B. Sc. Chemistry Examination, 2022

(3rd Year, 6th Semester, CBCS, Supplementary)

Chemistry

Paper – DSE/Chem/TH/03

Photo Chemistry - II and Spectroscopy + Statiistical Thermodynamics

Time : Two hours Full Marks : 40

Use a separate answer script for each unit.

UNIT – 6031-P

1. a) Derive general spectroscopic selection rules for the particle in a box system with a symmetric potential energy function. Show that the strength of interaction between a charge distribution and an electric field depends on the dipole moment of the charge distribution. 2+2

   b) Define molecular polarizability. Show that change in molecular polarizability is essential for Raman activity. If the bond length of H_2 is 0·07417 nm, what would be the spacings of the lines in pure rotational Raman spectrum of H_2? 1+2+2

   c) In vibration-rotation spectrum $(v = 0 \rightarrow 1)$ of HF, the rotational constants are found to be slightly different, $B_{v=0} = 20.6\ \text{cm}^{-1}$ and $B_{v=1} = 19.8\ \text{cm}^{-1}$. Calculate the percentage increase of bond length on going from $v = 0$ to 1. What effect does this lengthing of the bond have on the spacing of the lines for the P- and R-branch spectra? 2+2

   d) The vibrational wavenumbers of the following molecules in their $v = 0$ states are: HCl: 2885 cm^{-1}; DCl: 1990 cm^{-1}; D_2: 2990 cm^{-1} and HD: 3627 cm^{-1}. Calculate the energy change, in kJ.mol^{-1}, of the reaction $\text{HCl} + \text{D}_2 \rightarrow \text{DCl} + \text{HD}$, and determine whether energy is liberated or absorbed. 2

   e) Why do microwave studies give directly an estimate of the abundance of isotopes by comparison of absorption intensities? 2

   f) Show that the rate constant of a unimolecular photochemical reaction can be simply expressed by the inverse of lifetime of the reactive species when the reaction with unit quantum yield occurs entirely from the state reached by the absorption. 3

UNIT – 6032-P

2. (a) Describe briefly a macro-state and a microstate of a classical thermodynamic system.

   (b) Define an ensemble and name ensembles for an open system and an isolated system.

   (c) Write a brief note on Gamma-phase space.

   (d) The canonical distribution function for a closed thermodynamic system is given by, $P_j = \frac{e^{-\beta E_j}}{Q}$. Establish the expression involving P_j for average entropy of the system. [E_j is the energy of the system in its j[th] state, Q is the canonical ensemble partition function and $\beta = 1/k_B T$.] 3+2+2+3

3. (a) Describe the basic assumptions of Einstein's model to describe temperature dependence of specific heat of simple molecular solids at lower temperature range.

   (b) Find an expression for pressure of a gaseous system contained in volume V, at temperature T, containing N particles, each with individual mass m. The canonical partition function associated with the system is given as,

$$Q = \left(\frac{V - Nb}{N}\right)^N \cdot \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} e^{\frac{N^2 a}{V k_B T}};$$

   (a, b : *two constants; Other symbols have their usual meanings*)

   (c) State the statistical mechanical definition of thermodynamic temperature of a system. Comment on whether a system may be associated with negative absolute temperature value under some special condition. 3+4+3