until the pressure balances. The initial temperature and volume are 473 K and 20 L respectively. Calculate the final temperature and the work done. 3+2
