लक्ष्यं विश्रमानम्

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 6th Semester Examination, 2023

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) The first rotational spectral line of CO (C = 12.00, O = 16.00) appears at 3.842 cm^{-1} at 298 K. Explain the effect on the first rotational spectral line if the carbon atom of the molecule is replaced with its higher isotope, that is, $^{13}C^{16}O$. 2

   (b) How many normal modes of vibration are possible for (i) HBr (ii) OCS (linear) (iii) SO_2 (bent)? 1+1+1

   (c) Show that a diatomic molecule dissociates into atoms if it is present in the vibration state of vibrational quantum number (v) 3

$$v = \frac{1}{2x_e} - \frac{1}{2}$$

   where, x_e is the anharmonicity constant.

   (d) The molecule $^{14}N^{16}O$ when subjected to IR radiation shows absorption at 1876.06 cm^{-1} and 3724.20 cm^{-1} as fundamental and first overtone respectively. Calculate 4

   (i) the equilibrium vibrational frequency.
   (ii) anharmonicity constant.
   (iii) zero-point energy.
   (iv) the position of the first 'hot band'.

   (e) How can you differentiate between $^{\cdot}CH_3$ radical and $^{\cdot}CD_3$ radical using ESR spectroscopy? ($I = \frac{1}{2}$ for H, $I = 1$ for D). 2

2. (a) Which of the following molecule(s) are microwave active? State with reason. 2

   D_2 , D_2O , CCl_4 , SF_6

   (b) Explain how does the position of the most intense rotational line of HCl change due to 2

   (i) isotopic substitution of H by D
   (ii) decrease of temperature.

(c) A linear molecule having the formula AB_2 is suspected to have the structure either BAB or BBA. How can you ascertain the structure to the molecule using its IR and Raman spectra? 3

(d) The vibrational energy levels of a diatomic molecule are given as 2

$$\varepsilon_v(\text{cm}^{-1}) = 215.02\left(v+\frac{1}{2}\right)\left[1-0.0038\left(v+\frac{1}{2}\right)\right]$$

Find the zero-point energy of the molecule in eV.

(e) The ^{1}H-NMR spectrum of dimethyl nitrosoamine [O=N–N$(CH_3)_2$] shows two peaks at low temperature but only one peak at higher temperature (~ 200°C). — Explain. 2

(f) The Larmor frequency of ^{1}H at 1 tesla (T) is 42.57 MHz. If the magnetogyric ratios for ^{1}H and ^{13}C are 26.75×10^7 rad.T^{-1}.s^{-1} and 6.72×10^7 rad.T^{-1}.s^{-1}, respectively. What is the Larmor frequency of ^{13}C, in MHz at 1 tesla? 3

UNIT-II

3. (a) What do you mean by photostationary state? How is it different from a chemical equilibrium? 2

(b) The mechanism for photochemical decomposition of HI may be outlined as follows 2+1

$$HI + h\nu \longrightarrow H + I$$

$$H + HI \longrightarrow H_2 + I \text{ (rate constant } k_2)$$

$$I + I \longrightarrow I_2 \text{ (rate constant } k_3)$$

Show that the quantum efficiency with respect to decomposition of HI is equal to 2. Is a quantum efficiency greater than unity acceptable? Justify your answer.

(c) Define molar absorptivity. Is it an intensive property? On what factors does it depend? 3

(d) A dye solution of concentration 0.74 mgL^{-1} absorbs 40% of radiation of wavelength 610 nm in a cell of thickness 1 cm. Calculate (i) the molar mass of the dye compound, (ii) the energy of one einstein in the incident radiation in S.I. unit. (Given: $\varepsilon = 9.6 \times 10^4$ M^{-1}cm^{-1}) 2+2

4. (a) State and explain Franck-Condon principle. 2

(b) Dimerization of Anthracene attains photostationary state. The plausible mechanism of the dianthracene formation is 3

$$A + h\nu \longrightarrow A^* \qquad \text{Rate} = I_a$$

$$A^* + A \xrightarrow{k_2} A_2 \qquad k_2 \text{ is rate constant}$$

$$A^* \xrightarrow{k_3} A + h\nu' \qquad k_3 \text{ is rate constant}$$

$$A_2 \xrightarrow{k_4} 2A \qquad k_4 \text{ is rate constant}$$

where, A is Anthracene monomer and A_2 is dianthracene and A^* is photoexcited state of Anthracence. Show that at very high concentration of Anthracene monomer, the concentration of dianthracene is independent of monomer concentration.

(c) The quantum yield for the photodissociation of ICN(g) into I(g) and CN(g) by a 306 nm pump pulse is 1.00. If the radiant energy of the pump pulse is 1.55×10^{-4} J, determine the number of CN(g) radicals created per pulse if only 0.100% of the incident light is absorbed by the ICN(g) sample. 3

(d) Compare and contrast (with suitable reasoning) between fluorescence and phosphorescence with reference to the following points: 4
(i) wavelength, (ii) intensity, (iii) radiative lifetime, (iv) temperature at which they are usually observed.

UNIT-III

5. (a) Show that the surface tension and surface energy of a liquid are numerically equal. 2

(b) Show that the work of adhesion between two immiscible liquid phases α and β is given as 3

$$w_A^{\alpha\beta} = \frac{1}{2}(w_C^{\alpha} + w_C^{\beta}) - \gamma^{\alpha\beta}$$

where, w_C^{α} and w_C^{β} denote the work of cohesion for phases α and β, respectively, and $\gamma^{\alpha\beta}$ denotes the interfacial tension between the two phases. Hence comment on the condition for miscibility of the two liquid phases.

(c) The adsorption of a gas on a solid surface obeys the Langmuir isotherm with $K = 0.78\ \text{kPa}^{-1}$ at 30°C. Calculate the pressure at which the fractional surface coverage is (i) 20%, and (ii) 80%. Provide a physical justification of your result (variation of fractional surface coverage with pressure). 3

(d) What is 'Zeta potential'? Explain the stability of lyophobic colloids with the help of zeta potential. 1+2

(e) State and explain Schulze-Hardy rule. 1+2

6. (a) Derive Laplace equation for excess pressure inside a spherical bubble suspended in air. 3

(b) Adsorption of CO on charcoal at 273 K follows Langmuir isotherm. A plot of P (kPa) / V (cm^3) versus P (kPa) is linear with a slope of 0.01 and y-intercept of 0.5. What is the equilibrium constant, K in (kPa^{-1}) for the adsorption? 3

(c) Find the energy required in breaking 1 mL of water into small droplets having an average radius of 10^{-5} cm. The surface tension of water is 72 dyn cm^{-1} at 298 K. 3

(d) The surface tension (γ) of a liquid is found to vary according to the following relationship due to adsorption of a solute 3

$$\frac{\gamma}{\gamma^0} = 1 - \beta \ln\left(1 + \frac{c}{\alpha}\right)$$

where, γ^0 is the surface tension of the pure liquid, c is the concentration of the solute, α, β are constants. Using Gibbs adsorption isotherm show that

$$\Gamma = \frac{\beta\gamma^0}{RT}\left(\frac{\frac{c}{\alpha}}{1+\frac{c}{\alpha}}\right)$$

(e) What is Critical Micelle Concentration (CMC)? What is the effect of temperature on CMC? 1+1

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