P.G. Semester-II Examination, 2023

CHEMISTRY

Course ID : 21453 **Course Code : CHEM203C**

Course Title : Physical Chemistry

Time : 2 Hours Full Marks : 40

The figures in the right-hand margin indicate 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) Write the equivalent points for the following operations:

      (i) *c* glide perpendicular to *a* axis

      (ii) 2_1 screw parallel to *b* axis

   f) Draw stereographic projections for the following point groups :

      (i) mm2 (ii) 3m

   g) Two reactions of the same order have identical activation energies whereas entropies of activation differs by 50 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) Calculate the number of thermally accessible quantum levels for the translational motion of H_2 molecule confined to a 2000 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) Why does atomic scattering factor (f_a) vary with resolution ($\sin\theta/\lambda$)? Plot a graph of f_a vs. $\sin\theta/\lambda$ for sulphur, selenium and tellurium atoms.

(ii) Identify systematic absences for a BCC lattice. (2+l)+2=5

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

f) Show that the ground state wave function $\psi_0 = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\alpha x^2}$ is an eigen-function of the operator corresponding to one dimensional harmonic oscillator with eigen-value, $\frac{1}{2}h\nu_0$. 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) What is Brillouin zone?

ii) Calculate the difference in Bragg angle θ, for the α_1 and α_2 reflections from the same (*hkl*) planes for Cu $K\alpha_1\left(\lambda = 1.54050\,\text{Å}\right)$ and Cu $K\alpha_2\left(\lambda = 1.54434\,\text{Å}\right)$ when α_1 reflection appears at (i) 45° and (ii) 60°.

iii) 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. l+3+(2+2+2)=10

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