

M.Sc. 4th Semester Examination, 2021

CHEMISTRY

(Physical Chemistry Practical)

Paper: CHEM 405E (PR)

Course ID: 41465

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) Distinguish between order and molecularity. What is a pseudo-first order reaction? Why is rate constant of hydrolysis of ester dependent on catalyst concentration? How does rate constant vary with temperature? What is the dimension of rate constant which follows an n -th order rate equation?

3+2+2+2+1 = 10

b) Define specific and equivalent conductance. How do they change with dilution? What is the physical significance of Λ_0 ? Calculate the ionic strength of a solution by mixing 50 mL of 0.02 M $K_4Fe(CN)_6$ and 50 mL of 0.03 M $K_3Fe(CN)_6$.

2+3+2+3 = 10

c) Define standard and formal potential. What are the advantages of calomel electrode? At 25°C, the standard electrode potential for the Ag^+/Ag electrode is 0.7991V and solubility product of AgI is 8.2×10^{-17} . Calculate the standard electrode potential for $I^-/AgI/Ag$. "EMF is an extensive property"- comment.

2+2+4+2 = 10

- d) What are acid-base indicators? What is the mechanism behind colour change of an indicator? 'For strong acid weak base titration methyl orange is suitable, but for weak acid strong base phenolphthalein is suitable' – why? Distinguish between absorption and adsorption. 2+3+3+2 = 10
- e) State the “bottle-neck” principle in kinetics. Discuss quantitatively the effect of addition of KCl solution on the rate of the reaction, $S_2O_8^{2-} + 2I^- = I_2 + 2SO_4^{2-}$. The first order rate constant (k) for pyrolysis of t-butyl chloroacetate follows the equation,
 $\log k (\text{min}^{-1}) = 33.91 - 18000/T$
 (i) How long will it take for one mole to decompose 75% at 227°C.
 (ii) Calculate the energy of activation. 2+4+(2+2) = 10
- f) Explain the term photosensitization. Give one example of a photosensitized process which is of immense utility to mankind. What are the main differences between “fluorescence” and “phosphorescence”. On irradiation of propionaldehyde at 30°C with light having wavelength of 3020 Å, the quantum yield for CO is estimated to be 0.54. The intensity of incident light is 15,000 erg/s. Find the rate of formation of CO. 2+1+2+2+3 = 10
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