Reg. No ..... Name **17P3633**

MSc DEGREE END SEMESTER EXAMINATION- OCTOBER-NOVEMBER 2017

SEMESTER 3 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY

COURSE : **16P3CHET11 / 16P3CPHT11 ; PHYSICAL CHEMISTRY - III**

(For Regular - 2016 admission)

Time : Three Hours Max. Marks: 75

Section A
Answer any 10 (2 marks each)

1. Give an account of Lyndemann theory of unimolecular reaction mechanism.
2. The quantum yield of H_2-Cl_2 reaction is very high. Explain.
3. What is cage effect?
4. Apply the Bronsted – Bjerrum equation to predict the effect of increasing ionic strength of the medium on the following reaction, $CH_3COOC_2H_5 + OH^-$? Products.
5. Derive the relationship between ion conductance and ionic mobility at infinite dilution
6. The compound CH_3-CH=CH -CHO has a strong absorption in the ultraviolet at 46, 950 cm^{-1} and a weak absorption at 30,000 cm^{-1}. Justify these features in terms of the structure of the molecule.
7. 3-buten-2-one has a strong absorption at 213 nm and a weaker absorption at 320 nm. Justify these features and assign the ultraviolet absorption transitions.
8. Explain the term 'concentration quenching'.
9. With the help of an energy diagram, explain how the solvent polarity favors the exciplex formation and subsequent emission?
10. Define electrophoresis.
11. Sketch the variation of surface pressure of films with the pressure applied.
12. Explain the electrical phenomenon which arises due to a nondiffusible ion across a semi permeable membrane.
13. Give the merits of TPD.

10 x 2 (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. Write briefly about Taft relationship
15. Considering the deactivation processes of the singlet excited state in the absence and presence of a quencher, derive the Stern-Volmer equation which expresses the ratio of the fluorescence quantum yields in the presence and absence of a quencher.
16. Describe the mechanism of fluorescence. In what respect is a fluorescence spectrum not the exact mirror image of the corresponding absorption spectrum?
17. Write briefly on "bonding of adsorbate to solid".

Bunch II (Problem Type)

18. The rate constant of a second order reaction was found to be 0.134 $Lmol^{-1}s^{-1}$ at 300 K and 0.569 $Lmol^{-1}s^{-1}$ at 450K. Calculate the activation energy of the reaction. Also calculate the Pre-exponential factor for the reaction.
19. The conductance of a cell containing an aqueous 0.0560 *M* KCl solution is 0.0239 O^{-1}. When the same cell is filled with an aqueous 0.0836 *M* NaCl solution, its conductance is 0.0285 O^{-1}. Given that the molar conductance of KCl is 1.345×10^2 O^{-1} mol^{-1} cm^2, calculate the molar conductance of the NaCl solution
20. Radiation of wavelength 2500 A° 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.
21. For a 1.01×10^{-4} M aqueous solution of n-butanoic acid at 27^0C, dn / dc = $-0.081 Nm^2mol^{-1}$. If we use the Gibbs adsorption equation, determine the surface excess of butanoic acid and also calculate the average surface area available to each molecule.

5 x 5 (25)

Section C
Answer any 2 (15 marks each)

22. Discuss briefly Semenoff-Hinshelwood theory of branching chain reaction.
23. Discuss the effect of ionic strength on the rate of a reactions in solution explaining primary salt effect and secondary salt effect.
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 the postulates of the Isotherms for (i) monolayer adsorption and (ii) multilayer adsorption. Use any one method to find the surface area of the adsorbent.

2 x 15 (30)