

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

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

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LIBRARY2. The rotational constant for H^1Cl^{35} is observed to be 10.5909 cm^{-1} .

- Calculate the rotational constant for D^2Cl^{37} .
- 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: $[\text{PtCl}_4]^{2-} + \text{OH}^- \rightarrow \text{Pdt}$, 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

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