



JARAMOGI OGINGA ODINGA UNIVERSITY OF SCIENCE AND TECHNOLOGY
SCHOOL OF BIOLOGICAL AND PHYSICAL SCIENCES
UNIVERSITY EXAMINATION FOR THE DEGREE OF BACHELOR OF EDUCATION
SCIENCE
3RD YEAR 1ST SEMESTER 2016/2017 ACADEMIC YEAR
MAIN CAMPUS

COURSE CODE: SCH 301

COURSE TITLE: CHEMICAL THERMODYNAMICS AND EQUILIBRIUM

EXAM VENUE: LAB CHEM

STREAM: (BSC)

DATE: 20/04/16

EXAM SESSION: 2.00 – 4.00 PM

TIME: 2 HOURS

Instructions:

- 1. Answer question 1 (compulsory) and ANY other 2 questions.**
- 2. Candidates are advised not to write on the question paper.**
- 3. Candidates must hand in their answer booklets to the invigilator while in the examination room.**

Question 1 (30 marks)

- a) Define the following thermodynamic systems. (3 marks)
- Isolated system
 - Closed system
 - Open system
- b) Draw a well labeled P-V diagram for the Carnot's cycle. Using the diagram, show that the maximum net work done is expressed as:
 $W_M = RT_2 \ln V_2/V_1 - RT_1 \ln V_3/V_4$ where W_m = net work done.

(7 marks)

- c) 100g of ice at 0°C is dropped into an insulated beaker containing 150g of H₂O at 100°C. Calculate ΔS for the process that occurs, given that the heat of fusion of ice is 80 joule gram⁻¹ and the heat capacities of H₂O and ice to be 4.2 and 2.1 joule degree⁻¹gram⁻¹ respectively. (5 marks)
- d) Briefly explain the important applications of the third law of thermodynamics. What are its failures? (5 marks)
- e) The molecular heat of vaporization of H₂O is 40740 Joule gram⁻¹ at 373.3 K. Calculate the entropy change. (4 marks)
- f) Show that for a reversible process consisting of one mole of an ideal gas and involving only pressure – volume work; the entropy change at constant temperature is represented by the expression.

$$(\Delta S)_T = R \ln (P_1/P_2) \quad (6 \text{ marks})$$

- g) Explain the terms, Helmholtz Free Energy (A) and Gibbs Free Energy (G). How are they related? (4 marks)

Question 2 (20 marks)

- a) Briefly describe the properties of Gibbs free energy. (2 marks)
- b) Show that for one mole of perfect gas under isothermal process at 1 atmospheric pressure, the change in Free Energy. $\Delta G = RT \ln P$.

(4 marks)

- c) The vapour pressure of liquid A is 70 mmHg at 80°C. This vapor pressure is 0.5 mmHg greater than that of solid A at the same temperature. At 79°C, the vapour pressure of the liquid is 1.00 mmHg greater than that of solid. ΔH_{vap} is 36.0kJ (a) estimate the melting point of A. (b) Calculate the heat of fusion of A and its heat of sublimation. (4 marks)
- d) Briefly explain the significance of Clapeyron equation.

$$dP/dT = \frac{\Delta H_{\text{vap}}}{T^2} \quad (4 \text{ marks})$$

- e) Consider an equilibrium establishment in which one of the two phases is gaseous, Show how the relationship below, which is used for measurement of vapour pressure of liquids and solids can be established from Clapeyron equation. What is the relationship called?

$$\ln p_2/p_1 = \frac{\Delta H_{vap}(T_1 - T_2)}{RT_2T_1}$$

(6 marks)

Question 3

- a) Define the term chemical potential. (2 marks)
 b) Show that for a multicomponent system where moles of various components exist, Free Energy is related to chemical potential by the following equation:

$$dG = Vdp - SdT + \sum u_i dn_i$$

Where u_i = chemical potential and n = number of moles of various components.

(3 marks)

- c) Describe briefly how chemical potential can be applied to explain the behavior of an ideal solution. (3 marks)
 d) Derive the relation $F = C - P + 2$

Where the symbol F , C and P represent degree of freedom, component and phase, respectively. (4 marks)

- e) Explain the application of phase rule to the equilibrium of different phases of H_2O . Label neatly the various portions in the phase diagram. (4 marks)
 f) Using illustration(s) where possible explain how chemical potential can be used to study phase equilibrium. (4 marks)

Question 4

- a) State Henry's Law. (2 marks)
 b) Give conditions for the applicability of Henry's Law. (2 marks)
 c) Suppose that the vapor of an ideal solution contains X_A mole fraction of component A and x_b mole fraction of component B of the pure liquids A and B, respectively. If $P^{\circ} A$ and $P^{\circ} B$ are the vapors pressure of the pure liquids A and B, show that Raoult's Law implies

$$P = (P^{\circ} A - P^{\circ} B X_B + P^{\circ} A$$

P = TOTAL vapor pressure. (5 marks)

- d) Benzene and toluene for nearly ideal solutions. If at 300k, $P^{\circ}_{\text{toluene}} = 36.06 \text{ mm Hg}$ and $P^{\circ}_{\text{benzene}} = 105.0 \text{ mmHg}$. Compute the vapor pressure of the two solutions if they exist in one and two moles, respectively in the solution.
(5 marks)
- e) A mixture of acetone and carbon disulphide for, a non-ideal solution over most of the concentration range. Using a plot of vapor pressure versus mole fraction, predict the nature of deviation from Raoult's Law. Explain the expected observation(s). (6 marks)

Question 5

- a) Given that the standard free energy for the reaction shown below is -457.2 kJ , what is the equilibrium constant at 298 K ?



- b) For a certain process, $\Delta H^{\circ} = 155 \text{ kJ}$ and $\Delta S^{\circ} = 150 \text{ J/K}$. What is the minimum temperature this process will be spontaneous? (3 marks)

- c) Given the equilibrium constant, K_c , for the following reaction at 25°C ,
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad K_c = 3.6 \times 10^8$
 Calculate the equilibrium constant, K_p , for the same reaction at the same temperature. ($R = 0.08206 \text{ L}\cdot\text{atm/K}\cdot\text{mol}$). (3 marks)

- d) The equilibrium for the conversion of iso-butane and n-butane is
 $\text{n-butane} \rightleftharpoons \text{iso-butane} \quad K_1 = 2.5$
 What is the value of the equilibrium constant for the following reaction?
 $\text{iso-butane} \rightleftharpoons \text{n-butane} \quad K_2 = ?$ (3 Marks)

- e) If $K_c = 0.66$ for the reaction, $\text{NOBr}(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + 1/2 \text{ Br}_2(\text{g})$, at a particular temperature, what is K_c for the following reaction?
 $2 \text{ NOBr}(\text{g}) \rightleftharpoons 2 \text{ NO}(\text{g}) + \text{Br}_2(\text{g})$? (3 marks)

The element mercury, Hg, is a silvery liquid at room temperature. The normal freezing point of mercury is -38.9°C , and its molar enthalpy of fusion is $\Delta H_{\text{fusion}} = 2.29 \text{ kJ/mol}$. What is the entropy change of the system when 50.0 g of $\text{Hg}(\text{l})$ freezes at the normal freezing point?

(5 marks)