WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 6th Semester Examination, 2024

CEMACOR14T-CHEMISTRY (CC14)

PHYSICAL CHEMISTRY-IV

Time Allotted: 2 Hours | Full Marks: 40

The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

Answer any *three* questions taking *one* from each unit

UNIT-I

1. (a) What are 'Stokes' and 'anti-Stokes' lines in Raman spectrum? Why are Stokes lines being more intense than anti-Stokes lines? 2+2

   (b) The wave number of vibration of HCl^{36} molecule is 2990 cm^{-1}. Calculate the force constant of HCl bond. 3

   (c) The symmetric stretching of CO_2 is IR inactive but Raman active. — Explain. 3

   (d) (i) The difference in population between the α and β spin states of an electron in ESR spectroscopy is very low. But the system does not saturate. Explain why? 2+2

   (ii) What magnetic field strength must be applied to a free proton for spin transition to occur at 60.0 MHz? Magnetogyric ratio for ^1H is 26.7522×10^7 $rad.T^{-1}.s^{-1}$.

2. (a) Bond length of a homonuclear diatomic molecule cannot be determined spectroscopically. Justify or criticize the statement. 2

   (b) The rotational spectrum of HF molecule has lines 41.5 cm^{-1} apart. Calculate the moment of inertia and bond length of HF molecule. 3

   (c) State the effect of anharmonicity on the vibrational spectra of heteronuclear diatomic molecule. 3

   (d) Give the example of model system where the energy gap between successive levels 2

   (i) remains the same and (ii) increases.

   (e) For an unbound electron, what will be the value of Lande' factor (g-factor)? State the difference between NMR and ESR spectroscopy in terms of (i) population ratio of the two levels and (ii) line frequency. 1+3

UNIT-II

3. (a) A molecule on proper excitation undergoes photochemical dissociation. Explain this by drawing the potential energy curves for the ground state and the excited state of the molecule. 2

(b) The molar extinction co-efficient of $KMnO_4$ is 2.20×10^3 $M^{-1}cm^{-1}$. Calculate the percent transmission for a cell of path length 1 cm filled with 0.10 mM solution of $KMnO_4$. 3

(c) Define 'quantum yield' of a photochemical reaction. What inferences can be drawn if the quantum yield of a photochemical reaction is different from unity? 3

(d) What are the different radiative and non-radiative paths by which the excited state of a molecule can decay? Explain with the help of Jablonski diagram. 4

4. (a) What is a photosensitized reaction? Explain with an example. 2

(b) The molar extinction coefficient of a substance in water is 475 m^2/mol, what will be the path length of the cell to reduce the intensity of the transmitted beam to 20% of the initial value for 0.126 M solution of the substance in water? 3

(c) State Stark-Einstein law of photochemical equivalence. 2

(d) Ozone decomposes to $O_2(g)$ and $O(g)$ with a quantum yield of 1.0 when it is irradiated with radiation of wavelength 300 nm. If Ozone is irradiated with power of 100 Watt, how long it will take for 0.020 mol of $O_3(g)$ to decompose? 3

(e) Life time of phosphorescence is greater than that of fluorescence. — Explain. 2

UNIT-III

5. (a) What are the inherent assumptions in the Langmuir model of surface adsorption? Using Langmuir model, derive an expression for the fractional coverage of a gas, adsorbed on a solid surface, as a function of its pressure. 4

(b) A spherical soap bubble of volume $\pi/6$ cm^3 stands suspended in air. What is the excess pressure inside the bubble? 2

Given: the interfacial tension for the soap solution-air interface is 27 dyne/cm.

(c) Write down Gibbs adsorption equation and mention the significance of the term 'surface excess'. For a dilute solution, the surface tension often varies linearly with solute molar concentration (c) as $\gamma = \gamma^\circ - bc$, where γ° denotes the surface tension of the pure solvent. Show that the surface excess is $\Gamma = (\gamma^\circ - \gamma)/RT$. 4

(d) Define contact angle whenever a liquid comes in contact with a solid surface. The condition for wetting and non-wetting of the solid surface by the liquid can be explained in terms of the contact angle. — Explain. 4

6. (a) For multi-layer adsorption, write down BET equation. Mention the significance of the terms involved. Using this equation, how can the surface area of a solid adsorbent be measured? 4

(b) Calculate the increase in surface energy when one drop of water molecule of radius 2 mm is divided into ten droplets. Surface tension of water is 72 dyne/cm. 3

(c) Define surface tension. Graphically Represent the variation of surface tension (γ) of a liquid with temperature (T). Explain the significance of the point on the graph at critical temperature. 1+3

(d) Define (i) Tyndall effect (ii) Electrophoresis (ii) Electro osmosis. 3

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