M.Sc. 1st Semester Examination, 2021

CHEMISTRY

Course Title: Physical Chemistry

Course Code: CHEM 103C

Course ID: 11453

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 five* of the followings: 2×5 = 10

(a) Write down the full mathematical expression of ion association constant for an electrolyte in solution. Define each term associated in the said expression.

(b) If the activity co-efficient for $CaCl_2$ in 0.1 M solution is 0.515, what is the mean activity co-efficient of the ion?

(c) Write down the Tafel equation, which relates current and over potential for any electrolytic solution.

(d) Show that $[x^n, p_x] = \frac{1}{2\pi i} n x^{n-1}$, where n is positive.

(e) What is the wavelength of an H^+ ion (mass = 1.7×10^{-27} kg) moving with a velocity equal to (1/100)-th of that of the light?

(f) Write down Hammett Equation. What is its limitation?

(g) Explain the influence of dielectric constant of a solution on the rate of a bimolecular reaction.

2. Answer *any four* of the followings: 5×4 = 20

(a) (i) Prove that S_2 and i operations are effectively same.

(ii) What do you mean by indistinguishable configurations in group theory? 3+2 = 5

(b) What do you mean by a 'symmetry element' and a 'symmetry operation'? Find out the symmetry elements present in the following molecules: (i) NH_3 and (ii) H_2O. 2+3 = 5

(c) Calculate the average potential and kinetic energies of a harmonic oscillator in the ground state. Compare these with the classical results. 5

(d) Outline briefly Lindeman scheme for determining the rate constant of a gas phase reaction: 'A $\rightarrow$ B'. Show that the reaction obeys a first order kinetics at high pressure. What will be its order at low pressure? 3+1+1 = 5

(e) Derive the expression of rate constant according to double sphere activated complex model. What are the limitations of this model? 4+1 = 5

(f) (i) Show that the operator $\hat{p}_x$ for linear momentum is Hermitian. What is its physical significance? 3

(ii) Prove that the operator $\frac{h}{2\pi i} x\left(-\frac{d}{dx}\right)$ is not Hermitian. 2

3. Answer *any one* of the followings: 10×1 = 10

(a) (i) Define symmetry factor (β) for an electron-transfer reaction. From that, derive the popular Butler-Volmer equation, which relates the electric field and the rate of electron transfer for an electrolyte solution.

(ii) What are the limitations of collision theory?

(iii) Write down the expression of rate constant of a reaction according to Transition-State Theory. Explain the terms therein. (1+4)+2+3 = 10

(b) (i) For a particle in the states n = 2 and 3 of a one dimensional box of length L, find the probabilities that the particle is in the region $0 \leq x \leq L/4$.

(ii) Explain the influence of pressure on reaction rate in terms of volume of activation. Show the correlation graphically between volume of activation and entropy of activation for reaction in aqueous solution**.** 5+(3+2) = 10