

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

- What is the fundamental absorption of an anharmonic oscillator?
- Zero point energy is the basic difference between the wave mechanical and classical approaches to molecular vibration.— Justify or criticise.
- Illustrate Franck-Condon Principle with a diagram.
- What is the essential condition of Raman activity of a molecule?
- Why secondary processes usually do not follow the law of photochemical equivalence?
- What are 'photosensitized reactions'? Give one example useful to mankind.
- What is the difference between an 'Activated complex' and a 'Reaction intermediate'?
- Calculate the excess pressure inside a soap bubble ( $\gamma = 0.03$  N/m) of radius 2 mm.
- Write two main differences between physisorption and chemisorption.
- What is gold number?
- What is the CGS unit of  $\mu^2/3$  kT? (The symbols have their usual significance.)
- Why does phosphorescence have lower intensity than fluorescence?

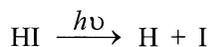
2. (a) If the total relative population at an energy  $E_J$  is  $\propto (2J + 1) \exp\left(\frac{-E_J}{kT}\right)$ ,show that at  $J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$ , the population will be maximum.(b) Plot the population vs. rotational quantum number of two isotopes of carbon monoxide  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$ .  
3+2

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10. (a) Calculate the energy required in breaking 1 cc of water into droplets having radius  $10^{-5}$  cm, given  $\gamma_w = 72$  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  $\text{BaCl}_2$  is added to arsenious sulphide solution peptized by a small amount of  $\text{H}_2\text{S}$ ? 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  $70.62 \text{ cm}^3 \text{ mol}^{-1}$  at 351 K and  $62.47 \text{ cm}^3 \text{ mol}^{-1}$  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 ( $\alpha$ ) versus displacement coordinate ( $\xi$ ) for different vibrational modes of  $\text{CO}_2$  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  $\text{AB}_2$ . 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—



Show that the quantum efficiency with respect to HI is 2, but that with respect to  $\text{I}_2$  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 :
- $$[\text{CoBr}(\text{NH}_3)_5]^{2+} + \text{OH}^- \longrightarrow [\text{Co}(\text{NH}_3)_5\text{OH}]^{2+} + \text{Br}^-$$
- 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  $2540 \text{ \AA}$  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  $8.81 \times 10^8$  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