B.Sc. 6th Semester (Honours) Examination, 2024 (CBCS)

Subject : Chemistry

Course:CC-XIV

(Physical Chemistry-IV)

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) A spherical air bubble is created within a liquid of surface tension 72 dyne/cm. If the volume of the bubble is $\pi/6$ cm^3, calculate the excess pressure inside the bubble.

(b) Define isoelectric point for a colloid. Mention dispersed phase and dispersion medium in fog.

(c) What are the transitions responsible for NMR spectrum? Write the essential condition for a molecule to be infrared active.

(d) The graph of $\log\frac{x}{m}$ vs. log p for an adsorption process is a straight line inclined at an angle of 45° with intercept equal to 0·6020. Calculate the mass of gas adsorbed per unit mass of adsorbent at the pressure of 0·4 atm.

(e) Phosphorescence of aromatic hydrocarbon is usually observed at low temperature in rigid matrix. — Explain.

(f) The rotational constants for CO in the ground and the first excited vibrational states are 1·9 and 1·6 cm^{-1}, respectively. Calculate the percentage change in internuclear distance due to vibrational excitation.

(g) Which of the following molecules are rotational Raman active?

Br_2, HBr, HCN, CS_2

Name one photosensitizer of plant origin.

(h) Predict the high resolution NMR spectra of CH_3CH DCl.

2. Answer *any two* questions: 5×2=10

(a) (i) Justify that Gibbs' surface excess can take up both positive and negative values.

(ii) A capillary tube of radius 0·001 cm is inclined at an angle 45° to the surface of a liquid. The liquid wets the wall. It has a density of 0·85 g/cc and surface tension of 36 dyne/cm. Calculate d, the distance along the capillary to the meniscus. 2+3

(b) (i) Find the number of normal modes of vibration of H_2O molecule and explain which of these are IR and Raman active.

(ii) For a proton the gyromagnetic ratio is $26{\cdot}752\times10^7$ rad T^{-1}. Calculate the Lamor frequency (in MHz) in a 21·1 Tesla magnetic field. 3+2

(c) (i) Write the expression of zeta potential and show how this expression helps to explain the mechanism of coagulation of lyophobic sol.

(ii) In the scheme below,

$$P \underset{K_1}{\overset{I_a}{\rightleftharpoons}} 2Q \xrightarrow{K_2} R$$

I_a represents the intensity of the light absorbed. Assuming that the quantum yield of the first step is one, calculate the steady state concentration of Q. 2½+2½

(d) How do HCl and DCl differ in respect of vibrational and rotational spectra (assuming the molecules to behave as rigid rotor and harmonic oscillator)?

How many times does a molecule $^1H^{35}Cl$ rotate per sec in the J = 1 rotational level? Given B ($^1H\ ^{35}Cl$) = 10·6 cm^{-1}. 2+3

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

(a) (i) Why is non-rigidity effect of a rotor pronounced at high J values? State the condition for a rigid diatomic rotor to be microwave active and state the corresponding selection rule.

(ii) Adsorption of N_2 on TiO_2 was carried out at 75K. A plot of $\frac{z}{(1-z)v}$ versus $Z\left(Z = {}^{P}/_{P^0}\right)$ gives a straight line with an intercept, 4×10^{-6} mm^{-3} and slope 1×10^{-3} mm^{-3}. Calculate the volume corresponding to the monolayer coverage.

(iii) Show the electronic transitions involved in formaldehyde molecule. State Stark–Einstein law of photochemical equivalence. 4+3+(2+1)

(b) (i) Using the formula for the energy levels for the Morse potential, $\varepsilon_n = h\nu\left(n+\frac{1}{2}\right) - \frac{(h\nu)^2}{4D_e}\left(n+\frac{1}{2}\right)^2$ deduce the expression of energy spacing between adjacent levels. For $^1H^{35}Cl$, De = $7{\cdot}41\times10^{-19}$J and ν = $8{\cdot}97\times10^{13}sec^{-1}$, calculate the smallest value of n for which $\varepsilon_{n+1} - \varepsilon_n < 0\cdot5(\varepsilon_1 - \varepsilon_0)$.

(ii) Graphically represent the variation of surface tension of a liquid with temperature why free falling raindrops appear spherical in shape.

(iii) Mention differences between water in oil and oil in water emulsion. 5+(1+2)+2

(c) (i) Classify the following molecules in terms of symmetric top, spherical top and asymmetric top:

SF_6, BCl_3, C_6H_6, CH_2Cl_2

(ii) Write an expression for the spin energy level of a nucleus having a nuclear spin I placed in a magnetic field H. Define flocculation value for a sol.

(iii) A reaction responds to both red and violet light (λ = 800 nm and 400 nm, respectively) with an equal quantum yield. Will there be more photochemical reaction per 400 J of light energy in the red than in the violet or vice-versa?

(iv) A laser Raman spectrometer operating at 532 nm is used to record the vibrational spectrum of Cl_2 having its fundamental vibration at 560 cm^{-1}. Calculate the position of Stokes line corresponding to this vibration. 2+3+3+2

(d) (i) What are the different radiative and non-radiative paths by which the excited state of a molecule can decay? Explain with the help of Jablonski diagram.

(ii) In a photochemical decomposition of $C_2H_4I_2$ according to the reaction $C_2H_4I_2 \rightarrow C_2H_4+I_2$ using a light of wavelength 4240 Å, the iodine liberated after 20 minutes required 41·15 ml of 0·005(N) sodium thiosulphate solution. The intensity of light source was $9{\cdot}15\times10^3$ erg^{-1}. Calculate the quantum yield assuming complete absorption of energy.

(iii) Consider the adsorption of $H_2(g)$ by a metal into its surface followed by rapid dissociation of the molecules into atoms which occupy a surface site. Calculate the fraction of the surface θ when both adsorption and desorption processes take place simultaneously. Calculate the value of θ in case of very small and very high concentrations. 3+3+(2+1+1)