B.Sc. 6th Semester (Honours) Examination, 2025 (CBCS)

Subject : Chemistry

Course: CC-XIV

(Physical Chemistry)

Time: 2 Hours **Full Marks: 40**

The figures in the right hand 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) At 20°C the surface tension of water is three times that of CCl_4—Give reasons.

(b) ^{12}C and ^{16}O do not show NMR spectra—Explain.

(c) The dissociative chemisorption of $X_2(g)$ on a metal surface follows Langmuir adsorption isotherm. Calculate the fraction of surface coverage of X at 1·0 atm pressure. [Adsorption constant (K) = 4·0 atm^{-1}]

(d) Explain why the rotational spectrum is observed for ICl but not for I_2 or Cl_2.

(e) Write down the selection rule in NMR spectroscopy. Mention the separation between first stoke and first anti-stoke lines in Raman spectra.

(f) For a photochemical reaction $2A + B \longrightarrow 3C$ express $\frac{d[A]}{dt}$ and $\frac{d[C]}{dt}$ in terms of I_a and quantum yield (ϕ).

(g) How many normal modes of vibrations are there for acetylene molecule? Which molecules will show infrared absorption spectra:

H_2, CH_3Cl, NH_3, N_2, H_2O

(h) What do you understand by 'Zeta potential'?

2. Answer *any two* questions: 5×2=10

(a) (i) Why does the surface energy increase on dispersion of a large water drop into smaller droplets? Why equivalent conductance decreases beyond CMC?

(ii) Flocculation value of $MgSO_4$ for $Fe(OH)_3$ sol is 0·22. Calculate the amount of $MgSO_4$(mg) required for coagulation of 50ml $Fe(OH)_3$ sol. (2+1)+2

(b) (i) At 292K, the surface tension of solution of butyric acid in water 'γ' can be accurately given by the equation $\gamma = \gamma_0 - a \ln (1 + bC)$ where 'C' is the conc. of butyric acid and γ_0 is the surface tension of water, while a and b are constants. Set up the expression for the excess conc. of solute per sqcm of surface as a function of C.

(ii) If 0.001M of a substance quenches the efficiency of fluorescence by 20%, calculate the Stern-Volmer constant. 3+2

(c) (i) Derive the expression for the transition frequency of stokes and antistokes lines for a linear molecule by considering only rotational energy.

(ii) The symmetric stretching mode of vibration of CO_2 is Raman active but IR inactive — Justify. 3+2

(d) (i) The fundamental and first overtone transition of NO molecule are found at 1876 cm^{-1} and 3724 cm^{-1}. Evaluate the equilibrium vibration frequency and exact zero point energy of NO.

(ii) Tabulate the differences between fluorescence and phosphorescence. 3+2

3. Answer *any two* questions: 10×2=20

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

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

(ii) The rotational spectrum of HI is found to have its first line at 12·8 cm^{-1}. Find out which particular transition for HI will produce most intense spectral line at 300 K.

(iii) State the selection rule for Rotational Raman and Vibrational Raman spectroscopy. Explain why with increasing vibrational quantum number value, the spectral lines gradually crowd together. 3+3+(2+2)

(b) (i) Predict theoretically the NMR spectra of diethylether.

(ii) Explain wetting of a solid by a liquid in terms of relative values of adhesional work between (solid and liquid) and the cohesional work of liquid.

(iii) At a magnetic flux density of 1·65T the frequency of seperation between protons in benzene and TMS is 510·5Hz. Calculate the chemical shift [given: g = 5·585, $\beta_N = 5{\cdot}05 \times 10^{-27} JT^{-1}$]

(iv) Explain why the angle of contact of mercury with glass is obtuse while that of water with glass is acute? 2+3+3+2

(c) (i) The following mechanism has been proposed for the dimerization of Anthracene (A) in benzene solution.

$$A + h\nu \xrightarrow{K_1} A^*$$

$$A^* + \xrightarrow{K2} A_2$$

$$A^* \xrightarrow{K_3} A + h\nu_f$$

Using steady state approximation for A* prove that quantum yield of A_2 is independent of the intensity of the light absorbed.

(ii) Radiation of wavelength 2500°A was passed through a cell containing 10 ml of a solution which was 0·05 molar in oxalic acid and 0·01 molar in uranyl sulphate. After absorption of 80 Joules of radiation energy, the concentration of oxalic acid was reduced to 0·04 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength.

(iii) Addition of excess $AgNO_3$ to NaCl solution gives positively charged AgCl sol, while $AgNO_3$ solution on treating with excess of NaCl solution yields negatively charged AgCl sol. Explain the phenomena.

(iv) Write down the condition(s) for stopping the electrophoresis of a colloidal solution.

3+4+2+1

(d) (i) Adsorption of phenol from its aqueous solution on to fly ash obeys Freundlich isotherm. At a given temperature from 10 mg g^{-1} and 16 mg g^{-1} aqueous phenol solution, the concentration of adsorbed phenol are measured to be 4 mg g^{-1} and 10 mg g^{-1} respectively. Calculate the concentration (in mg g^{-1}) of adsorbed phenol from 20 mg g^{-1} aqueous solution of phenol.

(ii) Write down the effect of temperature and pressure on adsorption. State Stark–Einstein law of photochemical equivalence.

(iii) Draw the potential energy diagram of CO ($K = 1870\ Nm^{-1}$) and F_2 ($K = 450\ Nm^{-1}$) showing at least four energy levels in each case.

(iv) Represent the colloid formed by addition of 100 mL 0·1M $AgNO_3$ solution to 50 mL 0·1M KI solution. Mention the sign of ΔH and ΔS in micellization process.

3+(2+1)+2+(1+1)

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