Name: **Enrolment No:**	UPES

UNIVERSITY OF PETROLEUM AND ENERGY STUDIES

End Semester Examination, May 2019

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)

S. No.		Marks	CO
Q 1	Write the names of four colligative properties of the solution.	**4**	**CO4**
Q 2	Evaluate the expression of $\left(\frac{\partial U}{\partial V}\right)_T$ for the van der Waals gas which obeys the equation of state $P(V-b)=RT$. (Hint $dU = TdS - PdV$)	**4**	**CO1**
Q 3	What is Trouton's rule? Which of the following liquids: benzene, water and cyclohexane, follow Trouton's rule? Explain with reasoning.	**4**	**CO1**
Q 4	An aqueous solution containing 0.25 g of a solute was dissolved in 20 g of water, frozen at -0.42 ^oC. Find out the molar mass of the solute. (Heat of fusion of ice at 0^oC is 334.7 J/g and R=8.314 $JK^{-1}mol^{-1}$)	**4**	**CO4**
Q 5	The partial molar volumes of acetone and chloroform in a mixture ($x_{acetone}$ =0.53) was 74.17 cm^3 mol^{-1} and 80.24 cm^3mol^{-1}, respectively. Find out the density of the solution.	**4**	**CO2**
SECTION B (Attempt all Questions; internal choice is given for question number 9)			
Q 6	**(a)** Derive the Clausius inequality. **(b)** For an ideal gas $\overline{C_p} = 5/2R$. Calculate the change in entropy suffered by 3 mol of the gas on being heated from 300 K to 600 K at **(i)** constant pressure and **(ii)** constant volume.	**4+6**	**CO1**
Q 7	**(a)** What are intensive and extensive variables? Classify the following into intensive and extensive variables: **(i)** enthalpy **(ii)** molar volume and **(iii)** heat capacity. **(b)** Using thermodynamic square find out the Maxwell relation of	**5+5**	**CO1**

	(i) $\left(\frac{\partial T}{\partial V}\right)_S$ and **(ii)** $\left(\frac{\partial S}{\partial V}\right)_T$		
Q 8	**(a)** Given the following information: $A + B \rightarrow C + D \quad \Delta H° = -10.5\ kJ$ $C + D \rightarrow E \quad \Delta H° = 15.0\ kJ$ Calculate the $\Delta H°$ for each of the following reactions: **(i)** $2C + 2D \rightarrow 2A + 2B$ **(ii)** $2E \rightarrow 2A + 2B$ **(b)** The volume of an aqueous solution of KCl, at 25 ^{0}C was found to obey the relation, $V/cm^3kg^{-1}=1.03+16.62\ (m)+1.77\ (m)^{3/2}+0.12\ (m)^2$; where "m" is in mol/kg. Find the partial molar volume of the components at m=0.1 mol kg^{-1} by explicit differentiation.	**2+8**	**CO1 & CO2**
Q 9	**(a)** Calculate the maximum work that can be done by a reversible heat engine operating between 400 and 100 K if 500 J is absorbed at 400 K. **OR** $\Delta H_{vaporization}$ of a substance is 45.7 kJ/mol, and its normal boiling point is 72.5°C. Calculate ΔS, ΔS_{surr} and ΔG for the vaporization of one mole of this substance at 72.5°C and 1 atm. **(b)** With reference to the formation of ammonia, discuss the effect of change of concentration and temperature on chemical equilibrium, according to Le Chatelier principle. **OR** SO_2 and SO_3 (0.10 mole each) were mixed in a two liter flask at 300 K. Equilibrium was attained as: $2SO_{2(g)} + O_{2(g)} \overset{300K}{\Longleftrightarrow} 2SO_{3(g)}$ The equilibrium pressure was 281.68 kPa. Find out the mole fraction of oxygen at equilibrium and the value of K_p°.	**5+5**	**CO1 & CO3**
SECTION-C (**Attempt all Questions; internal choice is given for question number 11**)			
Q10	**(a)** State Planck's statement of third law of thermodynamics. Show and explain the schematic plot of variation of entropy of a substance heated from 0 K (solid) to a temperature (T) in the gas phase **(b)** Derive the v*an't Hoff* equation. A reaction has a value of K_p=0.026 at 25°C and ΔH_{rxn}° =32.4 kJ/mol; Calculate the value of K_p at 37°C. (R=8.314 $JK^{-1}mol^{-1}$).	**10+10**	**CO1 & CO3**
Q 11	**(a)** One mole of Zn(s) is heated from 300 K to 1500 K. Calculate the entropy changes from the following data: melting point of Zn = 692 K, boiling point of Zn = 1180 K, enthalpy of fusion=7.53 kJ/mol, enthalpy of vaporization = 115.9 kJ/mol, specific heat capacity of Zn in solid, liquid and gaseous phases are 0.384, 0.512 and 0.312 J g^{-1} K^{-1} respectively, molar mass of Zn = 65.38 g	**8+6+6**	**CO1, CO1 and CO4**

	mol^{-1}. **OR** Derive $dS = \frac{C_V}{T}\, dT + \frac{\alpha}{\beta} dV$, where α and β are coefficient for thermal expansion at constant pressure and isothermal compressibility coefficient respectively. Under what conditions is $dG \leq 0$ a condition that defines the spontaneity of a process? Explain. **(b)** The standard enthalpy of combustion of anthracene ($C_{14}H_{10}$) is -7163 kJ/mol. Calculate the standard enthalpy of formation of anthracene. Given that $\Delta H_f^{H_2O} = -286 \frac{kJ}{mol} and\ \Delta H_f^{CO_2} = -393 \frac{kJ}{mol}$ **OR** Given the thermochemical equations: $H_{2(g)} + C_3H_{6(g)} \rightarrow C_3H_{8(g)} \quad \Delta H° = -124\ kJ$ $5O_{2(g)} + C_3H_{8(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)} \quad \Delta H° = -2220\ kJ$ $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H° = -286\ kJ$ Calculate the standard enthalpy of combustion of propene. **(c)** The vapour pressures of pure CCl_4 and $SnCl_4$ at 25°C are 114.9 and 238 mm Hg, respectively. Assuming ideal behavior, calculate the total vapour pressure of a mixture containing 10 gm of CCl_4 and 15 g of $SnCl_4$. (M.W. of CCl_4=154 and $SnCl_4$=170). **OR** Explain how the degree of association of a non-electrolyte can be determined from the measurement of a colligative property.		

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SECTION A (Attempt all Five Questions)

S. No.		Marks	CO
Q 1	The molar heat of vaporization of water at 100 ^{o}C is 40.585 kJ. To 1000 g of water, 5.6 g of glucose was dissolved to get glucose solution. Find out the boiling temperature of the solution. (R=8.314 $JK^{-1}mol^{-1}$)	**4**	**CO4**
Q 2	Evaluate the expression of $\left(\frac{\partial H}{\partial P}\right)_T$ for the van der Waals gas which obeys the equation of state $P(V-b)=RT$. (Hint $dH = TdS + VdP$)	**4**	**CO1**
Q 3	Show that for a system decrease in the value of Helmholtz free energy at constant temperature represents the maximum amount of work that can be obtained from the system.	**4**	**CO1**
Q 4	Write a short note on Raoult's laws. Mention its two industrial applications.	**4**	**CO4**
Q 5	The volume of an aqueous solution of NaCl, at 25^{o}C was expressed as a function of the amount "**m**" in one kg of solvent in the following form: $V/cm^3 = 1000.94 + 16.4\ (m/mol) + 12.14\ (m/mol)^{3/2} - 0.0027\ (m/mol)^{5/2}$ Find the partial molar volume of NaCl.	**4**	**CO2**

SECTION B (Attempt all Questions; internal choice is given for question number 9)

Q 6	**(a)** Show that the criteria of spontaneity is $dS > \frac{Q_{irrev}}{T}$. **(b)** For an ideal gas $\overline{C_v} = 3/2R$. Calculate the change in entropy suffered by 4 mol of the gas on being heated from 400 K to 500 K at **(i)** constant pressure and **(ii)** constant volume.	**4+6**	**CO1**

Q 7	**(a)** What are the state and path functions? Classify the following into state and path functions: **(i)** enthalpy **(ii)** entropy and **(iii)** heat capacity. **(b)** Using thermodynamic square find out the Maxwell relations of **(i)** $\left(\frac{\partial P}{\partial S}\right)_V$ and **(ii)** $\left(\frac{\partial P}{\partial T}\right)_V$	**5+5**	**CO1**
Q 8	**(a)** Given the following information: $A + B \rightarrow C + D \quad \Delta H° = -10.5\ kJ$ $C + D \rightarrow E \quad \Delta H° = 15.0\ kJ$ Calculate the $\Delta H°$ for each of the following reactions: (i) $3C + 3D \rightarrow 3A + 3B$ (ii) $2E \rightarrow 2A + 2B$ **(b)** Calculate the Δ_{mix}G and Δ_{mix}S, for mixing the constituents of air (N_2-78 mole %, O_2-20 mol % and H_2-2 mole %) at 300 K, to get 2 moles of air, assuming them as ideal mixture.	**2+8**	**CO1 & CO2**
Q 9	**(a)** Calculate the maximum work that can be done by a reversible heat engine operating between 350 and 100 K if 900 J is absorbed at 350 K. **OR** The value of ΔH_{fusion} of a substance is 35.7 kJ/mol, and its normal melting point is 20°C. Calculate ΔS, ΔS_{surr} and ΔG for the fusion of one mole of this substance at 20°C and 1 atm. **(b)** With reference to the formation of ammonia in Haber process, discuss the effect of changes of concentration and temperature on chemical equilibrium, according to Le Chatelier principle. **OR** Derive the thermodynamic derivation of relation between free energy change and reaction quotient of following type. $aA + bB \Leftrightarrow cC + dD$	**5+5**	**CO1 & CO3**
SECTION-C (**Attempt all Questions; internal choice is given for question number 11**)			
Q10	**(a)** State the third law of thermodynamics. Show and explain the schematic plot of variation of entropy of a substance heated from 0 K (solid) to 1000 K (gas). **(b)** Explain the various terms used in v*an't Hoff* equation. A reaction has a value of K_p=0.036 at 25°C and ΔH°_{rxn}=34.2 kJ/mol; Calculate the value of K_p at 47 °C. (R=8.314 $JK^{-1}mol^{-1}$).	**10+10**	**CO1 & CO3**

Q 11	**(a)** One mole of Cu(s) is heated from 300 K to 1500 K. calculate the entropy changes from the following data: melting point of Cu = 692 K, boiling point of Cu = 1180 K, enthalpy of fusion=7.53 kJ/mol, enthalpy of vaporization = 115.9 kJ/mol, specific heat capacity of Cu in solid, liquid and gaseous phases are 0.384, 0.512 and 0.312 J g^{-1} K^{-1} respectively, molar mass of Cu = 63.5 g mol^{-1}. **OR** Derive $dS = \frac{C_P}{T}\, dT + V\beta dP$, where β is the isothermal compressibility coefficient. Under what conditions is $dA \leq 0$ a condition that defines the spontaneity of a process? Explain. **(b)** The standard enthalpy of combustion of naphthalene ($C_{10}H_8$) is -5134 kJ/mol. Calculate the standard enthalpy of formation of naphthalene. Given that $\Delta H_f^{H_2O} = -286 \frac{kJ}{mol}$ and $\Delta H_f^{CO_2} = -393 \frac{kJ}{mol}$ **OR** Given the thermochemical equations: $H_{2(g)} + C_3H_{6(g)} \rightarrow C_3H_{8(g)} \quad \Delta H° = -134\ kJ$ $5O_{2(g)} + C_3H_{8(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)} \quad \Delta H° = -2120\ kJ$ $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H° = -286\ kJ$ Calculate the standard enthalpy of combustion of propene. **(c)** Explain how the degree of dissociation of a non-electrolyte can be determined from the measurement of a colligative property. **OR** Component P (0.6 mole) and R (0.4 mole) were mixed at 27°C to form an ideal solution. Calculate the Δ_{mix}V, Δ_{mix}G and Δ_{mix}S of the solution. (R= 2 Cal $K^{-1}mol^{-1}$).	**8+6+6**	**CO1, CO1 and CO4**