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) $Al_2(SO_4)_3$ is more active than Na_2SO_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 ρ 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°.

(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 $H_2(g)$ onto glass is endothermic (ΔH 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

$$A + h\nu \longrightarrow A^* \quad I_a$$

$$A^* + Q \xrightarrow{K_q} A + Q$$

$$A^* \xrightarrow{K_f} A + h\nu_f$$

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 ± 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 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 ^1H NMR spectrum of Ethanol molecule. 3+(2+2)+(1+2)

(b) (i) If H_2 molecule behaves like a harmonic oscillator with a force constant $K = 573$ N/m, Calculate the vibrational quantum number corresponding to its 4·5 eV dissociation energy. [Given, $M_H = 1{\cdot}67 \times 10^{-27}$ 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 intersity of $1{\cdot}4 \times 10^{-3} Js^{-1}$, 80·1% was adsorbed in a litre of solution during an exposure of 1150 s. The concentration of Br_2 decreased by $7{\cdot}5 \times 10^{-2}$ 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 mm^3 at STP (0°C and 1 atm pressure); at 3·00 torr it was calculated to be 8·5 mm^3. Assuming that benzene molecule occupies 30 $Å^2$ 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
