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# M.Sc. DEGREE (C.S.S.) EXAMINATION, JANUARY 2016

## Third Semester

Faculty of Science

Branch III: Chemistry

CH 3C 11—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.

- Explain the significance of rate determining step in a multistep reaction.
- 2. Explain the principle of SEM.
- 3. Distinguish between activated complex and transition state.
- 4. Write London equation for calculating activation energy.
- 5. Explain Bioluminescence with example.
- 6. Define Zeta potential.
- 7. How does temperature influences photochemical reaction?
- 8. What is the condition under which BET isotherm approximates to Langmuir adsorption isotherm?
- 9. Write Stern-Volmer equation. Represent graphically.
- 10. Explain with one example anionic surfactants.
- 11. Write Gibb's adsorption isotherm. Explain the term involved.
- 12. Unimolecular gas phase reaction follows 1<sup>st</sup> order kinetics at high pressure and 2<sup>ml</sup> order at low pressure. Why?
- 13. What is potential energy surface? Explain its significance.

 $(10 \times 1 = 10)$ 

#### Section B

Answer any five questions by attempting not more than 3 questions from each bunch.

Each question carries a weight of 2.

BUNCH 1 (SHORT ESSAY TYPE)

- Explain the principle of Surface Enhanced Raman Spectroscopy.
- 15. Describe the stabilizing action of surfactants.

Turn over

16. The decomposition of N2O5 takes place according to the following mechanism. Derive the rate law.

$$N_2O_5 \xleftarrow{\frac{h_1}{k-1}} NO_2 + NO_3$$
 $NO_2 + NO_3 \xrightarrow{h_2} NO_2 + O_2 + NO$ 
 $NO + NO_3 \xrightarrow{h_3} 2NO_2$ 

17. Explain primary and secondary kinetic salt effect.

# BUNCH 2 (PROBLEM TYPE)

- 18. Biacetyl triplets have a quantum yield of 0.25 for phosphorescence and a measured lifetime of the triplet state of 10 milliseconds. The phosphorescence is quenched by a compound Q with a diffusion controlled rate of 10<sup>10</sup> I mol <sup>-1</sup>s <sup>-1</sup>. What concentration of Q is required to reduce the phosphorance yield to half?
- 19. The relaxation time for attaining equilibrium in  $A + B \xrightarrow{k} C$  has been found to the 100  $\mu$ s.

The equilibrium constant of the reaction is  $10^{10}$ . Evaluate the rate constants  $k_1$  and  $k_{-1}$ .

- 20. In an experiment to measure quantum efficiency of a photochemical reaction, the absorbing substance was exposed to 490 nm light from a 100 W source for 45 minutes. The intensity of transmitted light was 40 % of the intensity of the incident light. As a result of irradiation, 0.344 mol of the absorbing substance decomposed. Determine the quantum efficiency.
- 21. The intrinsic viscosity of a solution of poly isobutylene at 20°C is 180 cm³ per gram. If [n] is related to the viscosity-average molar mass  $M_{\rm visc}$  by the expression, [n] = 3.6 × 10<sup>-2</sup> ( $M_{\rm visc}$ ) <sup>0.64</sup>, calculate the molar mass of the polymer.

 $(5 \times 2 = 10)$ 

## 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) Derive Michelis-Menten equation for an enzyme catalysed reaction.
- 23. (a) Explain the principle of Auger and ESCA.
  - (b) Write a note on dimerization of anthracene.
- 24. (a) Greenhouse effect.
  - (b) Eley-Ridel mechanism.
- 25. (a) What are the assumptions in Transition state theory? Following the theory derive an equation for rate constant.
  - (b) Compare Transition state theory with Collision theory.

 $(2 \times 5 = 10)$