Name: Enrolment No:	UPES

UNIVERSITY OF PETROLEUM AND ENERGY STUDIES

End Semester Examination, May 2023

Programme Name: B. Sc. (Hons.) Chemistry **Semester : II**
Course Name : Physical Chemistry-II **Time : 03 hrs**
Course Code : CHEM 1006 **Max. Marks : 100**
Nos. of page(s) : 3

Instructions: Read all the below mentioned instructions carefully and follow them strictly

1) Write your name and enrollment no. at the top of the question paper.
2) Do not write anything else on the question paper except your name and roll number.
3) Attempt all the parts of a question at one place only.
4) Internal choices are given for question number 9 and 11.
5) CO1, CO2, CO3 & CO4 in the last column stand for course outcomes and are for official use only.

SECTION A
(Attempt all Five Questions) (5Qx4M=20Marks)

S. No.		Marks	CO
Q 1	Define partial molar properties. Explain with an example.	**4**	**CO1**
Q 2	Suppose we know that ΔG^0 = +3.40 kJ/mol for the reaction $H_2(g) + I_2(s) \rightarrow 2HI(g)$ at 25°C, then calculate the equilibrium constant. (Given: R = 8.314 J/K/mol)	**4**	**CO3**
Q 3	What are colligative properties? Give examples	**4**	**CO1**
Q 4	Draw the P-V diagram for Carnot cycle. What will be the efficiency of a Carnot's engine, considering the temperature of the source as T_1 and the temperature of the sink as T_2?	**4**	**CO2**
Q 5	The standard heats of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are -277.0, -393.5 and -285.5 kJ mol^{-1} respectively. Calculate the standard heat change for the reaction $C_2H_5OH(l) + 3O_2(l) \rightarrow 2CO_2(g) + 3H_2O(l)$	**4**	**CO3**

SECTION B
(Attempt all Questions; internal choice is given for question number 9) (4Qx10M= 40 Marks)

Q 6	**(a)** Determine the Gibbs Free energy (ΔG_{mix}) and entropy (ΔS_{mix}) of mixing for the formation of an equimolar mixture of two perfect gases (1.2 moles of N_2 and 1.2 moles of O_2) at a temperature of 298 K. **(b)** Calculate the standard molar entropy of vaporization of phosphorus trichloride, PCl_3, at its boiling temperature, 74°C, given that the standard molar enthalpy of vaporization of phosphorus trichloride is 30.5 kJ $mole^{-1}$.	**6+4**	**CO2**
Q 7	(a) What are the criteria of spontaneity in terms of Gibbs Free energy and	**5+5**	**CO2**

	Helmholtz Free energy? (b) Check whether the following reaction is spontaneous at 25℃ and 11000 ℃ $C(s) + H_2O(l) \rightarrow CO(s) + H_2(g)$ Given that ΔH and ΔS are 31400 Cal/mol and 32 Cal/deg at 25 ℃.		
Q 8	**(a)** The vapour pressure of pure CCl_4 (m.w. 154 g/mole) and $SnCl_4$ (m. w. 170 g/mole) at 25°C are 114.9 and 238.3 torr, respectively. Assuming ideal behavior, calculate the total vapour pressure of solution containing 15 gm of CCl_4 and 10 gm of $SnCl_4$. **(b)** Calculate the enthalpy of reaction for $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ at 450 K using the following crude guesses for the heat capacities: $C_P(N_2) = 3.5\,R$, $C_P(H_2) = 3.5\,R$, $C_P(NH_3) = 4R$. It is known that $\Delta H_f^0(NH_3(g), 298\ K) = -45.72$ kJ/mol.	**10**	**CO2**
Q 9	**(a)** Prove that $\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$ **OR** Derive the expression of entropy change (ΔS_{mix}) for mixing of two ideal gases. **(b)** With reference to the formation of nitric oxide (NO), discuss the effect of change of concentration and temperature on chemical equilibrium, according to Le Chatelier principle. $\frac{1}{2}N_{2(g)} + \frac{1}{2}O_2 \overset{Catalyst}{\Longleftrightarrow} NO$, ΔH= 90.75 kJ **OR** Derive the expression for ΔS_{syst}, ΔS_{surr} and ΔS_{total} for expansion or compression of an ideal gas under the following circumstances (i) Isothermal reversible change (ii) Isothermal reversible change involving free expansion	**5+5**	**CO3**
SECTION-C (**Attempt all Questions; internal choice is given for question number 11**) **(2Qx20M=40 Marks)**			
Q10	**(a)** Derive all the four Maxwell's relations. Using Maxwell's square write all criteria of spontaneity. **(b)** Derive the thermodynamic expression of boiling point elevation of a solution $\Delta T_b = T - T^* = K_b x_B$ where K_b is the boiling point elevation constant and x_B is the mole fraction of solute B.	**8+12**	**CO3**
Q 11	**(a)** State 3rd law of thermodynamics. Calculate the third law entropy of a substance at 500 K using the following data (i) Heat capacity (J/K/mol) of solid from 0 K to normal melting point 250 K: Cp (s) = 0.05T	**10+10**	**CO3**

(ii) Enthalpy of fusion = 7.5 kJ/mol

(iii) Heat capacity of liquid from 250K to normal boiling point 400 K $C_p(l)$ = 60 kJ/mol

(iv) Enthalpy of vaporization = 40 kJ/mol

(v) Heat capacity of gas from 400 K to 500 K at 1 atm : Cp (g) = 70 J/K/mol

OR

At low temperatures, the heat capacity of some metals has been found to follow a modified version of the Debye T^3 law, varying with temperature according to the relationship

$$C_p = aT^3 + bT$$

with the additional, linear term arising from the electrons. Derive an expression for the molar entropy of such a metal at a low temperature *T*.

(b) Show how following equation can be derived from a Carnot cycle operating between two temperatures T_1 and T_2: $\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$

OR

From master equation derive the following thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$