(b) Why is quantum yield of H_2-Cl_2 reaction more than H_2-Br_2 reaction ? **5**

(c) Discuss the Rice-Herzfield mechanism for the gas phase decomposition of acetaldehyde. **10**

6. (a) Define dynamic chain reaction and explain how chain can be broken in chain reactions. **3**

(b) Consider the following mechanism for an enzyme-catalysed reactions :

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

(complex)

Under steady state approximation, for [ES], show that this reaction ratio is given by :

$$n = \frac{k_2 [E]_0 [S]}{k_m + [S]}$$

where the symbols have their usual meanings. Show that the rate of reaction becomes Ist order if $k_m \gg [s]$. **12**

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BB293

M. Sc. EXAMINATION, May 2019

(Second Semester)

(B. Scheme) (Re-appear)

CHEMISTRY

CH506B

Physical Chemistry-II (Kinetics, Quantum Mechanics and Spectroscopy)

Time : 3 *Hours*] [*Maximum Marks :* 100

Before answering the question-paper candidates should ensure that they have been supplied to correct and complete question-paper. No complaint, in this regard, will be entertained after the examination.

Note : Attempt *Five* questions in all, selecting at least *one* question from each Unit. All questions carry equal marks.

Unit I

1. (a) What are the postulates of quantum mechanics ? **8**

(b) Write the operators for the three components of angular momentum. **6**

(c) Prove that the position operator $\hat{x}$ and the momentum operator $\hat{P}_x$ are Hermitian. **6**

2. (a) What do you understand by a particle in a three dimensional box of dimensions a, b and c ? State and explain the boundary condition apply. **8**

(b) For the simplex-case of $a = b = c$, explain the concept of degeneracy by writing the expressions for energy upto $n = 3$. **7**

(c) Show that if the eigen function of a Hermitian operator have different eigenvalues, they are orthogonal. **5**

Unit II

3. (a) Discuss the kinetics of consecutive 1st order reaction. **6**

(b) Describe activated complex theory and derive an expression for the rate constant on the basis of activated complex theory. **10**

(c) Explain the significance of steric factor P used in collision theory. **4**

4. (a) Discuss single and double sphere models in an ionic reaction. Which model explains the experimental results well ? **10**

(b) What are the influence of ionic strength on such ionic reaction ? **5**

(c) What are the advantages of activated complex theory over collision theory. **5**

Unit III

5. (a) Define photochemical reactions. How do they differ from thermal reaction ? **5**

(c) Explain how (i) one can evaluate Michaelis's constant by Lineweave-Burk Plot. **5**

Unit IV

7. (a) What are the selection rules for pure rotational Raman spectrum of a symmetric top molecule ? **6**

(b) Write notes on the Effect of isotopic substitution in rotational spectra.

(c) Give an account of electronic spectra for diatomic molecules. **7**

8. (a) Find the expression for the spacing between two adjacent rotational levels. How can the study of rotational spectra be used to find the moment of inertia and the internuclear distance of a molecular. **8**

(b) Why are pure rotational spectra studies only in the gaseous states of atoms and molecules ? **4**

(c) Give a brief account of organic change transfer complexes in electronic spectra. **8**

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