



MACHAKOS UNIVERSITY

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UNIVERSITY EXAMINATIONS 2019/2020

SCHOOL OF PURE AND APPLIED SCIENCES
DEPARTMENT OF PHYSICAL SCIENCES

FIRST YEAR EXAMINATION FOR THE DEGREE OF MASTER OF SCIENCE IN
CHEMISTRY

SCH 803: ADVANCED CHEMICAL THERMODYNAMICS

DATE: December, 2019

TIME: 2 Hours

INSTRUCTIONS:

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 20 marks).

Section A - Compulsory.

Q1. 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)

i) Ideal gas and a real gas (2 marks)

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

b) 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 (7 marks)

ii) Given the following information at 25 °C;

Substance	S (JK ⁻¹)	ΔH (kJ)
C (graphite)	6.9	-496
H ₂ (g)	141.0	-387
C ₂ H ₆ (g)	241.0	-1467

Determine if the following reaction is thermodynamically possible.



(7 marks)

c) At 25 °C and 1 bar, the molar volume of pure water is 18.07 cm³ mol⁻¹ and that of pure methanol is 40.75 cm³ mol⁻¹. If 100.0 cm³ of water was mixed with 100.0 cm³ of methanol at 25 °C,

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

iv) Given that the partial molar volumes in the above mixture are 17.74 cm³ mol⁻¹ for water and 38.76 cm³ mol⁻¹ for pure methanol, calculate the volume of the water-methanol mixture (4 marks)

Section B

Answer any two questions

Q2. 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) i) Derive the Gibbs- Duhem equation (4 marks)

Q3. 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 $\mu_+ = \mu_+^0 + RT \ln a_+ + z_+ F \phi$
(Explain all the terms used in the equation) (6 marks)

Q4. 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 $3.6 \times 10^4 \text{ Nm}^{-2}$ and $1.12 \times 10^4 \text{ Nm}^{-2}$, 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)

Q5. 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)