



MAASAI MARA UNIVERSITY

**REGULAR UNIVERSITY EXAMINATIONS
2017/2018 ACADEMIC YEAR
THIRD YEAR FIRST SEMESTER**

**SCHOOL OF SCIENCE
EXAMINATION FOR THE DEGREE OF
SCIENCE (CHEMISTRY) AND BACHELOR OF
EDUCATION (SCIENCE)**

**COURSE CODE: CHE 314
COURSE TITLE: THERMODYNAMICS AND
PHASE EQUILIBRIA**

DATE: 25TH APRIL, 2018

TIME: 0830 - 1030HRS

INSTRUCTIONS

- 1. The paper consists of four questions**
- 2. QUESTION ONE is compulsory and carries 30 marks**
- 3. Attempt any other two (2) questions, each carries 20 marks**

IMPORTANT DATA

$$C_p = 5R/2 \text{ Mol}^{-1} \text{ deg}^{-1}$$

$$C_v = 3R/2 \text{ Mol}^{-1} \text{ deg}^{-1}$$

$$R = 8.314 \text{ J Mol}^{-1} \text{ K}^{-1}$$

$$R = 0.0821 \text{ L atm. Mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

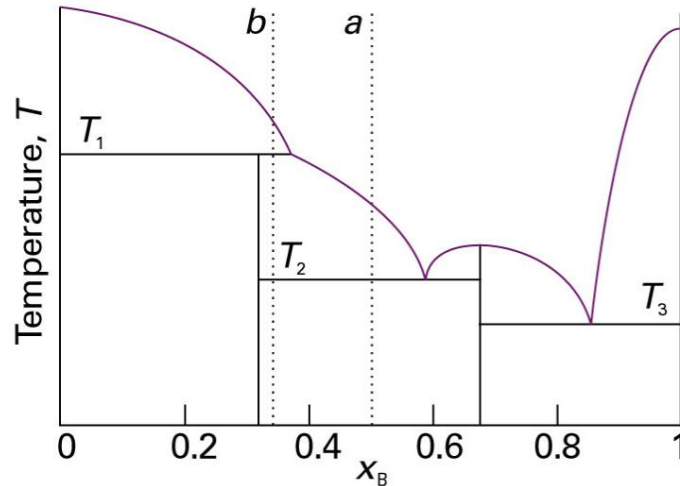
$$1 \text{ L atm} = 101.3 \text{ J}$$

$$1 \text{ atm} = 101325 \text{ Pa}$$

QUESTION 1 (30 MARKS) COMPULSORY

- a) Define the following terms
(i) Spontaneous process (ii) entropy (iii) Component (iv) Degree of freedom
[2 Marks]
- b) Calculate the change in entropy when two moles of oxygen is expanded isothermally until its volume triples. Assume the gas behaves ideal
[2 Marks]
- c) Given the standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ is 286 kJ. Calculate the entropy change of the surrounding when one mole of $\text{H}_2\text{O}(\text{l})$ is formed from its elements under standard conditions
[2 Marks]
- d) The standard molar entropies of water ice, liquid, and vapour are 37.99, 69.91 and 188.83 $\text{J K}^{-1} \text{ mol}^{-1}$, respectively. Sketch and appropriately label a graph that shows how the Gibbs energies of each of these phases vary with temperature.
[4 Marks]
- e) A certain substance X exists in two solid modifications, X_1 and X_2 , as well as liquid and vapour under a pressure of 1 atm. X_1 is stable at lower temperatures while X_2 is stable at higher temperatures. The transition from X_1 to X_2 is accompanied by an increase in molar volume. Both X_1 and X_2 are denser than the liquid phase. Draw the phase diagram for this one component system and label all the areas. (No metastable equilibria are observed.)
[5 Marks]
- f) In the chemical transformations given below, find for each the degrees of freedom. Show your reasoning and comment on the validity of your answers.
[6 Marks]
- (i) $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
- (ii) A mixture of N_2 , O_2 and NO in which the equilibrium
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ is established.
- (iii) $\text{S}(\text{rhombic}) \rightleftharpoons \text{S}(\text{monoclinic}) \rightleftharpoons \text{S}(\text{l}) \rightleftharpoons \text{S}(\text{g})$

- g) When water freezes at 0.00 °C its density changes from 1.000 g cm⁻³ to 0.917 g cm⁻³. Its enthalpy of fusion is 6.01 kJ mol⁻¹. Estimate the freezing point of water at 1000 atm. **[4 Marks]**
- h) Redraw the figure shown below in your answer book and then answer the questions which follow. The x axis should be drawn to scale



- Distinguish between congruent and incongruent melting. **[2 Marks]**
- On your figure label clearly the feature that denotes congruent melting and that which denotes incongruent melting. **[1 Mark]**
- On your figure mark the eutectic and the monotectic points. **[1 Mark]**
- What is the composition of the eutectic mixture and at what temperature does it melt? **[1 Mark]**
- What is the composition of the monotectic mixture and at what temperature does it melt? **[1 Mark]**

QUESTION 2 (20 MARKS)

- Draw and discuss the phase diagram of the carbon dioxide system **[7 Marks]**
- At 90 °C, the vapour pressure of 1,2-dimethylbenzene is 20 kPa and that of 1,3-dimethylbenzene is 18 kPa. What is the composition of a liquid mixture that boils at 90 °C when the pressure is 19 kPa? What is the composition of the vapor produced? **[8 Marks]**
- The magnesium-zinc is a two component system which involves the formation of an intermetallic compound MgZn₂. It has four phases. The melting point of Mg, MgZn₂, Zn 651, 575 and 420 °C. Draw the phase diagram for this system and label all the regions. **[5 Marks]**

QUESTION 3 (20 MARKS)

- a) A dilute solution of chloroform in acetone behaves as an ideal-dilute solution. The pure vapour pressure of acetone is 45.9 kPa at 35.2 °C. The Henry's law constant when the concentration of chloroform is expressed as a mole fraction is 19.3 kPa.
- (i) What is meant by an "ideal-dilute" solution? **[2 Marks]**
 - (ii) Calculate the vapour pressure of each component, the total pressure, and the composition of the vapour phase when the mole fraction of chloroform is 0.2, on the assumption that the conditions of the ideal-dilute solution are satisfied. **[5 Marks]**
 - (iii) Calculate ΔG of mixing for this solution. **[2 Marks]**
- b) At 39.9 °C the pure vapour pressure of ethanol is 130.4 Torr, and that of isooctane is 43.9 Torr. An ethanol-isooctane solution at 39.9 °C with $x_{\text{liquid}}(\text{ethanol}) = 0.9006$ has a vapour pressure of 185.9 Torr and $x_{\text{vapour}}(\text{ethanol}) = 0.6667$.
- (i) Calculate the activities and activity coefficients of both components in this solution on the Raoult's law basis. **[6 Marks]**
 - (ii) What do the above values of the activity coefficients indicate to you about this solution? **[2 Marks]**
- c) Four moles of an ideal gas are allowed to expand isothermally from 1 L to 10 L at 300 K. Calculate the change in free energy of the gas. **[3 Marks]**

QUESTION 4 (20 MARKS)

- a) Find $\Delta_{\text{mix}}G$, $\Delta_{\text{mix}}V$, $\Delta_{\text{mix}}S$ and $\Delta_{\text{mix}}H$ for mixing 500 g of hexane with 500 g of heptane at 30 °C. Assume an ideal solution. **[7 Marks]**
- b) (i) Define the term phase diagram **[1 Marks]**
(ii) Draw a phase diagram for a water system and label all the regions **[5 Marks]**
- c) The boiling point of water at a pressure 50 atm is 256 °C. Compare the theoretical efficiencies of a steam engine operating between the boiling point of water at **[3 Marks]**
- (i) 1 atm
 - (ii) 50 atm
- d) State the limitations of Henry's law on solubility of gases **[3 Marks]**
- e) Though eutectic mixtures have same melting points, they are not regarded as pure compounds. Explain **[1 Mark]**

END//