82

RAJARATA UNIVERSITY OF SRI LANKA

FACULTY OF APPLIED SCIENCES

B. Sc (General) Degree

Second Year Semester II Examination – April / May 2016

CHE 2201 PHYSICAL CHEMISTRY II

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

Planck's constant (h)	$= 6.626 \times 10^{-34}$ J s
Velocity of light (c)	$= 3 \times 10^{8}$ m s^{-1}
Mass of electron (m)	$= 9.1 \times 10^{-31}$ kg
Charge of electron (e)	$= 1.602 \times 10^{-19}$ C

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 EA . Explain the terms used in the equation.

(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 EA .

(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.
(50 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)

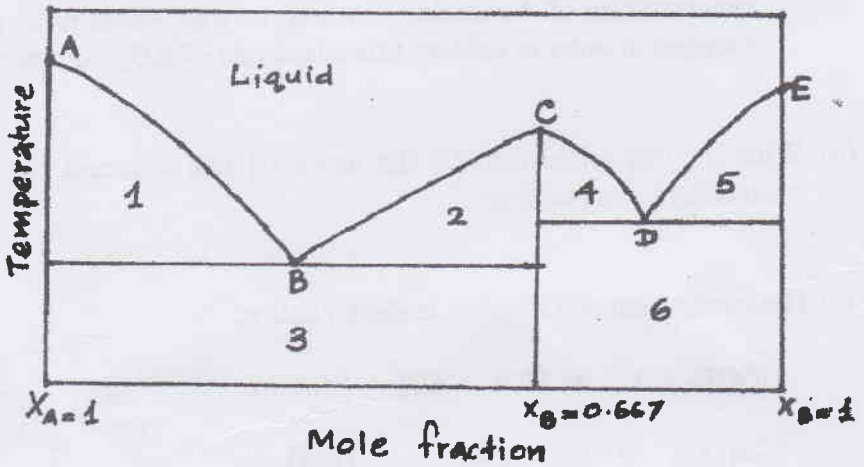
3. (a) Define the following terms.

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

(iv) Conjugate Solution: (v) 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 arks)

4. (a) De Broglie proposed that the wavelength of a particle like electron is given by $\lambda = \frac{h}{p}$, where p = mv and v, m and p are velocity, mass and momentum of an electron respectively. This hypothesis was verified experimentally through electron diffraction studies.

(i) What are the wavelengths of a microscopic particle such as electron and a macroscopic particle: Given that the velocity of an electron is 1.0×10^{6} m s^{-1}, mass and velocity of a macroscopic particle are 1.0 g and 10 cm s^{-1}, respectively.

(ii) Explain the property of values obtained for the wavelength of microscopic and macroscopic particles.

(iii) What is the De Broglie wavelength of an electron that has been accelerated through a potential difference of 100 V?

(30 Marks)

(b) (i) State the uncertainty principle.

(ii) Consider an electron moving in the 1^{st} orbital of the H atom with v= 1.0×10^{6} m s^{-1}. If the error in measurement of momentum is 1%, what is the uncertainty of position?

(iii) Mass and velocity of a large body are 0.2 kg and 10 m s^{-1}, respectively. The error in measurement is 0.1%. What is the uncertainty in the position? Comment on the values Δx, p and x.

(30 Marks)

(c) The energy of electronic levels is given by $E_n = \frac{n^2h^2}{8\,mL^2}$.

(i) Draw the energy level diagram of electronic distribution of hexatriene in a 1-D box model. L is the length of the molecule = 0.72 nm.

(ii) Calculate the wavelength of the molecule.

(iii) What will be the observation of the wavelength of butadiene? (Hint: reduced conjugation)

(40 Marks)

5. (a) (i) Write down the Clausius-Clapeyronequation for a univariant phase change, defining the symbols used. State the conditions under which this equation is applicable.

(15 Marks)

(ii) The vapour pressure of benzene is 0.153×10^5 N m^{-2} at 303 K and is 0.520×10^5 N m^{-2} at 313 K. Calculate the mean molar heat of evaporation of benzene over this temperature change.

(25 Marks)

(b) (i) Consider any two successive energy states identified by the quantum numbers n and (n+1), show that $\Delta E = \frac{h^2}{8\,mL^2}(2n+1)$

(iii) Write down the "zero point energy" expression for any particle constrained to move in a finite region.

(iv) What is the ground state energy for an electron that is confined to a 1-D box of length of 0.2 nm?

(v) Show that wave function $\phi = A \sin(kx) + B \cos(kx)$ is a general solution to the equation $\frac{d^2\emptyset}{dx^2} + k^2\emptyset = 0$, where $k^2 = \frac{8\pi^2 m}{h^2} E$ and A, B are the arbitrary constants introduced during integration.

(60 Marks)