

**B.Sc. 6th Semester (Honours) Examination, 2023 (CBCS)****Subject : Chemistry****Course : CC-XIV****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 questions:**

2×5=10

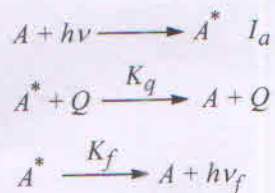
- (a)  $\text{Al}_2(\text{SO}_4)_3$  is more active than  $\text{Na}_2\text{SO}_4$  in coagulating a sol.
- (b) For the non-dissociative Langmuir type adsorption of a gas on solid surface at a particular temperature, the fraction of surface coverage is 0.6 at 30 bar. Calculate the Langmuir isotherm constant.
- (c) Low temperature and viscous medium are suitable for observing phosphorescence.— Explain.
- (d) A liquid of density  $\rho$  and surface tension  $T$  rises to a height  $h$  in a capillary tube of diameter  $D$ . What is the weight of the liquid in the capillary tube? Angle of contact is  $0^\circ$ .
- (e) Mention the differences of overtones and hot bands in the IR spectra.
- (f) What magnetic field is required for proton magnetic resonance at 220 MHz. [Given,  $g = 5.585$ ]
- (g) A 0.01M solution of a compound transmits 20% of visible light when the absorbing path length is 1.5 cm. What is the molar extinction coefficient of the substance?
- (h) What are Stokes and Anti-Stokes lines in the Raman spectra?

**2. Answer any two questions from the following:**

5×2=10

- (a) (i) "The chemisorption of  $\text{H}_2(\text{g})$  onto glass is endothermic ( $\Delta H$  is slightly positive)"— Comment.
- (ii) Derive an expression for the excess pressure inside a spherical soap bubble. 2+3
- (b) (i) Show that  $J_{max} = \sqrt{\frac{KT}{2Bhc}} - 1/2$  corresponding to maximum population of molecules in rotational spectra.
- (ii) Absorption and fluorescence spectra hold mirror image relationship.— Comment. 3+2

- (c) (i) The mechanism of quenching of fluorescence is



where  $I_a$  is the amount of exciting radiation absorbed per litre of solution per second,  $K_q$  is the rate constant for quenching,  $K_f$  is the rate constant for fluorescence and  $I_f$  is the amount of fluorescence radiation per litre per second. Formulate Stern–Volmer relation  $\frac{1}{I_f} = \frac{1}{I_a} \left[ 1 + \left( \frac{K_q}{K_f} \right) [Q] \right]$ . How the data should be plotted to determine the rate constant for quenching?

- (ii) Why the term  $\pm 2$  appears in the selection rule of pure rotational Raman transitions? 3+2
- (d) (i) For a soap solution  $\gamma = \gamma_0 - bc$ . Derive the corresponding equation of state of the adsorbed film by assuming Gibbs adsorption isotherm.
- (ii) If the  $J = 2$  to  $J = 3$  rotational transition for a heteronuclear diatomic molecule occurs at  $\lambda = 20$  mm, find the wavenumber for transition from  $J = 5$  to  $J = 6$  level in the same molecule. 2.5+2.5

3. Answer any two questions from the following: 10×2=20

- (a) (i) 1000 droplets of water having 2 mm diameter each coalesce to form a single drop. Surface tension of water is  $0.072 \text{ Nm}^{-1}$ . Calculate the energy loss in the process.
- (ii) Explain the basis of Franck–Condon principle. Explain why a photostationary state cannot be considered as an equilibrium state.
- (iii) What is nuclear magneton? Show the splitting pattern in high resolution  $^1\text{H}$  NMR spectrum of Ethanol molecule. 3+(2+2)+(1+2)
- (b) (i) If  $\text{H}_2$  molecule behaves like a harmonic oscillator with a force constant  $K = 573 \text{ N/m}$ . Calculate the vibrational quantum number corresponding to its 4.5 eV dissociation energy. [Given,  $M_{\text{H}} = 1.67 \times 10^{-27} \text{ kg}$ ]
- (ii) Write down the expression for the work of adhesion when a liquid spreads over a solid surface. Write down the effect of micelle formation over electrical conductivity and osmotic pressure.
- (iii) Show that the lines in rotational spectrum of a diatomic molecule are equispaced under rigid rotor approximation. 3+(2+2)+3



- (c) (i) "The nature of Raman spectrum of a substance depends on both the nature of molecules and the wavelength of incident radiation" — Justify or criticize.
- (ii) In photobromination of cinnamic acid, radiation at 435.8 nm with an intensity of  $1.4 \times 10^{-3} \text{ Js}^{-1}$ , 80.1% was adsorbed in a litre of solution during an exposure of 1150 s. The concentration of  $\text{Br}_2$  decreased by  $7.5 \times 10^{-2} \text{ mol m}^{-3}$  during this period. What is the quantum yield?
- (iii) The Morse potential is given by the expression  $(r) = D_e [1 - \exp\{-b(r - r_e)\}]^2$ . Show that for small displacement from equilibrium position, the above expression is approximated by a simple harmonic potential.
- (iv) How many normal modes of vibration are there for benzene molecule? 2+4+3+1
- (d) (i) Benzene adsorbed on graphite is found to obey the Langmuir adsorption isotherm. At a pressure of 1.00 torr, the volume of benzene adsorbed on a sample of graphite was found to be  $4.2 \text{ mm}^3$  at STP ( $0^\circ\text{C}$  and 1 atm pressure); at 3.00 torr it was calculated to be  $8.5 \text{ mm}^3$ . Assuming that benzene molecule occupies  $30 \text{ \AA}^2$  surface area, estimate the total surface area of graphite.
- (ii) Define gold number. Mention the conditions of observing Tyndall effect in colloidal solution.
- (iii) Explain how a lyophilic colloid helps in stabilizing a lyophobic colloid. 4+(2+2)+2