POSTGRADUATE SECOND SEMESTER EXAMINATION, 2022

CHEMISTRY

Course Code: CHEM 203C **Course ID: 21453**

Physical Chemistry

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 following questions: 2×5 = 10

   a) For azulene, fluorescence is observed for S_2 to S_0 transition. Comment.

   b) Define triplet state lifetime for a fluorescent molecule. How does it differ from radiative lifetime?

   c) Mention the main differences between a grand canonical and a micro-canonical ensemble.

   d) Why is silicon extensively used as semiconducting materials now-a-days?

   e) What are the limitations of X-ray powder diffraction (XRD)?

   f) Show that the first order reaction never goes to completion.

   g) Two reactions of the same order have identical activation energy but their entropies of activation differ by 100 $JK^{-1}mol^{-1}$. Calculate the ratio of their rate constants at any temperature.

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

   a) In a sample of atomic hydrogen, at 25°C, what proportion of atoms are in the first excited electronic state if it lays 1000 kJ mol^{-1} above the ground state? 5

   b) Establish the expression of equilibrium constant for any chemical reaction in terms of partition functions. 5

   c) Define and elaborate excimers and exciplexes. Write down the Stern-Volmer equation defining the terms therein. What is the unit of Stern-Volmer constant? 3+1+1 = 5

d) (i) Define N-type semiconductor with example.

(ii) Define Frenkel defect. Give one example.

(iii) Write two importance applications of superconducting materials. 2+2+1 = 5

e) Calculate the values of $\langle x \rangle$ and $\langle p_x \rangle$ for the simple harmonic oscillator in its ground state. 5

f) The quantum yield for the photochemical decomposition of HI is 0.2. In an experiment 0.01 moles of HI are decomposed. Calculate the number of photons absorbed. 5

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

a) (i) From equipartition law, estimate the molar heat capacity of water-vapour at 373 K, given,

θ_v = 5300, 2300 and 5400 K

θ_r = 40, 21 and 13 K.

Furnish proper justifications in each step.

(ii) Define dynamic quenching. How will you distinguish it from static quenching?

(iii) At least three energy levels are required for a LASER radiation. Explain.

5+2.5+2.5 = 10

b) (i) Discuss the Rice-Ramsperger-Kassel treatment for unimolecular reaction.

(ii) Explain graphically the effect of temperature on super conductor.

(iii) How many symmetry elements are there in a simple cube? Explain.

(iv) Define doping. 5+2+2+1 = 10