

2023

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) Molecular rotation about the bond axis cannot generate any microwave lines. Explain.
- (b) In vibrational spectra of a diatomics, the energy of the second overtone was found to be thrice that of the hot band. Comment on the observation.
- (c) Water can safely be used as a solvent in Raman spectroscopy but not in IR spectroscopy.
- (d) In microwave spectra, a molecule yields three different rotational constants. Comment on the symmetry of the molecule.
- (e) Identify in which of the following process/es spin inversion occur : Internal conversion, fluorescence, phosphorescence.
- (f) Name one bioluminescent chemical and one photosensitizer of plant origin.
- (g) Calculate the energy (in eV) of one Einstein radiation of wavelength 300 nm.
- (h) Define surfactant with one example.
- (i) Differentiate between absorption and adsorption.
- (j) What is Critical Micelle concentration?
- (k) Define isoelectric point for a colloid.
- (l) Dielectric constant of water (80) is much greater than air (1.00059). What is the implication of this information?

2. The rotational constant for H^1Cl^{35} is observed to be 10.5909 cm^{-1} .

- (a) Calculate the rotational constant for D^2Cl^{37} .
- (b) Find out the ratio of number of H^1Cl^{35} molecules with $J = 4$ to those with $J = 0$ at 300 K.

2+3

Please Turn Over

3. (a) The fundamental and first overtone transition of NO molecule are found at 1876 cm^{-1} and 3724 cm^{-1} respectively. Evaluate the equilibrium vibration frequency and exact zero point energy of NO.
(b) State the 'rule of mutual exclusion' in spectroscopy and illustrate with a suitable example. 3+2
4. (a) The Vibrational-Raman spectra of Cl_2 molecule shows a series of Stokes lines separated by 0.98 cm^{-1} along with the anti-Stokes lines. Calculate the Cl-Cl bond length.
(b) Despite the selection rule $\Delta J = \pm 1$ and equal transition probability for all the possible transitions, why intensity of all rotational lines in a microwave spectra are not same? Explain. 3+2
5. (a) For CO_2 , how many vibrational modes are there? Among them how many are IR active? Name those modes.
(b) The rotational spectrum of HI is found to have its first line at 12.8 cm^{-1} . Find out which particular transition for HI will produce the most intense spectral line at 300 K. 3+2
6. (a) State the selection rules for both the Rotational Raman and Vibrational Raman spectroscopy. Explain, why with increasing vibrational quantum number value, the spectral lines gradually crowd together.
(b) The fundamental vibration frequency of a homonuclear diatomic molecule is ' ν_0 '. Calculate the temperature at which the population of that molecule in its first excited state would be half of that of the ground state. 3+2
7. (a) 'The number of photons required to activate one molecule is called quantum yield'. Criticize the statement. If a system is found to absorb 3×10^{18} quanta of light per second to irradiate 0.002 mole of its molecules for 10 minutes, calculate the quantum yield of the process.
(b) The fact that fluorescence wavelength is often much longer than the irradiation wavelength is a consequence of the Frank Condon principle. Explain. 3+2
8. (a) The ϵ of 'B' (MW = 180) is $4 \times 10^3\text{ Lmol}^{-1}\text{cm}^{-1}$. Now if one litre of 'C' containing 0.1358 gm of 'B' shows an absorbance value of 0.411 in a 1cm quartz cell, calculate the % (w/w) of 'B' in 'C'.
(b) State major significances of the primary kinetic salt effect. If KCl is added to the reaction: $[\text{PtCl}_4]^{2-} + \text{OH}^- \rightarrow \text{Pdots}$, the rate of reaction decreases. Justify the claim. 2+3
9. (a) When a mixture of Hydrogen and Bromine is exposed to radiations of 450-550 nm, although they combine, the quantum yield is found to be as low as 0.01. Explain with proper reasoning.
(b) 0.01 molar solution of a compound transmits 20% of the Na-D line when the absorbing path is 1.50 cm. Calculate the molar extinction coefficient of the compound. 3+2
10. (a) When a capillary tube of diameter 2 mm is dipped into a liquid of specific gravity 0.8, it rises by 15 mm, making a contact angle 0° with the tube. Calculate the surface tension of the liquid in contact with the air and the glass tube. State the dimension and unit (in SI) of surface energy.
(b) To kill mosquito larva, kerosine oil is often sprinkled on the pool water. Explain. 3+2

11. (a) If there is 2% error in the determination of rotational constant 'B' of a diatomic molecule, calculate the percentage error in its bond length measurement.
- (b) Based on Stern's theory of electrical double layer, for a solid liquid interface, show how zeta potential differs from thermodynamic potential. 2+3
12. (a) Between Lyophobic and Lyophilic sols, which one is more stable and why? Explain, how the lesser stabilised one can be made stabilised using the more stabilised one.
- (b) Coagulation and peptization are reverse phenomena related with the lyophilic colloids. Criticize the sentence with proper reasoning. 3+2
13. (a) Surface tension and surface energy are numerically same.— Explain.
- (b) The % T of a solution of an acid base indicator (HIn) was determined at 590 nm under the following condition.
- (i) At pH 4.39, %T = 20
- (ii) At strong basic condition, %T = 5.4.

Assuming that at the given wavelength only the basic form (ie In^-) absorbs appreciably, determine pK_{In} . 2+3
