

**B.Sc 6<sup>th</sup> 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  $4\text{cm}^{-1}$ . 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  $\text{BaCl}_2$  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  $\text{CH}_2$  protons in a compound appears at  $\delta$  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  $\text{CO}_2$  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  $\lambda_{\text{max}} (\text{abs}) < \lambda_{\text{max}} (\text{fluorescence})$ .

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

(d) (i) Show that at low pressure ( $P < P^0$ ) 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  $D_{\text{dis}} = \frac{h\nu}{4x_e}$  where the symbols used have their usual significance.

(ii) 52.48 ml of the quartz container was filled up with  $\text{CH}_3\text{COCH}_3$  vapour at  $47^\circ\text{C}$  at 780 mm of Hg. The vapour was irradiated with radiation of wavelength 300 nm and intensity  $2.1 \times 10^{18} \text{ photons s}^{-1}$  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 of  $^1\text{H}$  NMR spectrum of acetaldehyde molecule with explanation.

(iv) Calculate the resonance frequency of  $^{19}\text{F}$  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  $18^\circ\text{C}$ , the surface tension  $\gamma$  of an aqueous solution of butyric acid is represented by the equation  $\gamma = \gamma_0 - 29.8 \log (19.64 C_2 + 1)$  where  $\gamma_0$ , the surface tension of water is  $0.073 \text{ Nm}^{-1}$  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  $1 \times 10^{-4}$  cm in aqueous suspension at  $25^\circ\text{C}$  migrates at a velocity of  $3 \times 10^{-8}$  cm/sec under potential gradient of 10 V/cm. Calculate zeta-potential at the quartz water interface ( $\eta$  of water = 0.89 centipoise, dielectric constant of water = 78.3).

(ii) For dimerization of anthracene  $2A \longrightarrow A_2$ , explain with sketch the change of fluorescence yield ( $\psi$ ) and quantum yield ( $\phi$ ) of the process with concentration of anthracene.

(iii) The photolysis of ozone follows (a)  $\text{O}_3 \xrightarrow{h\nu(I_{\text{abs}})} \text{O}_2 + \text{O}$ , (b)  $\text{O} + \text{O}_3 \xrightarrow{k_2} 2\text{O}_2$ , the quantum yield of reaction (a) is  $\phi_1$ , find an expression for the overall quantum yield ( $\phi_o$ ) of disappearance of  $\text{O}_3$ .

(iv) What is the criterion of a molecule to be NMR active. The rotational raman displacement for HCl molecule is  $41.6 \text{ cm}^{-1}$ . 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  $\nu = \frac{h}{4\pi^2 I} \sqrt{J(J+1)}$

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

(iii) When sufficient solution of  $\text{BaCl}_2$  is added to an arsenious sulphide solution, peptized by a small amount of  $\text{H}_2\text{S}$ , flocculation occurs and the solution becomes acidic – Explain.

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