UNIVERSITY OF NORTH BENGAL

B.Sc. Honours Part-III Examination, 2021

CHEMISTRY

PAPER-IX

PHYSICAL CHEMISTRY

Full Marks: 65

ASSIGNMENT

The figures in the margin indicate full marks.
All symbols are of usual significance.

1 Mark for neat and precise presentation

Answer any *four* questions 16×4=64

1. (a) On doubling the concentration of reactant, rate of the reaction is doubled. Find out the order of the reaction. 1
   (b) Distinguish between physical adsorption and chemisorption. 3
   (c) Explain adsorption isotherm and adsorption isobar. 2
   (d) Mentioning the assumptions derive the Langmuir adsorption isotherm. How will you derive Freundlich isotherm from this isotherm? 2+3+2
   (e) Explain the formation, stability and use of 'micelles'. 3

2. (a) Compare the characteristics of the first order reactions with those of the second order reactions. 3
   (b) Examine the order of the following reaction: 2

   $$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

   (c) Describe how you would determine the energy of activation of a chemical reaction from the temperature dependence of reaction rates. 5
   (d) A first order reaction is 40% complete in 30 minutes. How long will it take to be 80% complete? 3
   (e) Explain: "Zero-order reaction must be multistep and it goes into completion". 3

3. (a) Derive Bragg's equation for the diffraction of X-rays by crystals. 4
   (b) Both NaCl and KCl have similar geometric arrangements of positive and negative ions in their crystals, but their diffraction patterns are different. — Explain. 3
   (c) Show that 74% of the space in a crystal is occupied by atoms in a face centred cubic lattice. 3
   (d) Molybdenum (Molar mass = 95.94 g mol^{-1}) crystallises with a body centred cubic lattice has a density of 10.28 g cm^{-3}. Calculate the length of the unit cell and the distance between 110 planes. 3
   (e) Geometrically prove that a crystal cannot have a 5-fold rotation axis as well as an axis of greater than 6-fold symmetry. 3

4. (a) Set up the Schrodinger equation for a particle in a one-dimensional box. Show that the solution of this equation leads to the quantization of translational motion. Why a value of quantum number $n = 0$ is not permitted? 2+4+1

(b) Clearly explain the term degeneracy in quantum mechanics. Show that in a rectangular box of dimensions $l_x = a$ and $l_y = 2a$, there is an accidental degeneracy for the states ($n_x = 1,\ n_y = 4$) and ($n_x = 2,\ n_y = 2$). 2+3

(c) What do you mean by 'infrared active' and 'microwave active' molecules in spectroscopy? Give examples. 2

(d) Show that the de Broglie's hypothesis leads to Bohr's postulate of quantisation of angular momentum. 2

5. (a) What do you mean by photochemical reactions? Distinguish these from thermal reactions. 1+2

(b) State and explain Lambert-Beer law. Derive the integrated mathematical expression for this law. What is the significance of molar extinction coefficient? 2+3+1

(c) Explain singlet and triplet states. 2

(d) Distinguish between fluorescence and phosphorescence. 3

(e) How would you explain very high and very low quantum yields of some photochemical reactions? 2

6. (a) Derive the expression for the operator $\left(\hat{x} + \frac{d}{dx}\right)^2$. 3

(b) Verify that $f = \sin ax$ [where a is a constant] is not an eigen function of $\frac{d}{dx}$. 3

Modify the operator $\frac{d}{dx}$ so that the said function will be an eigen function.

Find out the eigen value.

(c) Verify whether the following operators will commute or not. 3

$\left(\hat{x} + \boldsymbol{i}\frac{d}{dx}\right)$, $\left(\hat{x} - \boldsymbol{i}\frac{d}{dx}\right)$

(d) Draw the sketches of ψ and ψ^2 for a particle in one dimensional box for the first five energy levels. Discuss about symmetry of the five wave functions. 5+2

7. (a) Show that the entropy is a logarithmic function of thermodynamic probability. 3

(b) How is molecular partition function defined? What is the effect of temperature on molecular partition function? 2+2

(c) For a system the energy levels are $0,\ \varepsilon,\ 2\varepsilon,\ 3\varepsilon$ and the degeneracy of the energy levels are 1, 1, 3, 5 respectively. Find out the molecular partition function at 300 K. 3

Given: $\varepsilon = 4.14 \times 10^{-21}$ J

(d) Derive Einstein's equation for the heat capacity of solid and arrive at Dulong-Petit law form this equation. 4+2

8. (a) Derive Michaelis-Menten equation. What is the significance of Michaelis constant? 3+1

(b) Discuss the structural differences between DNA and RNA molecules. 3

(c) Explain the Lock and Key theory of enzyme action. 2

(d) What is 'turnover number'? 1

(e) Show that the energy difference between two adjacent lines in the rotational spectrum of a rigid diatomic molecule is constant but the rotational intensities of transition occurring in the molecule are different. 3+3

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