

(7 pages)

Reg. No. :

Code No. : 7167

Sub. Code : PCHM 43

M.Sc. (CBCS) DEGREE EXAMINATION, APRIL 2019.

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. For a linear diatomic simple harmonic oscillator model, origin of perpendicular vibrations is

- (a) $\Delta J = 0$ and $\Delta v = \pm 1$
- (b) $\Delta J = \pm 1$ and $\Delta v = \pm 1$
- (c) $\Delta J = 0$ and $\Delta v = \pm 1, \pm 2, \pm 3$
- (d) Both (a) and (b)

2. The weak *I*_r band arises due to the $v = 1$ to $v = 2$ transition is known as

- (a) fundamental band
- (b) first overtone band
- (c) second overtone band
- (d) hot band

3. Which of the following is called red Laser?

- (a) He-Ne Laser (b) Ar-Laser
- (c) Ar⁺-Laser (d) Kr-Laser

4. Which of the following molecules is / are symmetric top?

- (a) Chloroform
- (b) Chloromethane
- (c) Phosphorous trichloride
- (d) All of these

5. The 1967 Nobel prize for the contributions to fast reaction kinetics was won by

- (a) Manfred Eigen (b) Norrish
- (c) Porter (d) All of them

Page 2

Code No. : 7167



6. Absolute Reaction Rate Theory (ARRT) was developed by

- (a) Eyring
- (b) Polanyi
- (c) Evans
- (d) All of them

7. For a reaction between two ions, the plot of $\log k$ versus $\sqrt{\mu}$ gives a straight line with slope equal to +2. What are the charges of the ions?

- (a) -2 and -1
- (b) -2 and +1
- (c) +2 and -1
- (d) Both (b) and (c) are correct

8. The reaction, $H + O_2 \rightarrow HO + O$, is an example of

- (a) chain initiation
- (b) propagation
- (c) chain branching
- (d) termination

Page 3

Code No. : 7167

9. Which of the following processes is an example of heterogeneous catalysis involving solid catalyst and gaseous reactants?

- (a) Hydrogenation of alkenes by Wilkinson catalyst
- (b) Haber process for the production of ammonia
- (c) Contact process for the manufacture of sulphuric acid
- (d) All of these

10. In enzyme catalysis the rate / [S] vs rate plot is called

- (a) Michaelis - Menton plot
- (b) Lineweaver - Burk plot
- (c) Eadie's plot
- (d) Langmuir - Rideal Plot

PART B — (5 × 5 = 25 marks)

Answer ALL questions, choosing either (a) or (b), each answer should not exceed 250 words.

11. (a) How many modes of vibrations are there for H_2O molecule? Sketch the symmetry of fundamental modes of vibrations of them.

Or

(b) The force constant of CO molecule is 1840 Nm^{-1} . Calculate the vibrational frequency in cm^{-1} . The atomic masses are $^{12}\text{C} = 19.923 \times 10^{-27} \text{ kg}$ and $^{16}\text{O} = 26.564 \times 10^{-27} \text{ kg}$.

Page 4

Code No. : 7167

[P.T.O.]



12. (a) Describe the quantum theory of Raman effect.

Or

- (b) What do you mean by polarized and depolarized Raman line? In what way it is related to the symmetry of vibrations?

13. (a) Discuss the kinetics of reactions taking place in flow systems involving stopped flow.

Or

- (b) Describe the Lindemann hypothesis for the study of unimolecular reaction.

14. (a) Derive Hammett equation and give the significances of substituents and reaction constants.

Or

- (b) What are chain reactions? Give their characteristics.

15. (a) Give the expression for BET adsorption isotherm and explain the terms in it.

Or

- (b) Explain the effect of pH and temperature on the rate of enzyme catalysed reactions.

Page 5 Code No. : 7167

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b), each answer should not exceed 600 words.

16. (a) Given that $\bar{\nu}_e = 536.10 \text{ cm}^{-1}$ and $x_e \bar{\nu}_e = 3.4 \text{ cm}^{-1}$ for $^{23}\text{Na}^{19}\text{F}$ gas. Calculate the frequencies of first and second vibrational overtone transitions.

Or

- (b) Describe the vibration-rotation spectra of diatomic molecules with the help of energy level diagram and give the selection rules for P, Q and R branch lines.

17. (a) Describe the principle, characteristics and types of Lasers used in Raman spectroscopy.

Or

- (b) Describe the applications of IR and Raman spectroscopy in the determination of structure of molecules with proper examples.

18. (a) Describe the thermodynamic formulation of transition state theory.

Or

- (b) (i) Describe the application of NMR method in the study of fast reactions.
(ii) Write a note on Slater theory of unimolecular reactions.

Page 6 Code No. : 7167



19. (a) Derive an equation for the influence of pressure of solvent on rate and explain the significance of volume of activation.

Or

- (b) Explain the kinetics and mechanism of $\text{H}_2\text{-Br}_2$ reaction with the help of steady state approximation.

20. (a) Discuss Freundlich adsorption isotherm and Langmuir adsorption isotherm.

Or

- (b) What do you mean by acidity function? Explain the general pattern of 'acid-base catalysed reactions with the help of $\log k$ vs pH plot.
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