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 $^{13}C^{16}O$ will be smaller than that of $^{12}C^{16}O$ – 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 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 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 λ_{max} (abs) < λ_{max} (fluorescence).
(ii) During micellization of surfactant in aqueous medium entropy increases – Explain. 3+2=5
(d) (i) Show that at low pressure (P < P^o) 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 x 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 $D_{dis} = \frac{h\upsilon}{4x_e}$ 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 $CH_3COCH_3 \longrightarrow C_2H_6 + CO$, and assuming ideal behavior of vapour)

(iii) Show the splitting pattern in high resolution of ^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}F = 5.255, β_N = 5.05 × 10^{-27} 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 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 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 $2A \longrightarrow A_2$, 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) $O_3 \xrightarrow{h\upsilon(I_{abs})} O_2 + O$, (b) $O + O_3 \xrightarrow{k_2} 2O_2$, 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 1.61×10^{-27} 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 $BaCl_2$ 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 $^1H^{127}I$ is 2309 cm^{-1}. Calculate the force constant for this molecule in Nm^{-1} 2+4+2+2=10