

Reg. No

Name

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

Time : Three Hours

Max. Marks: 75

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

1. What are the demerits of Lyndemanns unimolecular mechanism?
2. The quantum yield of H_2-Cl_2 reaction is very high. Explain.
3. What is meant by potential energy surface of the reaction, $A + B-C \rightarrow A-B + C$?
4. Explain the Bronsted catalysis law.
5. Write a note on the influence of pH on catalytic reactions
6. What is the effect of dilution on specific conductivity and equivalent conductivity?
7. Derive the relationship between ion conductance and ionic mobility at infinite dilution
8. Why conduction of proton in ice is fifty times faster than in water at $0^\circ C$?
9. What is an actinometer? Describe how a uranyl oxalate actinometer may be used.
10. A certain system absorbs 2×10^{16} quanta per second. At the end of 20 minutes, it is observed that 0.002 mole of the irradiated substance has reacted. What is the quantum yield of the process?
11. What is streaming potential?
12. Distinguish between positive and negative adsorptions.
13. Explain the chemistry of coagulation of a colloid.

(2 x 10 = 20)

Section 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 the thermodynamic formulation of reaction rate.
15. Give an account of the influence of temperature on ion conductances. Write the relation between conductance and temperature which is analogous to Arrhenius rate equation
16. Write a note on the photochemistry of vision.
17. Give an account of Reflection absorption Infrared spectroscopy in the study of solid surfaces.

Bunch II (Problem Type)

18. For a homogeneous gaseous reaction, the rate constants are $3.0 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ and $1.2 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ at 629K and 700K respectively. Calculate the energy of activation and Frequency parameter.

19. Represent the equation that shows the effect of dielectric constant of the medium on the rate a reaction and apply to discuss the effect of increasing dielectric constant of the medium on the rate of the following reactions,
- a) $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{NO}_2^- \rightarrow [\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+} + \text{Br}^-$ and
 b) $\text{CH}_2\text{ClCOO}^- + \text{OH}^- \rightarrow \text{CH}_2\text{OHCOO}^- + \text{Cl}^-$
20. Calculate the ionic strength of the following solutions at 298 K. a) 0.10 m Aluminium sulphate
 b) 0.25 m Potassium sulphate c) 0.02 m Calcium chloride and 0.1 m KCl
21. A solution containing $0.49 \text{ mols liter}^{-1}$ of oxalic acid and 0.01 moles of uranyl nitrate were prepared. 10 ml of this solution was exposed to radiation of wavelength 2550. When $8.8 \times 10^{-2} \text{ kJ}$ of radiation had been adsorbed, the concentration of oxalic acid was found to have been reduced to 0.038 M. Calculate the quantum yield

(5 x 5 = 25)

Section C

Answer any 2 (15 marks each)

22. a) What are the assumptions in Transition state theory?
 b) Using the statistical mechanical treatment of the equilibrium and considering of the activated complex through the col as a very loose vibration, derive an equation for the rate constant of bimolecular reactions.
23. Describe the Semenov Hinshelwood theory of branching chain reaction. Explain the lower and upper explosion limits with reference to the kinetic equations
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. Give an account of the electrokinetic effects. Give their applications

(15 x 2 = 30)