F 4680 (Pages : 2) Reg. No.....

Name.....

M.Sc. DEGREE (C.S.S.) EXAMINATION, JANUARY 2017

Third Semester

Faculty of Science

Branch III : Chemistry

CH3 C11—CHEMICAL KINETICS, SURFACE CHEMISTRY AND PHOTOCHEMISTRY

(2012 Admission onwards)

Time : Three Hours Maximum Weight : 30

Section A

Answer any **ten** *questions.*
Each question carries a weight of 1.

1. What do you mean by branching chain reaction ?
2. Explain the term steady state approximation.
3. Distinguish between excimers and exciplexes.
4. Distinguish between prototropic and protolyptic mechanism with example.
5. Define steric factor. Explain how is it related to entropy of activation ?
6. Explain thermoluminescence with example.
7. Explain the principle of Auger Electron Spectroscopy.
8. What are the general properties of emulsion ?
9. Spontaneous adsorption is exothermic. Why ?
10. What are micelles ?
11. Explain with one example anionic and cationic surfactants.
12. What do you mean by delayed fluroscence ?
13. What is potential energy surface ? Explain its significance.

(10 × 1 = 10)

Section B

Answer any **five** *questions by attempting not more than* 3 *questions from each bunch.*
Each question carries a weight of 2.

BUNCH I (Short Essay Type)

14. Derive Stern-Volmer equation. Represent graphically.
15. Write a short note on Langmuir Unimolecular theory of adsorption.

16. The decomposition of NO_2Cl takes place according to the following mechanism. Assuming steady state for Cl derive the rate law. What is the apparent rate co-efficient.

$$NO_2Cl \xrightarrow{k1} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{k2} NO_2 + Cl_2$$

17. Explain the principle and working of solar cells.

BUNCH II (Problem Type)

18. Photobromination of cinnamic acid to dibromocinnamic acid was carried out in blue light of wavelength 440 nm using light intensity of $1.5 \times 10^{-3} JS^{-1}$. An exposure of 20 minutes produced a decrease of 0.075 millimoles of bromine. The solution absorbed 80% of the light passing through it. Calculate the quantum yield of the reaction.

19. A second order reaction has a rate constant $k = 2.5 \times 10^{-3}$ Lmol S^{-1} at 25°C. Its energy of activation is 48 $KJmol^{-1}$. Calculate $\Delta S^{\#}$ for the reaction, assuming that the reaction takes place in solution.

20. For an enzyme-substrate system obeying the simple Michelis-Menten mechanism, rate of product formation when the substrate concentration is very large, has the limiting value 0.02 mol dm^{-3}. At a substrate concentration of 250 mg dm^{-3}, the rate is half this value. Calculate k_1/k_{-1} assuming that $k_1 >> k_{-1}$.

21. 0.106 mg of stearic acid (M = 284 g mol^{-1}) is found to cover 500 cm^2 of water surface at the point where surface pressure just begins to rise sharply. Estimate the cros-sectional area a, per stearic acid molecule and thickness *t*, of the surface film of stearic acid on water. Density of stearic acid = 0.85 g cm^{-3}.

(5 × 2 = 10)

Section C

Answer any **two** *questions.*
Each question carries a weight of 5.

22. (a) Explain the principle of Lasers in the study of photochemical kinetics.

    (b) Explain briefly mechanism of heterogeneous catalysis with example.

23. (a) Explain the E-type and P-type delayed fluroscence.

    (b) Derive Michelis-Menten equation.

24. Write notes on :

    (a) Flash photolysis.

    (b) Eley-Ridel mechanism.

    (c) NMR and ESR methods of studying fast reactions.

25. (a) Describe how the limitations of the Lindemann theory of unimolecular reaction are overcome by the Hinshelwood and RRK modification.

    (b) compare Transition state theory with Collision theory.

(2 × 5 = 10)