

B.Sc 6th Semester (Honours) Examination, 2022 (CBCS)

Subject: Chemistry

(Physical Chemistry-IV)

Paper: CC-14

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 from the following: **2 x 5 = 10**

(a) Show graphically the variation of molar conductivity and surface tension with concentration for SDS solution with proper reason.

(b) The separation between the rotational lines in the spectrum of $^{13}\text{C}^{16}\text{O}$ will be smaller than that of $^{12}\text{C}^{16}\text{O}$ – Justify.

(c) In the pure microwave spectrum of XY molecule, the adjacent lines are separated by 4cm^{-1} . If the molecule is irradiated by a radiation of $30,000\text{ cm}^{-1}$, find the position of first stokes line.

(d) Addition of 5.0 ml of 0.006M BaCl_2 to 10 ml of arsenic sulphide sol just causes the complete coagulation. Calculate the flocculation value of the effective ion.

(e) The meniscus of Hg in a glass tube is convex upward – Explain

(f) The signal for CH_2 protons in a compound appears at δ 4.6. Calculate the difference in frequency expressed in Hertz between this signal and TMS signal in a 300 MHz instrument.

(g) At 460 nm a blue filter transmits 72.7% of the light and a yellow filter 40.7 % of the light. What is the transmittance value at the same wavelength, of two filters in combination?

(h) Why do electrolytes increase the surface tension of liquid? – Elucidate in the light of Gibbs adsorption isotherm.

2. Answer any two questions from the following: **5 x 2 =10**

(a) (i) The symmetric stretching mode of vibration of CO_2 is Raman active but IR inactive – Justify.

(ii) The limbs of vertical U-tube have internal diameters of 1mm and 2 mm respectively. It is partially filled with a liquid of density 0.82g/ml and surface tension 50 dyne/cm. What is the difference in level of the liquid in the two limbs? **2+3=5**

(b) (i) For a diatomic molecule with $B = 0.35 \text{ cm}^{-1}$, find the quantum level from which the most intense spectral line will originate at 1000 K.

(ii) Phosphorescence has a long radiative lifetime and it occurs at a longer wavelength than fluorescence – Justify. $2.5 + 2.5 = 5$

(c) (i) Show the transitions leading to absorption and fluorescence schematically using potential energy diagram and hence show that $\lambda_{\max}(\text{abs}) < \lambda_{\max}(\text{fluorescence})$.

(ii) During micellization of surfactant in aqueous medium entropy increases – Explain. $3+2=5$

(d) (i) Show that at low pressure ($P < P^{\circ}$) BET isotherm reduces to Langmuir's adsorption isotherm.

(ii) Electro-Osmosis is a consequence of existence of electrical double layer at the solid-liquid interface – Justify the statement. $2.5 + 2.5 = 5$

3. Answer any two questions from the following: $10 \times 2 = 20$

(a) (i) The molecular dissociation energy is defined at a state where the vibrational energy of the diatomic molecule has its maximum value. Show that $D_{dis} = \frac{hv}{4x_e}$ where the symbols used have their usual significance.

(ii) 52.48 ml of the quartz container was filled up with CH_3COCH_3 vapour at 47°C at 780 mm of Hg. The vapour was irradiated with radiation of wavelength 300 nm and intensity 2.1×10^{18} photons s^{-1} for 30 minutes. Find out the increase in pressure (given, quantum yield = 0.1 and the dissociation reaction is $\text{CH}_3\text{COCH}_3 \longrightarrow \text{C}_2\text{H}_6 + \text{CO}$, and assuming ideal behavior of vapour)

(iii) Show the splitting pattern in high resolution ^1H NMR spectrum of acetaldehyde molecule with explanation.

(iv) Calculate the resonance frequency of ^{19}F nucleus in an NMR spectrometer operating at a magnetic field strength of 16.45 T [given, g factor of $^{19}\text{F} = 5.255$, $\beta_N = 5.05 \times 10^{-27} \text{ J T}^{-1}$]

$3+3+2+2=10$

(b) At 18°C , the surface tension γ of an aqueous solution of butyric acid is represented by the equation $\gamma = \gamma_0 - 29.8 \log(19.64 C_2 + 1)$ where γ_0 , the surface tension of water is 0.073 N m^{-1} and C_2 is the bulk concentration of the solute. Calculate, using Gibbs adsorption isotherm, the surface excess of butyric acid at concentration $C_2 = 0.01 \text{ mol dm}^{-3}$.

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

(iii) Mention differences between Oil in water emulsion and Water in oil emulsion. Justify the condition of spreading of one liquid over another. 3+3+(2+2)=10

(c) (i) A quartz particle of diameter 1×10^{-4} cm in aqueous suspension at 25°C migrates at a velocity of 3×10^{-8} cm/sec under potential gradient of 10 V/cm. Calculate zeta-potential at the quartz water interface (η of water = 0.89 centipoise, dielectric constant of water = 78.3).

(ii) For dimerization of anthracene $2\text{A} \longrightarrow \text{A}_2$, explain with sketch the change of fluorescence yield (ψ) and quantum yield (φ) of the process with concentration of anthracene.

(iii) The photolysis of ozone follows (a) $\text{O}_3 \xrightarrow{h\nu(I_{abs})} \text{O}_2 + \text{O}$, (b) $\text{O} + \text{O}_3 \xrightarrow{k_2} 2\text{O}_2$, the quantum yield of reaction (a) is φ_1 , find an expression for the overall quantum yield (φ_o) of disappearance of O_3 .

(iv) What is the criterion of a molecule to be NMR active. The rotational raman displacement for HCl molecule is 41.6 cm^{-1} . Calculate the internuclear distance between the atoms in angstrom. (reduced mass for HCl is $1.61 \times 10^{-27} \text{ kg}$) 3+2+2+(1+2)=10

(d) (i) Show that the frequency of rotation of a rigid rotator increases with increase in rotational quantum number (J) by the relation $\nu = \frac{\hbar}{4\pi^2 I} \sqrt{J(J+1)}$

(ii) Derive Langmuir Adsorption Isotherm mentioning all the assumptions involved in it.

(iii) When sufficient solution of BaCl_2 is added to an arsenious sulphide solution, peptized by a small amount of H_2S , flocculation occurs and the solution becomes acidic – Explain.

(iv) The fundamental vibrational frequency of ${}^1\text{H}{}^{127}\text{I}$ is 2309 cm^{-1} . Calculate the force constant for this molecule in Nm^{-1} 2+4+2+2=10