WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 6th Semester Examination, 2021

CEMACOR14T-CHEMISTRY (CC14)

PHYSICAL CHEMISTRY-IV

Time Allotted: 2 Hours | Full Marks: 40

The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

Answer any *three* questions taking *one* from each unit

UNIT-I

1. (a) Draw schematically the Potential energy diagram of an anharmonic oscillator indicating hot band transition and dissociation energy. For HF molecule with anharmonicity constant 0.0218 and equilibrium oscillation frequency of 2990 cm^{-1}, find the vibrational quantum number at the dissociation level. 4

   (b) The rotational Raman spectra of $^{35}Cl_2$ has a spacing of 2.94 cm^{-1} between the 1st Stokes and Anti-Stokes line. What will be the bond length of the molecule? How will the spacing change on replacing Cl by its heavier isotope? 3

   (c) State the difference between NMR and ESR spectroscopy in terms of (i) population ratio of the two levels (ii) line frequency. 3

   (d) The most intense line of a rotational transition of HCl is the 10 to 11 transition at 25°C. Will the position of this line change on (i) replacing H by D (ii) increasing the temperature. 4

2. (a) The first vibrational transition of $^{1}H^{35}Cl$ is 2886 cm^{-1}. Calculate the wave number for the same transition in CO taking the force constant to be 20% higher than that for HCl. Also calculate the ratio of the zero-point energy for HCl to that of CO. 2+2

   (b) The difference in population between the α and β spin states of an electron in ESR spectroscopy is very low. But the system does not saturate. Explain why? 2

   (c) Predict the intensity distribution in the hyperfine splitting lines of the ESR spectrum of the radical CD_3 (I = 1 for D). 3

   (d) Will the frequency of rotation of the molecules $^{1}H^{35}Cl$ and $^{2}H^{35}Cl$ differ in the (i) ground state (ii) 1st excited state? 3

   (e) How does the infrared spectrum of a molecule differ in case of a harmonic and an anharmonic oscillator model? 2

UNIT-II

3. (a) How will the molar absorbance of a sample at a particular wavelength change if the solution is half diluted and the path length is doubled? Will its value change with the change in wavelength of the incident light? 3

(b) Draw the $1/\Phi$ vs [M] plot for the reaction $A \rightarrow B + C$ having the following mechanism and indicate the value of slope, and intercept. 3

(i) $A \xrightarrow{h\nu} A^*$

(ii) $A^* + M \xrightarrow{k_1} M + A$

(iii) $A^* \xrightarrow{k_2} B + C$

(c) Name the processes involved in singlet to singlet and singlet to triplet transition. Which of these processes will be enhanced in presence of iodine atom in the system? 3

(d) In a photochemical reaction A → 2B + C, the quantum yield with 500 nm light is 2.1×10^2. If 2.28 moles of B is formed upon exposure to light, how many photons were absorbed by A? 3

4. (a) For a particular cell, E at 20°C, 25°C and 30°C are 0.0663V, 0.06839V and 0.07045V respectively. Calculate ΔG, ΔS and ΔH for the reaction at 25°C. 5

(b) The absorption spectra of O_2 shows a vibration structure with continuum at 56876 cm^{-1}. The upper electronic state dissociates into one ground state and one excited state atom (Excitation energy of atom is 15875 cm^{-1}). Estimate the ground state dissociation energy of oxygen in KJ/mole. Explain your answer with proper diagram. 2+2

(c) Name the phenomenon where an electronic spectra gives a continuum in-between two regions of line spectra. 1

(d) The photochemical reaction $SO_2 + Cl_2 \rightarrow SO_2Cl_2$, $\Phi = 1$. Will the rate of this reaction be temperature dependent? Explain your answer. 2

UNIT-III

5. (a) Define surface excess. Derive Laplace's equation of excess pressure inside a spherical bubble, suspended in air. 1+3

(b) Justify/criticize: When work of adhesion is greater than half of the work of cohesion, wetting occurs. 3

(c) Using Stern model of electric double layer, describe zeta potential of a colloidal system. How is zeta potential and coagulation affected by adsorption of oppositely charged ions on the colloidal surface. 4

(d) A quartz particle of diameter 1×10^{-14} cm in aqueous suspension at 25°C ($\eta_w = 0.8903$ CP) migrate with a velocity of 3×10^{-3} cm/sec under an applied potential gradient of 10 V/cm. Calculate the zeta potential. (Given, the dielectric constant of water is 78.30) 3