

Name:

Enrolment No:



## UNIVERSITY OF PETROLEUM AND ENERGY STUDIES

End Semester Examination, May 2019

Programme Name: B. Sc. (Hons.) Chemistry

Course Name : Physical Chemistry-II

Course Code : CHEM 1006

Nos. of page(s) : 3

Semester : II

Time : 03 hrs

Max. Marks : 100

**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.
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- 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 °C. Find out the molar mass of the solute. (Heat of fusion of ice at 0°C is 334.7 J/g and $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$ )	4	CO4
Q 5	The partial molar volumes of acetone and chloroform in a mixture ( $x_{\text{acetone}} = 0.53$ ) was $74.17 \text{ cm}^3 \text{ mol}^{-1}$ and $80.24 \text{ cm}^3 \text{ mol}^{-1}$ , 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) $\left(\frac{\partial S}{\partial V}\right)_T$		
<b>Q 8</b>	<p>(a) Given the following information:</p> $A + B \rightarrow C + D \quad \Delta H^\circ = -10.5 \text{ kJ}$ $C + D \rightarrow E \quad \Delta H^\circ = 15.0 \text{ kJ}$ <p>Calculate the <math>\Delta H^\circ</math> for each of the following reactions:</p> <p>(i) <math>2C + 2D \rightarrow 2A + 2B</math></p> <p>(ii) <math>2E \rightarrow 2A + 2B</math></p> <p>(b) The volume of an aqueous solution of KCl, at 25 °C was found to obey the relation,  <math>V/\text{cm}^3\text{kg}^{-1} = 1.03 + 16.62(m) + 1.77(m)^{3/2} + 0.12(m)^2</math>; where “m” is in mol/kg.            Find the partial molar volume of the components at <math>m = 0.1 \text{ mol kg}^{-1}</math> by explicit differentiation.</p>	2+8	CO1 & CO2
<b>Q 9</b>	<p>(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.</p> <p style="text-align: center;"><b>OR</b></p> <p><math>\Delta H_{\text{vaporization}}</math> of a substance is 45.7 kJ/mol, and its normal boiling point is 72.5°C. Calculate <math>\Delta S</math>, <math>\Delta S_{\text{surr}}</math> and <math>\Delta G</math> for the vaporization of one mole of this substance at 72.5°C and 1 atm.</p> <p>(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.</p> <p style="text-align: center;"><b>OR</b></p> <p>SO<sub>2</sub> and SO<sub>3</sub> (0.10 mole each) were mixed in a two liter flask at 300 K. Equilibrium was attained as:</p> $2\text{SO}_{2(g)} + \text{O}_{2(g)} \xrightleftharpoons{300\text{K}} 2\text{SO}_{3(g)}$ <p>The equilibrium pressure was 281.68 kPa. Find out the mole fraction of oxygen at equilibrium and the value of <math>K_p^\circ</math>.</p>	5+5	CO1 & CO3
<b>SECTION-C (Attempt all Questions; internal choice is given for question number 11)</b>			
<b>Q10</b>	<p>(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</p> <p>(b) Derive the <i>van't Hoff</i> equation. A reaction has a value of <math>K_p = 0.026</math> at 25°C and <math>\Delta H_{\text{rxn}}^\circ = 32.4 \text{ kJ/mol}</math>; Calculate the value of <math>K_p</math> at 37°C. (<math>R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}</math>).</p>	10+10	CO1 & CO3
<b>Q 11</b>	<p>(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<sup>-1</sup> K<sup>-1</sup> respectively, molar mass of Zn = 65.38 g</p>	8+6+6	CO1, CO1 and CO4

mol<sup>-1</sup>.

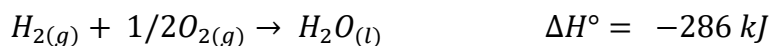
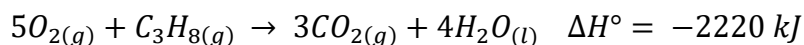
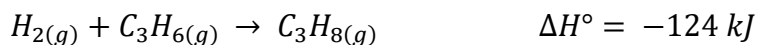
**OR**

Derive  $dS = \frac{C_V}{T} dT + \frac{\alpha}{\beta} dV$ , where  $\alpha$  and  $\beta$  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<sub>14</sub>H<sub>10</sub>) 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:




Calculate the standard enthalpy of combustion of propene.

- (c) The vapour pressures of pure CCl<sub>4</sub> and SnCl<sub>4</sub> 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<sub>4</sub> and 15 g of SnCl<sub>4</sub>. (M.W. of CCl<sub>4</sub>=154 and SnCl<sub>4</sub>=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 °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. ( $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$ )	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°C was expressed as a function of the amount "m" in one kg of solvent in the following form: $V/\text{cm}^3 = 1000.94 + 16.4 (m/\text{mol}) + 12.14 (m/\text{mol})^{3/2} - 0.0027 (m/\text{mol})^{5/2}$ 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 $\bar{C}_v = 3/2R$ . 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
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Q 7	<p>(a) What are the state and path functions? Classify the following into state and path functions:            (i) enthalpy (ii) entropy and (iii) heat capacity.</p> <p>(b) Using thermodynamic square find out the Maxwell relations of            (i) <math>\left(\frac{\partial P}{\partial S}\right)_V</math> and (ii) <math>\left(\frac{\partial P}{\partial T}\right)_V</math></p>	5+5	CO1
Q 8	<p>(a) Given the following information:  <math>A + B \rightarrow C + D \quad \Delta H^\circ = -10.5 \text{ kJ}</math>  <math>C + D \rightarrow E \quad \Delta H^\circ = 15.0 \text{ kJ}</math>            Calculate the <math>\Delta H^\circ</math> for each of the following reactions:            (i) <math>3C + 3D \rightarrow 3A + 3B</math>            (ii) <math>2E \rightarrow 2A + 2B</math></p> <p>(b) Calculate the <math>\Delta_{mix}G</math> and <math>\Delta_{mix}S</math>, for mixing the constituents of air (<math>N_2</math>-78 mole %, <math>O_2</math>-20 mol % and <math>H_2</math>-2 mole %) at 300 K, to get 2 moles of air, assuming them as ideal mixture.</p>	2+8	CO1 & CO2
Q 9	<p>(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.</p> <p style="text-align: center;"><b>OR</b></p> <p>The value of <math>\Delta H_{\text{fusion}}</math> of a substance is 35.7 kJ/mol, and its normal melting point is 20°C. Calculate <math>\Delta S</math>, <math>\Delta S_{\text{surr}}</math> and <math>\Delta G</math> for the fusion of one mole of this substance at 20°C and 1 atm.</p> <p>(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.</p> <p style="text-align: center;"><b>OR</b></p> <p>Derive the thermodynamic derivation of relation between free energy change and reaction quotient of following type.</p> $aA + bB \rightleftharpoons cC + dD$	5+5	CO1 & CO3
<b>SECTION-C (Attempt all Questions; internal choice is given for question number 11)</b>			
Q10	<p>(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).</p> <p>(b) Explain the various terms used in <i>van't Hoff</i> equation. A reaction has a value of <math>K_p=0.036</math> at 25°C and <math>\Delta H_{rxn}^\circ=34.2 \text{ kJ/mol}</math>; Calculate the value of <math>K_p</math> at 47 °C. (<math>R=8.314 \text{ JK}^{-1}\text{mol}^{-1}</math>).</p>	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<sup>-1</sup> K<sup>-1</sup> respectively, molar mass of Cu = 63.5 g mol<sup>-1</sup>.

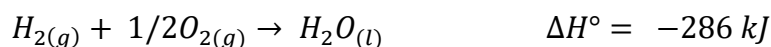
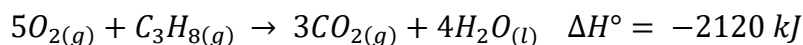
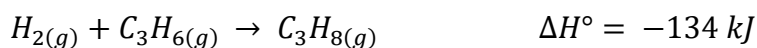
**OR**

Derived  $dS = \frac{C_P}{T} dT + V\beta dP$ , where  $\beta$  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<sub>10</sub>H<sub>8</sub>) 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:



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  $\Delta_{mix} V$ ,  $\Delta_{mix} G$  and  $\Delta_{mix} S$  of the solution. (R= 2 Cal K<sup>-1</sup>mol<sup>-1</sup>).

8+6+6

CO1,  
CO1  
and  
CO4