

M. Sc DEGREE END SEMESTER EXAMINATION - OCTOBER 2022**SEMESTER 3 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY****COURSE : 16P3CHET11 / 16P3CPHT11 : PHYSICAL CHEMISTRY - III***(For Supplementary - 2016/2017/2018/2019/2020 Admissions)*

Time : Three Hours

Max. Marks: 75

PART A**Answer any 10 (2 marks each)**

1. What happens to over all reaction rate when iodine is replaced by bromine in the halogenations of acetone in aqueous solution?
2. Examine the defects of Lindemann theory of unimolecular reactions?
3. What do you mean by acid function?
4. What is the action of promoters in a catalysis?
5. Write the Hammett equation and mention its significance.
6. State Kohlrausch's law of independent migration of ions. How the conductance of acetic acid obtained using the results of ion conductances ?
7. Define ionic strength of an electrolyte solution introduced by Lewis and Randal. What is ionic strength of 0.01 m aq. NaCl solution ?
8. Derive the relationship between ion conductance and ionic mobility at infinite dilution
9. The compound $\text{CH}_3\text{-CH=CH-CHO}$ has a strong absorption in the ultraviolet at $46,950\text{ cm}^{-1}$ and a weak absorption at $30,000\text{ cm}^{-1}$. Justify these features in terms of the structure of the molecule.
10. Explain Photostationary state with an example.
11. Distinguish between positive and negative adsorptions.
12. What is Freundlich adsorption isotherm?
13. Give any two postulates of Langmuir theory.

(2 x 10 = 20)**PART B****Answer any 5 questions by attempting not more than 3 questions from each of the following bunches (5 marks each)****Bunch I (Short Essay Type)**

14. Give Semenov—Hinshelwood mechanism for explosive reactions.
15. Give the evidence for the formation of triple ions obtained from the experiment conducted by Fuoss and Kraus
16. Write note on (a) Photosensitization (b) pulse radiolysis
17. Write a note on different types of colloids. Give examples.

Bunch II (Problem Type)

18. A second order reaction has a rate constant $k = 2.5 \times 10^{-3}\text{ L mol}^{-1}\text{ s}^{-1}$ at 25°C . Its energy of activation is 48 kJ mol^{-1} . Calculate ΔS for the reaction, assuming that the reaction takes place in solution.
19. The volume of activation for a certain reaction is $-4 \times 10^{-6}\text{ m}^3\text{ mol}^{-1}$ at 300K . Calculate the pressure required to double the rate constant at 10^5Pa .

20. The equivalent conductances of sodium acetate, hydrochloric acid and sodium chloride at infinite dilution are 91.0, 426.16 and 126.45 $\text{ohm}^{-1} \text{cm}^2$, respectively at 25°C. Calculate the equivalent conductance at infinite dilution for acetic acid.
21. Radiation of wavelength 2500 Å was passed through a cell containing 10 ml of a solution which was 0.05 M in oxalic acid and 0.01 M in uranyl sulphate. After absorption of 80 joules of radiation energy, the concentration of oxalic acid was reduced to 0.04 M. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength. **(5 x 5 = 25)**

PART C

Answer any 2 (15 marks each)

22. Discuss briefly Semenov-Hinshelwood theory of branching chain reaction.
23. Derive Michaelis-Menten equation and discuss the effect of temperature and pressure on Enzyme catalysis?
24. How the formation of ionic atmosphere affect the activity coefficient of electrolyte. Derive the Debye-Huckel limiting law equation? Explain the graphical plot that validate DHLL equation.
25. Write briefly on (i) electrical properties of colloids and (ii) structure of micelle. **(15 x 2 = 30)**