

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:** **$2 \times 5 = 10$**

- (a) A spherical air bubble is created within a liquid of surface tension 72 dyne/cm. If the volume of the bubble is $\frac{\pi}{6} \text{ cm}^3$, 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?
 $\text{Br}_2, \text{HBr}, \text{HCN}, \text{CS}_2$
Name one photosensitizer of plant origin.
- (h) Predict the high resolution NMR spectra of $\text{CH}_3\text{CH DCl}$.

2. Answer any two questions: **$5 \times 2 = 10$**

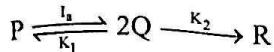
- (a) (i) Justify that Gibbs' surface excess can take up both positive and negative values.
(ii) A capillary tube of radius 0.001 cm is inclined at an angle 45° to the surface of a liquid. The liquid wets the wall. It has a density of 0.85 g/cc and surface tension of 36 dyne/cm. Calculate d, the distance 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 $26.752 \times 10^7 \text{ rad T}^{-1}$. 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,



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 ${}^1\text{H}{}^{35}\text{Cl}$ rotate per sec in the $J = 1$ rotational level? Given $B({}^1\text{H}{}^{35}\text{Cl}) = 10.6 \text{ cm}^{-1}$. 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 ($Z = P/P_0$) gives a straight line with an intercept, $4 \times 10^{-6} \text{ mm}^{-3}$ and slope $1 \times 10^{-3} \text{ mm}^{-3}$. 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, $\varepsilon_n = hv \left(n + \frac{1}{2}\right) - \frac{(hv)^2}{4D_e} \left(n + \frac{1}{2}\right)^2$ deduce the expression of energy spacing between adjacent levels. For ${}^1\text{H}{}^{35}\text{Cl}$, $D_e = 7.41 \times 10^{-19} \text{ J}$ and $v = 8.97 \times 10^{13} \text{ sec}^{-1}$, calculate the smallest value of n for which $\varepsilon_{n+1} - \varepsilon_n < 0.5(\varepsilon_1 - \varepsilon_0)$.

(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:



- (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 ($\lambda = 800 \text{ nm}$ 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 $\text{C}_2\text{H}_4\text{I}_2$ according to the reaction $\text{C}_2\text{H}_4\text{I}_2 \rightarrow \text{C}_2\text{H}_4 + \text{I}_2$ using a light of wavelength 4240 \AA , the iodine liberated after 20 minutes required 41.15 ml of $0.005(N)$ sodium thiosulphate solution. The intensity of light source was $9.15 \times 10^3 \text{ erg}^{-1}$. Calculate the quantum yield assuming complete absorption of energy.

- (iii) Consider the adsorption of $\text{H}_2(\text{g})$ 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)
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