

Exam. Code : 210403

Subject Code : 4835

M.Sc. Chemistry 3rd Semester

**ELECTROCHEMISTRY & CHEMICAL
DYNAMICS**

Course—XIX

Time Allowed—Three Hours] [Maximum Marks—50

Note :— Candidates are to attempt **FIVE** questions, **ONE** from each Section. **Fifth** question may be attempted from any Section. All questions carry equal marks.

SECTION—A

1. Discuss the thermodynamic treatment of electrified surfaces leading to the derivation of the Lippmann equation. 10
2. (a) Derive Butler-Volmer equation in the kinetics of the electrode reactions.
(b) Determine the effect that increasing the over potential from 0.50 V to 0.60 V has on the current density in the electrolysis of 1.0 M NaOH(aq), which is 1.22 mA cm⁻² at 0.50 V and 25°C. Take $\alpha = 0.50$. 5,5

SECTION—B

3. (a) Derive the mathematical expression for Arrhenius Pre-exponential factor.
- (b) The following data was obtained for the vapour phase decomposition of ethylene oxide into methane and carbon monoxide at 414.5°C :

t (min)	0	5	7
p (mm Hg)	116.51	122.56	125.72

t (min)	9	12	18
p (mm Hg)	128.74	133.23	141.37

Show that the reaction is first-order and calculate the rate constant. 5,5

4. Derive rate expression for unimolecular reactions according to Lindemann-Hinshelwood theory. 10

SECTION—C

5. Using steady state approximation, derive rate laws for (a) photochemical reactions of Hydrogen-Chlorine, and (b) chain reaction between Hydrogen and Bromine. 5,5

6. Discuss stopped flow method used for determining rate of fast reactions. Compare it with flash photolysis. 10

SECTION—D

7. (a) Evaluate the limiting current density at an electrode in which the concentration of Mg^{2+} ions is 1.5 mmol dm^{-3} at 25°C . The thickness of the Nernst diffusion layer is 0.32 mm . The ionic conductivity of Mg^{2+} at infinite dilution and 25°C is $10.60 \text{ mS m}^2 \text{ mol}^{-1}$.
- (b) Discuss the technique of cyclic voltammetry and account for the characteristic shape of a voltammogram. 3,7
8. (a) Discuss the mathematics of the polarographic wave obtained in the case of a dropping mercury electrode.
- (b) How polarography is used to analyze a mixture of reactants ? 6,4