(8 pages)   Reg. No. : ....

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M.Sc. (CBCS) DEGREE EXAMINATION, APRIL 2023

Fourth Semester

Chemistry – Core

PHYSICAL CHEMISTRY – IV

(For those who joined in July 2017 onwards)

Time : Three hours   Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. The molecule which is IR inactive but Raman active is

    (a) HCl
    (b) N_2
    (c) SO_2
    (d) Protein

2. In the Born-Oppenheimer approximation which one of the following order is correct

    (a) $E_{el} > E_{vib} > E_{rot} > E_{tr}$
    (b) $E_{el} > E_{rot} > E_{vib} > E_{el}$
    (c) $E_{vib} > E_{el} > E_{rot} > E_{tr}$
    (d) $E_{rot} > E_{vib} > E_{el} > E_{tr}$

3. A vibrational mode in a molecule will be Raman active if

    (a) the polarizability of the molecule changes during the vibration
    (b) it is IR active also
    (c) the polarizability of the molecule remains the same during the vibration
    (d) the excited normal modes have the same symmetry as are of the Cartesian coordinates

4. Consider the carbonyl stretching frequency in the IR spectro of the compounds (A) $CH_3 CONHCH_3$ (B) $Ph CONHCH_3$ (C) $CH_3 CONHPh$

    Which of the following is the correct increasing order of the carbonyl stretching frequency?

    (a) A < B < C
    (b) B < A < C
    (c) A < C < B
    (d) C < B < A

5. In the Lindemann mechanism of unimolecular reactions the observed order at low concentration is

    (a) 0.1
    (b) 1
    (c) 1.5
    (d) 2

6. Consider the following Statements :

    An increase in the rate of a reaction for a rise in temperature is due to

    1. the increase in the number of collisions
    2. the shortening of the mean free path
    3. the increase in the number of activated molecules
    4. the increase in pressure of the system

    Which of the statements given above are correct?

    (a) 1 and 2
    (b) 2 and 3
    (c) 1 and 3
    (d) 1, 3 and 4

7. Which of the following statements is in accordance with collision theory?

    I. Rate is directly proportional to collision frequency
    II. Rate depends upon orientation of atoms
    III. Temperature determines the rate

    (a) only III
    (b) only I and II
    (c) only II and III
    (d) all of these

8. In the mechanism of reaction

    $H_2 + Br_2 \rightarrow 2HBr$ the first step is

    (a) dissociation of H_2 into H radicals
    (b) dissociation of Br_2 into Br radicals
    (c) reaction of H radical with Br_2
    (d) reaction of Br radical with H_2

9. The aggregation of surfactant molecules is known as

    (a) Micelles
    (b) Clusters
    (c) Gel
    (d) Colloid

10. Which of the following is not a heterogeneous catalyzed reaction?

    (a) $2H_2 + O_2 \xrightarrow{pt} 2H_2O$
    (b) $CaCClO_2 \xrightarrow{NiO} CaCl_2 + O_2$
    (c) $2SO_2 + O_2 \xrightarrow{NO} 2SO_3$
    (d) $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$

PART B — (5 × 5 = 25 marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 250 words.

11. (a) Fundamental and First overtone transition of No molecule are centrad at 1876 cm^{-1} and 3724 cm^{-1} respectively. Evaluate

    (i) the equilibrium vibrational frequency and

    (ii) the exact Zero point Energy.

Or

(b) Explain the P and R branch lines of the vibration-tolation specturm.

12. (a) Write the differences between Raman and IR spectra.

Or

(b) Explain polarized and depolarized Raman lines.

13. (a) Explain flash photolysis technique for studying the kinetics of fast reactions.

Or

(b) Derive an expression for the relaxation time of fast reactions following first-order kinetics.

14. (a) Explain the influence of pressure on Reaction rates in solution.

Or

(b) Explain the kinetics of decomposition of O_4 and N_2O_5.

15. (a) Explain Gibbs adsorption isotherm.

Or

(b) Describe the solubilzation of micelles in the light of Laplace's law.

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b).

Each answer should not exceed 600 words.

16. (a) Describe the concept of overtones in vibrational spectra based on the anharmonicity and Harmonicity of the oscillator.

Or

(b) (i) Explain the applicability of Born-Oppenhemer approximation for the independent rotations and vibrations of a diatomic molecule. (4)

    (ii) Calculate the force constant for the bond in HCl from the put that the fundamental frequency is 8.667×10^{13} S^{-1}. (4)

17. (a) How many Normal modes of vibration are possible for the following molecules HBr, O_2, OCS (linear), SO_2 (bent), BCl_3, $HC \equiv CH$, CH_4 and CH_3I?

Or

(b) Account for the changes in the vibrational spectra of donor molecules upon coordination in the following complexes.

    (i) Terminal and bridged carbonyls

    (ii) Cis and Trans carbonyls.

18. (a) Explain and deuve equation to account for the influence of solvents on reaction between ions in solution according to ARR theory.

Or

(b) Derive Bronsted – Bjerum equation.

19. (a) Discuss the Lindemann theory of unimolecular reactions.

Or

(b) Describe Pulse method and stopped flow method for studying kinetics of fast reactions.

20. (a) Explain the kinetics of single substrate enzymatic reaction and derive the rate law.

Or

(b) Derive an expression for Freundlich adsorption isotherm explain its limitations and applications.

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