



MANGALORE UNIVERSITY

DEPARTMENT OF CHEMISTRY

M.Sc. CHEMISTRY

CH H 553: ELECTROCHEMISTRY AND REACTION DYNAMICS

COURSE OUTCOME:

- It is an advanced course on two different topics, electrochemical processes and theoretical aspects of chemical kinetics. The first part deals with concept and applications of electrocatalysis and processes taking place at the electrode and the solution interface.
- This course content trains students on alternate methods of synthesis using electrochemical concepts.
- Introduces the student to theoretical basis of understanding the rates of complex reactions,
- Arriving at the mechanism of various inorganic and organic reactions and knowledge of advanced techniques with the use of lasers in characterizing intermediates complex chemical reactions.

UNIT-I:

[15 hours]

Electrocatalysis -Introduction. Electrocatalysis in reactions involving adsorbed species, concept and process of electrogrowth on electrodes. deposition to crystallization, mechanism of electrogrowth. Special features of electrocatalysis. Hydrogen evolution and reactions. Electronation of oxygen and their mechanisms. 6hrs.

Photocatalysis: History of photocatalysis, principles and developments in photoelectrochemistry. Semiconductor-electrolyte solution interface. Effect of light at semiconductor interface. Capacity of space charge - Mott-Schottky plot. Photo cells-PEC cells and Phtogalvanic cells, surface effects in photoelectrochemistry. 5hrs

Ionic liquids - Introduction, characteristics of ionic liquids, models of simple ionic liquids, mixtures of simple ionic liquids. Hole model for liquid electrolytes. Transport phenomena in liquid electrolytes. Electronic conductance of alkali metals dissolved in alkali halides. 4hrs.

UNIT – II

[15 hours]

Electrode Processes: Charge transfer across the interface and its implications. Basic electrodic reactions: Butler - Volmer equation. Current potential laws at charged interface. Quantum aspects of charge transfer reactions. Concepts of over voltage, Theory of hydrogen and oxygen overvoltage. Mechanism of cathodic and anodic reactions, Dependence of current density on overvoltage: Tafel equation. Applications of electrode processes-(voltammetry, electrosynthesis, electrocatalysis, source of energy) 6 hrs.

The Electrified Interface: Electrification of an interfaces, experimental techniques used in studying interface (Low energy electron diffraction, X-ray photoelectron spectroscopy). The potential difference across Electrified interface. The accumulation and depletion of substances at an interface. Thermodynamics of electrified interface. Brief introduction to the structure of electrified interfaces(models) . 6hrs.

Kinetics of Composite Reactions: Inorganic reaction mechanism (decomposition of N₂O₅, and phosgene). Organic reaction mechanism- decomposition of acetaldehyde. Goldfinger-Letort-Niclause rules, combustion of hydrocarbon. 3hrs

UNIT – II

[15 hours]

Reaction Dynamics: A Review of Chemical Kinetics, and activation parameters. Statistical treatment of rates – Transition state theory and its applications to reactions in solution. Concept of tunneling. Conventional transition state theory (CTST) - equilibrium hypothesis, Applications of CTST to reaction between atoms, derivation of rate expression, thermodynamic formulation of conventional transition – state theory, limitations of CTST. Extension of TST.

7hrs.

Potential energy surfaces – Features & construction of them. Theoretical calculation of E_a. Features of potential energy surfaces (attractive and repulsive surfaces for exothermic reaction). A brief account on concept of stripping and rebound mechanisms. State-to-state kinetics and spectroscopy of transient species.

4hrs

Dynamics of unimolecular reactions - Lindemann, Hinshelwood, RRK & RRKM theories.

4 hrs.

REFERENCES:

1. Modern Electrochemistry, 2nd Ed. Vol.1, 2A &2B, J O M Bockris and A K N Reddy, (Plenum, New York) 1998.
2. Chemical and Electrochemical Energy Systems, Narayan & Viswanathan (Univ. Press, Hyderabad) 1998.
3. Fundamentals of Electrochemistry, Fulkner and A. J. Bard, Wiley India, 2006.
4. Ions in solution-Basic principles of chemical interactions, J. Burgeess (Chichester) 1999.
5. Electrochemistry-Principles, Methods and Applications, Brett and Brett, Oxford Science1993.
6. Chemical Kinetics, K. J. Laidler, Pearson Education, Anand Sons (India) 3rd ed., 2008.
7. Fundamentals of Chemical Kinetics, M.R. Wright, Harwood Publishing, Chichesrer, 1999.
8. Kinetics & Mechanisms of Chemical Transformations, J Rajaram& J C Kuriacose, Macmillan, Delhi, 2007.