[This question paper contains 4 printed pages.]

Sr. No. of Question Paper : 733 **G** **Your Roll No.....**

Unique Paper Code : 217305

Name of the Paper : Physical Chemistry – II (CHHT-307)

Name of the Course : **B.Sc. (H) Chemistry**

Semester : III

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions.
3. Q. No. **1** is compulsory.
4. Draw the graphs (wherever required) on your answer sheets. Graph paper is not required. Use of scientific calculator is permitted.

   $R = 8.314\ JK^{-1}\,mol^{-1}$; $N_A = 6.022 \times 10^{23}\ mol^{-1}$

1. Attempt any **five** of the following :

   (a) The magnitude of the boiling point elevation is less than that of the freezing point depression for a solution of the same concentration: Explain the statement in terms of chemical potential along with diagram.

   (b) Work done by the system in a reversible isothermal expansion of an ideal gas is greater than that of irreversible expansion: Justify the statement along with diagram.

   (c) Which would have the high entropy in gas phase at same temperature - Argon, ethane ?

   (d) Why ΔG is used more compared to ΔA to express the condition of spontaneity of the reaction ?

(e) A monobasic acid "A" has molecular weight M. The specific gravity is mentioned on the bottle of the acid "A" is Y g/cc and purity of the acid is Z% by weight. Find out the normality of the acid "A" in terms of M, Y and Z.

(f) Explain Hess's Law of constant heat summation with an example.

(g) C_p is always greater than C_v. (3×5)

2. Derive the following relations :

(a) $C_p - C_{v.} = \left[\left(\partial U/\partial V_T\right) + P\right]\left(\partial v/\partial T\right)_p$

(b) $\left(\partial H/\partial P\right)_T = V - T\left(\partial V/\partial T\right)_P$

(c) $\left(\partial T/\partial V\right)_S = -\left(\partial P/\partial S\right)_V$

(d) $TP^{-R/Cp,m}$ = Constant (4×3)

3. (a) Make a rough sketch of the following cycle on T-S diagram :

Step A. Isothermal expansion (at T_1) from P_1 to P_2.

Step B. Isochoric heating from P_2, T_1 to P_3, T_3.

Step C. Isobaric cooling from P_3, T_3, to P_1, T_1.

Find out the slope in each step.

(b) Write a short note on abnormal colligative properties of solutions and van't Hoff factor ?

(c) One mole of an ideal gas is allowed to expand isothermally at 27°C until its volume is tripled. Calculate ΔS_{sys} and ΔS_{univ} under the following conditions :

(i) Expansion is carried out reversibly.

(ii) Expansion is a free expansion. (4×3)

4. (a) For a certain gas, the following is true :

$$C_{v,m} = a + bT + cT^2 \quad \text{and} \quad P(V_m - B) = RT$$

Derive an expression for the entropy change of 1.0 mole of this gas that accompanies a change in its state from T_i, $V_{i,m}$ to T_f, $V_{f,m}$.

(b) Define molal depression constant. Derive thermodynamically an expression relating the freezing point depression of a solution with its molality.

(c) The bond enthalpy of $H_2(g)$ is 436 kJ mol^{-1} and that of $N_2(g)$ is 941.3 kJ mol^{-1}. Calculate the average bond enthalpy of an N-H bond in ammonia. ΔH_f^0 (NH_3) = –40.0 kJ mol^{-1}. (3×4)

5. (a) For a binary system show that

$dv_1 = -\frac{n_2}{n_1} dv_2$. What is the physical significance of this expression ?

(b) Explain the terms osmosis and osmotic pressure. Using the concept of chemical potential, derive an expression for the osmotic pressure of the solution in terms of its concentration.

(c) An ideal gas is allowed to expand reversibly and isothermally at 298K from a pressure of 1 bar to 0.05 bar. (i) What is the change in molar Gibbs energy ? (ii) What would be the change if the process occurs irreversibly ? (3×4)

6. Differentiate between :

(i) Differential and Integral enthalpy of solution.

(ii) Bond enthalpy and Bond dissociation enthalpy.

(iii) Exact and Inexact differential. (3×4)

7. (a) Prove that :

(i) $(\partial H/\partial P)_T = 0$ for an ideal gas

(ii) $(\partial U/\partial V)_p + P = C_p(\partial T/\partial V)_p$

(b) 5.13% (wt/v) solution of cane sugar is isotonic with a 0.9% (wt/v) solution of an unknown solute. Calculate molar mass of the solute. Molecular weight of cane sugar = 342 g/mol.

(c) The volume of an aqueous solution of sodium chloride at 25°C was found to obey the relation :

$$V/cm^3kg^{-1} = 1003 + 16.62\ (m/mol\ kg^{-1}) + 1.77(m/mol\ kg^{-1})^{3/2} + 0.12\ (m/mol\ kg^{-1})^2$$

Find the partial molar volume of the components at m=0.1 mol kg^{-1} by explicit differentiation. (3×4)

8. (a) At a total pressure of 2 atmospheres and 673K the equilibrium constant Kp for the following reaction is 1.64×10^{-4}. Calculate K_c and K_x.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(b) 100 g of water at 100°C is placed in thermal contact with 1 kg of ice at 0°C and the system is allowed to come into equilibrium. Calculate the entropy change for the original 100 g of water, for the original 1 kg of ice and for the total system. Take the specific heat capacity of water to be 4.18 $JK^{-1}g^{-1}$ and the enthalpy of fusion of ice to be 333 Jg^{-1}.

(c) A salt solution fails to quench thirst: Justify with reasons. (4,6,2)

9. (a) State and explain third law of thermodynamics. How is it useful in calculating the absolute entropy of a substance ?

(b) What do you understand by maximum flame temperature ? Prove that it is given by following relation :

$$T_f = T_0 + \left(-\Delta H_{T0}\right)/\sum C_{P(Products)}$$

(c) Explain the effect of addition of inert gas at equilibrium by deriving equilibrium constant (K_P) under the following conditions :

(i) When pressure is constant.

(ii) When volume is constant. (4,4,4)