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Reg. No. :

Code No. : 5886

Sub. Code : PCHM 43

M.Sc. (CBCS) DEGREE EXAMINATION, APRIL 2020.

Fourth Semester

Chemistry — Core

PHYSICAL CHEMISTRY — IV

(For those who joined in July 2017 onwards)

Time : Three hours

Maximum : 75 marks

PART A — ($10 \times 1 = 10$ marks)

Answer ALL questions.

Choose the correct answer.

1. What is the relation between restoring force, f to the displacement q in Hooke's law?
(a) $f = -kq$ (b) $f = kq$
(c) $f = -kq^2$ (d) $f = kq^2$
2. Which of the following molecules will not display an infrared spectrum?
(a) CO_2 (b) N_2
(c) Benzene (d) $\text{H-C} \equiv \text{C-H}$

3. In Raman spectroscopy, energy of change comes from
- (a) Photon (b) Electron
(c) Ion (d) Molecule
4. In Raman spectrum, if λ is the wavelength of incident radiation, then the Stoke's lines will have wavelength equal to
- (a) λ (b) $\lambda + \Delta\lambda$
(c) $\lambda + \Delta\lambda$ (d) λ^2
5. The factor introduced to make collision theory a more generalized one is called
- (a) Steric Factor (b) Hammett Factor
(c) Collision Factor (d) Arrhenius Factor
6. The minimum energy, above the internal energy, which the reacting molecule must possess so that their collision results in a reaction is known as
- (a) Threshold energy
(b) Average Potential Energy
(c) Average Kinetic energy
(d) Activation energy

7. Effect of ionic strength is
- (a) Ionic effect
 - (b) Electrophoretic effect
 - (c) Salt effect
 - (d) Solvent effect
8. Explosive reactions are the type of
- (a) Fast reactions
 - (b) Chain reactions
 - (c) Slow reactions
 - (d) Surface reactions
9. Adsorption of acetic acid on charcoal is an example for
- (a) Absorption (b) Physisorption
 - (c) Chemisorption (d) Both (b) and (c)
10. The transition of ions to micelle is
- (a) Reversible
 - (b) Irreversible
 - (c) Both (a) and (b)
 - (d) Neither (a) nor (b)

PART B — ($5 \times 5 = 25$ marks)

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

Each answer should not exceed 250 words.

11. (a) Homonuclear diatomic molecules do not show vibrational spectra. Explain why?

Or

- (b) Explain the effect of anharmonicity on the vibrational spectra of diatomic molecules.
12. (a) Consider the molecular vibrations of carbon dioxide and determine whether they are Raman active (or) not.

Or

- (b) What are the advantages of Raman spectroscopy over IR?
13. (a) Discuss the simple collision theory.

Or

- (b) How will you study Fast reaction by temperature jump method?
14. (a) Give the significance of volume of activation.

Or

- (b) Account for the first and second explosion limits in $\text{H}_2\text{-O}_2$ reaction.

15. (a) Derive Langmuir isotherm equation.

Or

- (b) Write a brief note on heterogeneous catalysis.

PART C — ($5 \times 8 = 40$ marks)

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

Each answer should not exceed 600 words.

16. (a) Explain the terms :

- (i) Overtones
- (ii) Combination of bands
- (iii) Selection rules for IR spectra
- (iv) Born-Oppenheimer approximation.

Or

- (b) How many normal modes of vibration are possible for the following molecules?

- (i) HBr
- (ii) O₂
- (iii) OCS (linear)
- (iv) SO₂ (bent)

17. (a) Explain:
- (i) Q-switching
 - (ii) Types of Lasers.

Or

- (b) Discuss the classical theory of Raman spectroscopy.
18. (a) Discuss the salient features of ARR Theory and write its thermodynamic formulation.

Or

- (b) State the limitations of Langmuir theory of unimolecular reaction and discuss Hinshelwood theory of unimolecular reaction.
19. (a) Discuss the Factors influencing reaction rates in solution.

Or

- (b) Using the Rice-Herzfeld mechanism for the formation of HBr in the reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$, and steady state treatment for [H] and [Br], derive the rate law and expression for the formation of HBr.

20. (a) Derive B.E.T. adsorption isotherm.

Or

(b) Discuss Michael is-Menton Kineics.
