2025

CHEMISTRY — HONOURS

Paper : CC-14

(Physical Chemistry - 5)

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question no.*** **1** and ***any eight*** questions from the rest.

1. Answer ***any ten*** questions : 1×10

(a) What is the fundamental absorption of an anharmonic oscillator?

(b) Zero point energy is the basic difference between the wave mechanical and classical approaches to molecular vibration.— Justify or criticise.

(c) Illustrate Franck-Condon Principle with a diagram.

(d) What is the essential condition of Raman activity of a molecule?

(e) Why secondary processes usually do not follow the law of photochemical equivalence?

(f) What are 'photosensitized reactions'? Give one example useful to mankind.

(g) What is the difference between an 'Activated complex' and a 'Reaction intermediate'?

(h) Calculate the excess pressure inside a soap bubble (γ = 0.03 N/m) of radius 2 mm.

(i) Write two main differences between physisorption and chemisorption.

(j) What is gold number?

(k) What is the CGS unit of $\mu^2/3\,kT$? (The symbols have their usual significance.)

(l) Why does phosphorescence have lower intensity than fluorescence?

2. (a) If the total relative population at an energy E_J is $\propto (2J + 1) \exp\left(-E_J/kT\right)$,

show that at $J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$, the population will be maximum.

(b) Plot the population vs. rotational quantum number of two isotopes of carbon monoxide $^{12}C^{16}O$ and $^{13}C^{16}O$. 3+2

Please Turn Over

10. (a) Calculate the energy required in breaking 1 cc of water into droplets having radius 10^{-5} cm, given γ_w = 72 dynes/cm.

(b) At what temperature surface tension will be zero? Justify your answer. 3+2

11. (a) Derive Gibbs adsorption isotherm.

(b) Describe the effect of adding the following solutes in water on its surface tension using Gibbs adsorption isotherm (i) KCl and (ii) Sodium dodecyl sulphate. 3+2

12. (a) Explain the origin of charge and stability of Lyophobic colloids with the help of Stern double layer theory.

(b) What happens when sufficient amount of $BaCl_2$ is added to arsenius sulphide solution peptized by a small amount of H_2S? 3+2

13. (a) How will you distinguish a polar molecule from a non-polar molecule with the help of temperature variation of molar polarization?

(b) The molar polarization of Fluorobenzene vapour is 70.62 cm^3 mol^{-1} at 351 K and 62.47 cm^3 mol^{-1} at 423 K. Calculate the dipole moment and distortion polarizability of the molecule. 2+3

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3. (a) 'Stokes lines can occur only if the molecule is originally in an excited vibrational or rotational state.'— Justify or criticize.

(b) Draw the curve of polarizability (α) versus displacement coordinate (ξ) for different vibrational modes of CO_2 and based on this, indicate which modes are Raman active. 2+3

4. (a) What are internal conversion and inter-system crossing? Explain with the help of a Jablonsky diagram.

(b) 'Low temperature and viscous medium are suitable for observing phosphorescence.'— Explain. 3+2

5. (a) Discuss the effect of anharmonicity on the vibrational spectra of a heteronuclear diatomic molecule.

(b) A linear molecule has the formula AB_2. Discuss how would you ascertain whether the molecule has the structure BAB or ABB using its Raman and IR spectra together. 3+2

6. (a) The mechanism of photochemical decomposition of HI is—

$$HI \xrightarrow{h\upsilon} H + I$$

$$H + HI \longrightarrow H_2 + I$$

$$I + I \longrightarrow I_2$$

Show that the quantum efficiency with respect to HI is 2, but that with respect to I_2 is one.

(b) How many HI molecules will be decomposed when 3070 J of energy is absorbed at 253 nm? 3+2

7. (a) Kinetics of the following reaction :

$$[CoBr(NH_3)_5]^{2+} + OH^- \longrightarrow [Co(NH_3)_5 OH]^{2+} + Br^-$$

was studied in aqueous solution of (i) 0.05 (N) NaCl and (ii) 0.001 (N) NaCl. State with reason whether rate constants remain same or different.

(b) Quantum yield may be as low as 0.01 and as high as 10^6. Does it contradict the Stark-Einstein law? 3+2

8. (a) 'Only those collisions that satisfy both the activation energy requirement and the specific molecular orientation are effective in producing products.'— Justify or criticize.

(b) 'A unimolecular gaseous reaction shows second order kinetics at low pressure.'— Explain using Lindemann mechanism. 3+2

9. (a) Radiation of wavelength 2540 A° was passed through a cell containing 10 ml of a solution of 0.0495 molar oxalic acid and 0.01 molar uranyl sulphate. After the absorption of 8.81×10^8 Ergs radiation, the concentration of oxalic acid was reduced to 0.0383 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength.

(b) Why aerosol is spherical in shape? 3+2