29

RAJARATA UNIVERSITY OF SRI LANKA

FACULTY OF APPLIED SCIENCES

B. Sc (General) Degree

Second Year Semester II Examination **(Repeat)** – April / May 2016

CHE 2201 PHYSICAL CHEMISTRY II

Answer **ALL FOUR** questions Time: **TWO** hours

Use of a non programmable calculator is permitted.

1. (a) A chemical process maintains the concentration of reactant B_2 at 1.6×10^{-6} mol dm^{-3}. B_2 reacts with another reactant A to yield AB_2 as follows

$$A + B_2 \rightarrow AB_2$$

(i) Write a differential rate equation in terms of A, B_2 and AB_2

In the above process, A is kept at a constant concentration of 8.0×10^{-6} mol dm^{-3}. If the rate constant for the reaction is 2.1×10^{-6} mol dm^{-3} at a temperature T, calculate

(ii) the rate of formation of AB_2 and (iii) the rate of consumption of B_2 at temperature T.

(iv) In a certain reaction at the same temperature T, it is necessary that the rate of formation of AB_2 should be increased to 1.1×10^{-4} mol $dm^{-3}s^{-1}$. Since the concentration of A remains constant, to what value must the B_2 concentration be changed in order to achieve this raised rate of AB_2 formation.

(30 Marks)

(b) What do you understand by the terms (i) rate constant (ii) pseudo order and (iii) mechanism of a reaction

(20 Marks)

(c) The mechanism of a reaction is shown below.

$$HOOH + I^- \rightarrow HOI + OH^- \quad \text{(slow)}$$

$$HOI + I^- \rightarrow I_2 + OH^- \quad \text{(fast)}$$

$$2OH^- + 2H_3O^+ \rightarrow 4\,H_2O \quad \text{(fast)}$$

(i) What is the overall reaction? (ii) Predict the rate law based on this mechanism (Hint: apply the steady state approximation).
(iii) Find the overall order of the reaction?

(50 Marks)

2. (a) Given a set of values of reactant concentration versus time, outline how you would determine whether the reaction exhibited first order kinetics or second order kinetics.

(30 Marks)

(b) (i) Write down the Arrhenius equation relating the rate constant k and the activation energy E_A . Explain the terms used in the equation.

(20 Marks)

(c) (ii) Describe how the activation energy could be measured experimentally and indicate how the data could be manipulated graphically to obtain a numerical estimate of E_A .

(iii) For a particular reaction. the rate constant is 1.78×10^{-4} dm^{-3} mol^{-1} s^{-1} at 190 ^{0}C and 1.38×10^{-3} dm^{-3} mol^{-1} s^{-1} at 370 ^{0}C. Evaluate the activation energy for the reaction.

(30 Marks)

(d) Explain how a catalyst serves to enhance the rate of a chemical reaction. What is the difference between heterogeneous and homogeneous catalysis?

(20 Marks)

3. (a) Define the following terms.

(i) Azeotropic mixture (ii) Triple point (iii) Eutectic point

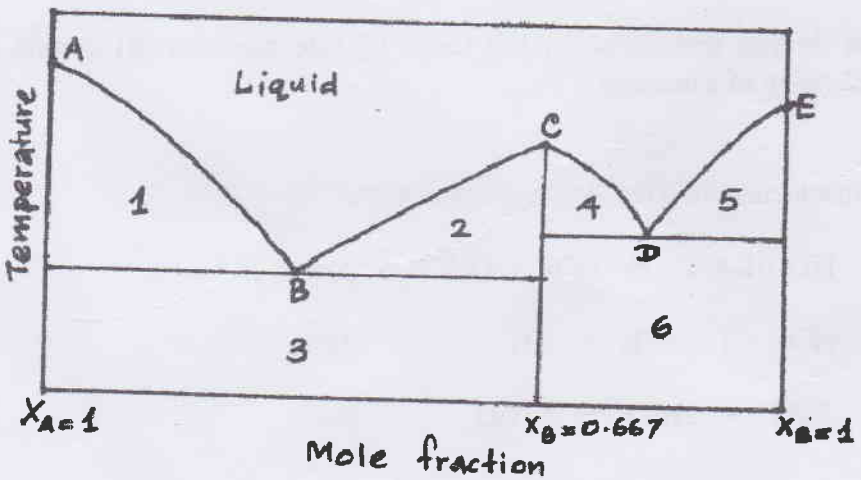
(iv) Congruent melting point

(20 Marks)

(b) Binary systems, which show a minimum or a maximum in their boiling point curves cannot be separated into pure components by fractional distillation. Explain.

(20 Marks)

(c) A phase diagram for the solid-liquid equilibria of a binary system is given below:



(i) What would be the empirical formula of the compound formed at point C?

(15 Marks)

(ii) Identify the phases present in the numbered areas 1, 2, 3, 4, 5 and 6?

(15 Marks)

(iii). Identify the figurative points A, B, C, D and E.

(15 Marks)

(iv). Calculate and interpret the degrees of freedom at point B.

(15 Marks)

4. (a) Distinguish between
(i) adsorption and absorption with an example
(ii) physisorption and chemisorption

(30 Marks)

(b) (i) Explain the mechanism of Heterogeneous catalysis with an example
(ii) Write down the expression for the Gibbs adsorption isotherm and identify all the terms in it.
(iv) Explain briefly how you would verify the validity of Freundlich Isotherm

(50 Marks)

(c) Action of soap is due to emulsification and micelle formation. Comment

(20 Marks)