Unique Paper Code	: 32171202_OC
Name of the Paper	: **Physical Chemistry II: Chemical Thermodynamics and its Applications**
Name of the Course	: B.Sc.(H) Chemistry
Semester	: II
Duration	: 3 hours
Maximum Marks	: 75

Instructions for Candidates:

i. Following details must be written on first page:
• University Roll No.:
• Unique Paper Code:
• Name:
• Class:
• Course:
• Semester:
• Paper Name:
ii. Put page numbers on every page of the answer script.
iii. Attempt any **four** questions in all. **Q. No.- 1** is **compulsory**.
iv. Marks are mentioned at the end of each question.
v. Attempt all parts of a question together.

1. Attempt any seven questions and give answers in brief.

(a) Does the equilibrium constants for reaction in solution is effected by the solvent?
(b) Addition of a non-volatile solute lowers the freezing point and elevates the boiling point of a solvent. Explain.
(c) Prove C_p-C_v=$VT\alpha^2/\kappa$
(d) Q is not a state function but become state function under certain conditions. Explain.
(e) If a steam engine is supplied 4000 J of heat and it performs 1000 J of work. Account for the rest of 3000 J of heat.
(f) Why with increase of pressure the melting point would decrease for Ice ↔ Water equilibrium.
(g) For the equilibrium $CO(g)+H_2O(g)\leftrightarrow CO_2(g)+H_2(g)$. What is the effect of pressure in this equilibrium?
(h) The observed value ΔH_f° for benzene is 82.9 kJ mol^{-1} while from theoretical calculation it was ΔH_f° 256 kJ mol^{-1}. Account for the great difference of 173 kJ mol^{-1}.
(i) Why, Joule-Thomson coefficient negative value corresponds to warming on expansion. (3×7)

2. (a) One mole of an ideal gas at 300K and 10^6Pa expands to 10^5Pa. Calculate W, Q, U, H for:

i. Isothermal – Reversible
ii. Isothermal – Irreversible
iii. Adiabatic – Reversible
iv. Adiabatic - Irreversible

(b) Prove, $TV^{\gamma-1}$= constant
PV^{γ}= constant

(c) Define Kirchhoff's Law. The heat of dissociation per mole of gaseous water at 18°C and 1 atm is 241750 J. Calculate its value at 63°C.
Given that:
$C_p (H_2O)$= 33.565 J K^{-1} mol^{-1}
$C_p(H_2)$ = 28.83 J K^{-1} mol^{-1}
$C_p(O_2)$= 29.12 J K^{-1} mol^{-1} (6×3)

3. (a) i. State second law of thermodynamics and prove entropy is a state function.
ii. Calculate the entropy change when $10dm^3$ of an ideal gas at 27°C is heated to 127°C at constant pressure of 1.01×10^5 Nm^{-2}. Given that, $C_{p,m}$=2.5R.

(b) i. Prove, – ΔG = - W_{net}
ii. Prove, Gibbs- Helmholtz equation $(G/T)_P= -\int H/T^2\, dT + I$

(c) i. Prove that isothermal reversible work of expansion is always greater in magnitude than that of irreversible expansion of an ideal gas.
ii. Define Hess's law of constant heat summation and explain its application. (6×3)

4. (a) i. Prove Gibbs-Duhem equation.
ii. Derive the formula for effect of temperature on chemical potential.

(b) i. What are limitations of ideal solubility law.
ii. Calculate the ΔG_{mixing}, ΔH_{mixing}, ΔS_{mixing}at 25°Cand 1 atm. When 10 moles of Helium are mixed with 10 moles of Neon.

(c) i. Explain the effect on RBC when they are placed in hypotonic and hypertonic solution.
ii. 0.45g of glucose of molecular weight 180g is placed inside a tube of unit area of cross section and closed at one end with a semipermeable membrane. The tube is kept in water at 27°C. Calculate, the height of solution inside the tube when equilibrium is attained and the osmotic pressure. Given that, density of solution =1.017 g cm^{-3} and g = 98 cm s^{-2} (6×3)

5. (a) i. Derive Van't Hoff equation in the form

$$d\ln K_p/dT = -\Delta H^\circ / RT^2$$

ii. For a reaction $X_2 \rightarrow 2X$, the equilibrium constant at 1225 K is 3.28×10^{-3} and the reaction is exothermic by 216.7 kJ mol^{-1}. Calculate ΔG° and ΔS° for the reaction at 1225 K.

(b) i. At 480 K and pressure of 1atm, a mixture consisting of N_2 and H_2 in the mole ratio of 1:3 contains 16% NH_3 at equilibrium. Calculate $K_p$for the reaction.

ii. Drive relationship between K_p, K_c andK_x

(c) i. Define Raoult's law and Henry's law. What are limitations of Henry's law?

ii. A solution of 1.0×10^{-2} kg of sodium chloride in 1000g freezes at -0.604°C. The molal depression constant of water K_f is 1.85 K kg mol^{-1}. Calculate the degree of dissociation of sodium chloride. (6×3)

6. (a) i. Define integral heat of solution, integral heat of dilution and integral heat of infinite dilution. Distinguish between them by taking an example.

ii. Calculate the enthalpy change for the reaction:

$$C_2H_4(g) + Br_2(g) \leftrightarrow C_2H_4Br_2(g)$$

The bond enthalpy of ΔH°_{C-H} = 415 kJmol^{-1},$\Delta H^\circ_{C=C}$=610kJmol^{-1}, ΔH°_{C-C} =348 kJmol^{-1}, ΔH°_{C-Br}=276 kJmol^{-1}, ΔH°_{Br-Br}= 193 kJ mol^{-1}.

(b) Define Le Chatelier'sPrinciple. What are the effects of pressure, temperature, concentration and catalyst on chemical equilibrium? Explain it by taking an example.

(c) i. Derive thermodynamic equation of boiling point elevation on addition of non-volatile solute in a solvent.

ii. The boiling point of chloroform was raised by 0.325 K when 5.141×10^{-4} kg of anthracene was dissolved in 3.5×10^{-2} kg of chloroform. Calculate the molar mass of solute. K_b= 3.9 K kg mol^{-1}. (6×3)