M.Sc. 2nd Semester Examination, 2021

CHEMISTRY

(Physical Chemistry Practical)

Paper: CHEM 205C (PR)

Course ID: 21465

Time: 2 Hours **Full Marks: 40**

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any four* of the following questions: 10×4 = 40

   a) Establish the relation between dissociation constant and degree of dissociation of a weak acid and hence elaborate the Ostwald's dilution law. How can you determine the degree of dissociation of a weak electrolyte experimentally? How does the degree of dissociation vary with temperature? 3+2+3+2 = 10

   b) What is the significance of $\wedge_o$? Explain how you will proceed to determine $\wedge_o$ for (i) NaCl and (ii) CH_3COOH. The thermodynamic dissociation constant of acetic acid is 1.75×10^{-5}. Calculate using Debye-Huckel theory, the degree of dissociation of 0.001M acetic acid in 0.05M $Ca(NO_3)_2$ [A = 0.51]. 2+4+4 = 10

   c) Write down the procedure to determine the cell constant of a conductivity cell. Describe the procedure in detail to determine λ_o of a weak electrolyte from a set of conductivity data of the weak electrolyte itself. What are the units of equivalent conductance and molar conductance? Write down the relation between these two. 2+4+2+2 = 10

d) For the reaction, A + B → products (initial concentrations of A & B are different) solve the rate equation and hence find the expression of the rate constant. What would happen if B is in large excess? Explain. What would be the order of the reaction if the rate constant has the unit mol dm^{-3} s^{-1}? How long will a first order reaction take to complete 85% of reaction, if it takes 20 minutes for 25% completion? 4+2+1+3 = 10

e) What do you mean by primary kinetic salt effect? Write down the relevant equation and explain each term. Discuss the effect of the charge of the reactant ions on the reaction rate. Demonstrate graphically the primary kinetic salt effect of the reaction, $[CO(NH_3)_5Br]^{2+}$ + Hg^{2+} → Product(s) and mention the slope value. Calculate the ratio of rate constants of the reaction, A^{+1} + B^{-2} → product, studied at 25°C in two water media with ionic strengths 0.001 and 0.01.

1+2+3+2+2 = 10

f) A first order process X → product requires 16 seconds for 75% decomposition. What is the half-life for the process? Two reactions have the same energy of activation but the entropies of activation differ by 10 SI units. Compare the specific rate constants for the two reactions.

Justify:

A) Zero order reaction is usually a multistep reaction.

B) Reaction of third and higher orders is usually not common.

2+4+2+2 = 10