RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SIXTH SEMESTER EXAMINATION, MAY 2025

THIRD YEAR [BATCH 2022-25]

Date : 05/05/2025 **CHEMISTRY (HONOURS)**

Time : 11 am – 1 pm **Paper : CC 13** Full Marks : 50

Unit –I

[Answer **any two**] [2×5]

1. a) For the reflection of X-rays from the faces of a crystal, derive the Bragg's equation
$$n\lambda = 2d\ sin\theta$$
b) A crystal having simple cubic crystal lattice has the length of its unit cell a_0 pm. One of its planes shows a first order Bragg diffraction at an angle 60°. Taking the wavelength of X ray as a_0 pm. Find the miller indices of the plane. [3+2]

2. a) Show qualitatively or otherwise that the interplanar distance in a cube (edge length a) having Miller indices (hkl) is given by
$$\boldsymbol{d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}}$$
b) An x-ray analysis fails to locate the position of H-atoms - Justify or criticize. [3+2]

3. a) Calculate the fraction of space occupied by atoms in a closed-packed face-centred cubic lattice of a single crystal of silver.
b) KCl has an f.c.c. lattice. But from X-ray diffraction experiment it appears to be simple cube. Explain. [3+2]

Unit –II

[Answer **any two**] [2×5]

4. a) What is law of photochemical equivalence? Explain with the definition of quantum yield.
b) 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 of radiation, the concentration of oxalic acid was reduced to 0.0383 molar. Calculate the quantum yield for the photochemical dissociation of oxalic acid. [2+3]

5. UV light of $\lambda = 313\ nm$ brings about the following photochemical reaction at 329K with a quantum efficiency of 0.174.
$$CH_3COCH_3(g) \rightarrow CH_4(g) + CO(g)$$
Calculate the number of molecule of CH_3COCH_3 decomposed when radiation for 2300 sec at the rate of 8.52×10^{-3} Js^{-1} takes place. [5]

6. a) Define molar extinction coefficient of a substance stating its unit.
b) The photochemical dimerization of anthracene(A) proceeds by the mechanism
$$A + h\nu \rightarrow A^*$$
$$A^* + A \rightarrow A_2$$
$$A^* \rightarrow A + h\nu_f \text{ (fluorescence)}$$
$$A_2 \rightarrow 2A$$
Applying steady state approximation to A^*, obtain the concentration of the dimer (A_2) in the photostationary state. [2+3]

Unit –III

[Answer **any three**] [3×6]

7. a) In a schematic spectral diagram show the line(s) you obtain in case of a (i) harmonic oscillator (ii) in the same diagram show the lines (fundamental, first overtone and hot bands) for the same oscillator if anharmonicity is considered. [no need to show overtones of hot band].
   b) A molecule has B=2.0 cm^{-1} and reduced mass $\mu=1.66\times10^{-27}$kg. Calculate the moment of inertia I and then determine the bond length r_e. [4+2]

8. a) The IR spectra of HCl shows a very intense absorption at 2886 cm^{-1}, a weaker one at 5668 cm^{-1} and a very weak one at 8347 cm^{-1}. Explain the observations (position of the bands and their intensity pattern) using proper equations. Hence also calculate the zero point energy of HCl.
   b) State and explain Frank-Condon principle. [4+2]

9. a) Discuss fluorescence and phosphorescence with the help of both potential energy and Jablonsky diagram.
   b) Infrared Raman spectrum of Cl_2 molecule shows a series of stokes lines separated by 0.98 cm^{-1} and a similar series of anti-stokes lines. Calculate the Cl-Cl bond length. [4+2]

10. a) Predict the spectra (rotational, vibrational, and/or Raman) observed for each of the following molecules and provide a short explanation
    (i) N_2 (ii) H_2O (iii) CO_2

    b) Draw **any two** transitions between potential energy curves
    (i) leading to dissociation to atom/atoms in their excited states
    (ii) showing phosphorescence
    (iii) showing different equilibrium geometries for ground and excited states
    c) Which one between fluorescence and phosphorescence has shorter lifetime and why? [3+2+1]

11. a) I being the moment of inertia of a molecule find out the expression necessary to tell transition between which two rotational states is most probable at a temperature T.
    b) Use Jablonski diagram to describe all 1^{st} order transitions after absorbing UV-Vis radiation. [3+3]

Unit –IV

[Answer **any two**] [2×6]

12. a) Define, with an example, a lyophilic colloid. How many such a colloid help in stabilizing a lyophobic colloid like a gold sol? Explain what do you mean by the term 'gold number'.
    b) If a water drop of 1mm radius is broken into a million droplets, calculate the increase in surface energy. [Given $\gamma = 72.75$ dynes m^{-1}] [4+2]

13. a) Derive Gibbs' adsorption equation for a two component system and comment on it.
    b) Derive Langmuir adsorption isotherm, clearly mentioning all the assumptions. [3+3]

14. a) "Colloid solutions are thermodynamically unstable." Comment.
    b) Under what condition, BET equation is converted to Langmuir equation?
    c) The volume of a liquid transported through porous diaphragm is 1.8 cc/sec. If the viscosity of the liquid is 8×10^{-3} poise, and the specific conductance of the solution is found to be 1.61×10^{-3} $ohm^{-1}cm^{-1}$. Calculate the zeta-potential in volts when the flowing current was found to be 6 amperes and dielectric constant of the liquid is 80. [1+2+3]

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