M.Sc. 2nd Semester Examination, 2021

CHEMISTRY

(Physical Chemistry)

Paper: CHEM 203C

Course Id: 21453

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) Mention the difference between the canonical and micro-canonical ensembles.

   b) Show that the thermal de-Broglie wavelength of a particle of mass 'm' at temperature T has the dimension of length.

   c) How is the light absorption related to the transmittance of a sample?

   d) Define constructive interference.

   e) What is doping? Give an example.

   f) Two reactions of the same order have identical activation energy but their entropies of activation differ by 50 $JK^{-1}mol^{-1}$. Calculate the ratio of their rate constants.

   g) The half-life of a reaction does not depend on the initial concentration of the reactants. Find the order of the reaction.

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

   a) Calculate the number of thermally accessible quantum levels for the translational motion of H_2 molecule confined to a 1000 cm^3 vessel at room temperature (25°C). 5

   b) Establish the Sackur-Tetrode equation for an ideal monoatomic gas. Mention its physical significance. 4+1 = 5

c) Define the terms: absorption, emission and excitation spectra. What do you mean by Stokes shift for a fluorescent molecule? Show it pictorially. 3+1+1 = 5

d) (i) Explain graphically the effect of temperature on semiconductor and super conductor.

(ii) What are the limitations of X-ray diffraction (XRD)? 3+2 = 5

e) For unimolecular reactions, discuss the Hinshelwood's treatment over the Lindemann-Christiansen hypothesis. 5

f) The quantum yield for the photochemical decomposition $2HI \longrightarrow H_2 + I_2$ at λ = 254 nm is 1.99. If 3070 J of energy is absorbed, find the number of moles of HI decomposed. 5

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

a) (i) Calculate the fraction of $N_2(g)$ molecules in the v = 0 and v = 1 vibrational states at 300 K. [Given, θ_v of N_2 = 3374 K]

(ii) Define excitation energy transfer. State the difference between radiative and non-radiative energy transfer.

(iii) Monochromatic light is passed through a cell (1 mm path length) containing 0.005 mol/dm^3 solution. The light intensity is reduced to 16%. Calculate the molar extinction co-efficient of the sample. What would be the transmittance if the path length is 2 mm? 3+(2+2)+3 = 10

b) (i) Some amount of heat is added to 1 mole of copper (Cu) at 0K that causes the temperature of Cu to rise to 0.02K. Find the number of microstates accessible to the Cu atoms. Molar specific heat of Cu is, $C_v = (7\times10^{-4}T)$ J.

(ii) Justify the following:

(A) Delayed fluorescence does not normally occur in aromatic hydrocarbons.

(B) The rate of solvent relaxation depends on solvent viscosity.

(C) For fluorophores, the excitation spectrum is usually identical in shape to their absorption spectrum. 4+(2+2+2) = 10