

MCHE-015

ASSIGNMENT BOOKLET

**M.Sc. in Chemistry Programme
(MSCCHEM)**

ADVANCED KINETICS AND ELECTROCHEMISTRY
(Valid from 1st July 2026 to 30th June 2027)

It is compulsory to submit the assignment before
filling in the examination form



School of Sciences
Indira Gandhi National Open University
New Delhi-110068
(2026-2027)

Dear Learner,

Please read the section on assignments in the Programme Guide for M.Sc. in Chemistry that we sent you after your enrolment. A weightage of 30 per cent, as you are aware, has been earmarked for continuous evaluation, which would consist of one tutor-marked assignment for this course. The assignment is in this booklet, and covers both the blocks of the course. The total marks of all the parts are 100, of which 40% are needed to pass it.

Instructions for Formatting Your Assignments

Before attempting the assignment please read the following instructions carefully:

1. On top of the first page of your answer sheet, please write the details exactly in the following format:

ENROLAMENT NO. :.....

NAME :.....

ADDRESS :.....

COURSE CODE :.....

COURSE TITLE :.....

ASSIGNMENT NO :.....

STUDY CENTRE :.....

DATE :.....

(Name and Code)

PLEASE FOLLOW THE ABOVE FORMAT STRICTLY TO FACILITATE EVALUATION AND TO AVOID DELAY.

2. Use only foolscap size paper (but not of very thin variety) for writing your answers.
3. Leave about 4 cm margin on the left, top and bottom of your assignment response sheet.
4. Your answers should be precise.
5. Submit the complete assignment answer sheets within the due date.
6. The assignment answer sheets are to be submitted to your Study centre within the due date. Answer sheets received after the due date shall not be accepted.

We strongly suggest that you retain a copy of your answer sheets.

7. This assignment is valid from 1st July, 2026 to 30th June, 2027. If you have failed in this assignment or fail to submit it by June 2027, then you need to get the assignment for the year 2027-2028, and submit it as per the instructions given in the Programme Guide.
8. You cannot fill the examination form for this course until you have submitted the assignment.

Wishing you good luck

Tutor Marked Assignment

Advanced Kinetics and Electrochemistry (MCHE-015)

Course Code: MCHE-015

Assignment Code: MCHE-015/TMA/26-27

Maximum Marks: 100

Note: Attempt all questions. The marks for each question are indicated against it.

1. Answer *any five* of the following in brief: (2 x 5 = 10)
- (a) Define the physical significance of the Steady-State Approximation (SSA) in facilitating the kinetic analysis of unstable intermediates.
 - (b) Define parallel and consecutive reactions by providing one distinct chemical example for each system.
 - (c) Explain the Stark-Einstein Law of photochemical equivalence and its specific application to the primary act of excitation.
 - (d) Identify the role and significance of the 'Induction Period' in the temporal evolution of consecutive reaction pathways.
 - (e) Describe the characteristic S-shaped (sigmoidal) curve observed in autocatalytic reactions and its mechanistic origin.
 - (f) Briefly explain the Lotka-Volterra model as a theoretical framework for describing oscillatory kinetics.
 - (g) State the fundamental mechanisms of solid-state reactions as proposed by Wagner.
2. (a) For three parallel reactions of the same order, the rate constants are k_1 , k_2 and k_3 and the energies of activation are E_1 , E_2 and E_3 , respectively. Prove that apparent overall energy of activation

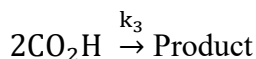
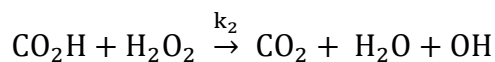
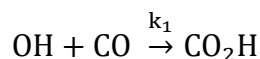
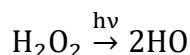
$$E = \sum_{i=1}^3 \frac{k_i E_i}{k_i} \quad (5)$$

- (b) Consider the following mechanism for an enzyme catalysis:



where E stands for enzyme, S for substrate, ES for enzyme–substrate complex and P for product. Applying steady state approximation for $[ES]$, derive the rate law for the formation of the product during the initial stages. (5)

3. (a) Explain the physical origin of the Arrhenius equation from a molecular dynamics perspective. What do the pre-exponential factor and the activation energy represent microscopically? (5)
- (b) The following mechanism has been proposed for the photodecomposition of H_2O_2 in the presence of carbon monoxide:



by utilizing the steady-state approximation for $\text{H}\cdot$ and $\text{CO}_2\text{H}\cdot$, show that the rate law for the reaction is given by

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -\phi I_a = \frac{k_2(2\phi I_a)^{\frac{1}{2}}}{(k_3)^{\frac{1}{2}}} [\text{H}_2\text{O}_2]$$

Where ϕ is the quantum yield and I_a is the intensity of absorbed radiation. (5)

4. (a) Explain the mechanism of the Belousov–Zhabotinskii (B–Z) reaction. Discuss the specific role of intermediate species in producing the non-linear oscillatory behaviour characteristic of this system. (5)

(b) Distinguish between diffusion-controlled and interface-controlled solid-state reactions. Evaluate how their respective rate laws differ based on the physical constraints of the solid phase. (5)

5. (a) Compare and contrast the inner-sphere and outer-sphere electron transfer mechanisms. Using Marcus theory, explain how molecular reorganization energy influences the rate of electron movement. (5)

(b) Reactant A undergoes two parallel first-order reactions to form B and C with rate constants $k_1 = 2.0 \times 10^{-4} \text{ s}^{-1}$ and $k_2 = 3.0 \times 10^{-4} \text{ s}^{-1}$ respectively. If the initial concentration of A is 1.0 M, calculate the percentage yield of B and the concentration of C remaining after 1000 s. (5)

6. Answer *any five* of the following in brief: (2 x 5=10)

- Define the 'Tafel Slope' and evaluate its significance in determining the rate-determining step of an electrode reaction.
- What is meant by overpotential (η) in an electrolytic cell and how does it relate to cell polarization?
- Explain the fundamental principle of Electrocrystallisation during metal deposition at the cathode.
- Identify and briefly describe two primary environmental factors that accelerate the corrosion of metallic structures.
- State the theoretical thermodynamic efficiency limit of a fuel cell and compare it with the Carnot efficiency of a heat engine.

- (f) Define charge transfer resistance and explain its role in electrochemical impedance spectroscopy.
- (g) Describe the role and requirement of an electrocatalyst in a hydrogen evolution reaction (HER).
7. (a) (i) Discuss the concept of quantization of charge transfer and explain its importance in multistep reactions. (2)
- (ii) A reaction has $i_0 = 2 \times 10^{-4} \text{ A/cm}^2$ and $\alpha = 0.5$, $n = 1$, $\eta = 0.1 \text{ V}$. Calculate the current density using Butler–Volmer equation. (3)
- (b) Derive the Butler-Volmer equation for a single-step electron transfer. Explain the mathematical simplification that allows this equation to yield the Tafel equation under conditions of high overpotential. (5)
8. (a) Compare and contrast Cyclic Voltammetry (CV) and Chronoamperometry. Evaluate their relative strengths in identifying redox reversibility and determining diffusion coefficients. (5)
- (b) Classify fuel cells on the basis of their operating principles and electrolyte systems. Describe their working principles and electrochemical reactions of any four types of fuel cells. (5)
9. (a) Discuss the electrochemical mechanism of rusting in iron. Evaluate the effectiveness of cathodic protection (sacrificial anode method) in preventing large-scale infrastructure degradation. (5)
- (b) A neutral solution containing 0.5 g of copper is electrolysed until all the copper is plated and the electrolysis is continued for 7 mins longer. The current is maintained at an average of 1.20 amp throughout the electrolysis. On the basis of 100% current efficiency,
- (i) calculate the time required for complete deposition of copper.
- (ii) what volume of gas evolved during the entire electrolysis? (5)
10. (a) Explain the 'Volcano Plot' in electrocatalysis. Critique how the adsorption energy of intermediates guides the selection of optimal electrode materials for energy conversion. (5)
- (b) Describe the operational and structural differences between Secondary Batteries and Supercapacitors. Specifically, compare their performance in terms of energy density versus power density. (5)

END OF ASSIGNMENT