MACHAKOS UNIVERSITY

University Examinations 2019/2020Academic year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

FIRST YEAR FIRST SEMESTER EXAMINATION FOR

MASTER OF SCIENCE IN CHEMISTRY

SCH 803: ADVANCED CHEMICAL THERMODYNAMICS

DATE: 28/11/2019 **TIME: 2.00-5.00 PM**

INSTRUCTIONS TO CANDIDATES

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 15 marks).

SECTION A - COMPULSORY.

QUESTION ONE (30 MARKS)

a) Using examples, differentiate the following terms as used in thermodynamics

i. Species and substances (2 marks)

ii. Homogeneous mixture and a solution (2 marks)

iii. Ideal gas and a real gas (2 marks)

iv. Ideal dilute solution and an ideal liquid mixture (2 marks)

b) Discuss the concept of partial molar quantity determination (5 marks)

c) Spontaneous processes are thermodynamically irreversible. Using the concepts of thermodynamics;

i) Define a spontaneous reaction and explain **three** ways that are used to determine the spontaneity of a chemical reaction (4 marks)

ii) Given the following information at 25 ºC;

Substance	S (JK^{-1})	ΔH (kJ)
$C_{(graphite)}$	6.9	-496
$H_{2\,(g)}$	141.0	-387
$C_2H_{6\,(g)}$	241.0	-1467

Determine if the following reaction is thermodynamically possible.

$2C_{(graphite)} + 3H_{2(g)} \rightarrow C_2H_{6\,(g)}$ (5 marks)

c) At 25 ºC and 1 bar, the molar volume of pure water is 18.07 $cm^3\ mol^{-1}$ and that of pure methanol is 40.75 $cm^3\ mol^{-1}$. If 100.0 cm^3 of water was mixed with 100.0 cm^3 of methanol at 25 ºC,

i) Determine the mole fraction of pure methanol in the mixture (4 marks)

ii) Given that the partial molar volumes in the above mixture are 17.74 $cm^3\ mol^{-1}$ for water and 38.76 $cm^3\ mol^{-1}$ for pure methanol, calculate the volume of the water-methanol mixture (4 marks)

SECTION B: ANSWER ANY TWO QUESTIONS

QUESTION TWO (20 MARKS)

a) i) Derive the Debye –Huckel equation (5 marks)

ii) Explain the applications of Debye –Huckel theory (4 marks)

b) By the aid of equations, explain the fugacity of a pure gas (2 marks)

c) Derive the Gibbs- Duhem equation (4 marks)

QUESTION THREE (20 MARKS)

a) Explain three methods of evaluating the activity coefficients of nonelectrolyte substances (9 marks)

b) Show that the chemical potential of a cation is given by $\mu_+ = \mu^o_+ + RT\ln a_+ + z_+F\emptyset$ (Explain all the terms used in the equation) (6 marks)

QUESTION FOUR (20 MARKS)

a) i Calculate the vapour pressure of a solution containing 11.7 g benzene (MW = 78) and 4.6 g methylbenzene (MW = 92) at 50 °C, if the vapour pressures of the pure components at this temperature are 3.6×10^4 Nm^{-2} and 1.12×10^4 Nm^{-2}, respectively. (5 marks)

ii Using equations, show that a certain solvent obeys the Raoult's law for fugacity (5 marks)

b) The concept of entropy is used to derive an expression for the maximum efficiency of an engine. Such an engine must function in cycles. Briefly explain the Carnot Cycle and derive the formula used to calculate the efficiency of an engine (5 marks)

QUESTION FIVE (20 MARKS)

a) i) State Henry's law. (1 mark)

ii) Calculate the solubility of carbon dioxide in water at 0 °C and a pressure of 3.00 atm. The solubility of carbon dioxide is 0.348 g/100 mL in water at 0 °C and 1.00 atm. (4 marks)

b) Show that the change in Gibbs's free energy (ΔG) for a process at a constant temperature and pressure is given by $\Delta G = \Delta A + P\Delta V$ (where A is the Helmholtz Free energy function, P is pressure and V is the volume) (5 marks)

c) Derive the equation of state of a real gas and compare it with that of a real gas mixture (5 marks)