RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. in Applied Sciences
Second Year Semester II Examination– September/ October 2020

CHE 2201 – PHYSICAL CHEMISTRY II

Answer any **FOUR** questions. Time: Two (02) hours

$R = 8.314\ J\ K^{-1}\ mol^{-1}$, $F = 96{,}485\ C\ mol^{-1}$
A non-programmable calculator is permitted

1.

(a) What is time independent Schrödinger's equation?

(20 marks)

(b) Given $\varphi(x) = Acos(Bx)$. Find the eigenvalue of the operator $\hat{C} = \frac{d^2}{dx^2}$. Find out whether $\hat{C} = \frac{d}{dx}$. is an eigen operator.

(20 marks)

(c) Find the voltage of electrons in an electron microscope have to be accelerated to get a wavelength of 0.1 nm. An electron is confined to a one-dimensional, infinitely deep potential energy well of width x = 50 pm.

(i) What is the least energy (in eV) the electron can have?

(ii) Compute the energy level of the first excited state and the second excited state. Draw the energy level diagram.

(60 marks)

2.

(a) (i) State the Gibbs phase rule and define the terms

(20 marks)

(ii) Determine the number of degrees of freedom (i) at the triple point of water and (ii) for CH_3COOH dissolved in water

(20 marks)

(b) Draw pressure vs. composition diagram for a solution composed of $C_2H_4Cl_2$ and C_2H_5OH if (i) pressure at each composition is calculated according to Roults law and (ii) the solution deviates from Raoult's law in the positive direction. ($C_2H_4Cl_2$ is more volatile than C_2H_5OH)

(20 marks)

(c) Draw and label temperature vs. composition phase diagrams for (i) and (ii) in part (b)

(20 marks)

(d) Partially miscible liquids A and B form upper consolute point of its phase diagram. Mixing of 25 g of A and 60 g of B forms two phases at 25°C. If the weight of B in phase I is 15% and that of B in phase II is 80%. Draw the phase diagram and calculate the masses of each phase in equilibrium.

(20 marks)

3.

(a) (i) Derive the integrated form of Clausias-Clapeyron equation for a solid⇋ liquid equilibrium system. Given that, $\frac{dP}{dT} = \frac{\overline{\Delta S}}{\overline{\Delta V}}$

(30 marks)

(ii) The heat of vaporization of hexane is 30.8 kJ mol^{-1}. The boiling point of hexane at a pressure of 1.00 atm is 68.9℃. What will be the boiling point at a pressure of 0.50 atm?

(20 marks)

(b) (i) Use an appropriate phase diagram to explain the fractional distillation of ethanol-water mixture.

(25 marks)

(ii) A mixture of water and acetone at 0.99 atm boils at 70 °C. Calculate the percentage composition of the mixture. Vapour pressure of acetone and water at 70 °C are 1.58 atm and 0.312 atm respectively.

(25 marks)

4.

(a) The process of breathing maintains the concentration of O_2 in human blood in the lungs at 1.6×10^{-6} mol of O_2 per dm^3 of blood. The O_2 reacts with haemoglobin (Hb) to yield oxy haemoglobin (HbO_2)

Hb concentration in the lungs is kept constant at 8.0×10^{-6} mol dm^{-3}. The rate constant of the reaction at body temperature is 2.1×10^{6} dm^3 $mol^{-1}s^{-1}$.

(i) Write the differential rate law for the formation of HbO_2

(10 marks)

(ii) Calculate the rate of formation of HbO_2 and the rate of consumption of O_2

(10 marks)

(iii) In certain illnesses it is necessary that the rate of formation of HbO_2 should be increased to 1.1×10^{-4} dm^3 $mol^{-1}s^{-1}$ since the Hb concentration remains constant. To what value must the concentration of O_2 be changed in order to increase the rate of formation of HbO_2

(20 marks)

(b) (i) Derive the integrated rate law for the first order reaction, A→P

(20 marks)

(ii) How do you experimentally prove that the above reaction follows first-order kinetics?

(20 marks)

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(iii) If 3.0 g of substance **A** decomposes for 36 minutes the mass of unreacted **A** remaining is found to be 0.375 g. What is the half life of this reaction if it follows first-order kinetics?

(20 marks)

5.

(a) (i) What do you understand by the term "mechanism" of a reaction?

(10 marks)

(ii) The decomposition of ozone dramatically changes in the presence of chlorine atoms as a catalyst as follows.

$$Cl + O_3 \xrightarrow{k_1} ClO + O_2$$

$$ClO + O \xrightarrow{k_2} Cl + O_2$$

Write the net reaction and show how rate equation for the O_3 decomposition is obtained by using the steady-state approximation.

(30 marks)

(b) (i) Explain the effect of temperature and a catalyst on a rate of a reaction

(30 marks)

(ii) For the gas-phase reaction, $H_2 + I_2 \rightarrow 2\ HI$, rate constants at temperature of 373.15 K, and 473.15 K are 8.74×10^{-15} L mol^{-1} s^{-1} and 9.53×10^{-10} L mol^{-1} s^{-1} respectively. Evaluate the Arrhenius parameters for the above reaction.

(30 marks)