

UNIVERSITY OF MADRAS
B.Sc. DEGREE COURSE IN CHEMISTRY
SYLLABUS WITH EFFECT FROM 2020-2021

BCY-DSC12

CORE-XII: PHYSICAL CHEMISTRY- II

Learning Outcomes

1. Learning the basics of chemical kinetics
2. Understanding the basics of catalysis and adsorption
3. Introduced to the fundamentals of photochemistry
4. Learning the basics of computational chemistry
5. Learning the fundamentals of electrochemical cells

Semester	Subject Title	Total Hours	Credit
VI	PHYSICAL CHEMISTRY- II	75	5

UNIT I: CHEMICAL KINETICS

(20hrs)

Rate of reaction- Average and instantaneous rates, factors influencing rate of reaction - molecularity of a reaction - rate equation - order and molecularity, Rate laws - Rate constants - derivation of rate constants and characteristics for zero, first, second and third order (equal initial concentration) - Derivation of time for half change. Methods of determination of order of reactions - Experimental methods of determination of rate constant of a reaction - Volumetry, manometry and polarimetry.

Effect of temperature on reaction rate - temperature coefficient - concept of activation energy - energy barrier - Arrhenius equation. Theories of reaction rates - Collision theory - derivation of rate constant of bimolecular gaseous reaction - Failure of collision theory. Theory of absolute reaction rates - Derivation of rate constant for a bimolecular reaction - significance of entropy and free energy of activation. Comparison of collision theory and ARRT.

UNIT II: CATALYSIS AND ADSORPTION

(15 hrs)

Catalysis - general characteristics of catalytic reactions, auto catalysis, promoters, negative catalysis, poisoning of a catalyst - theories of homogenous and heterogenous catalysis - Kinetics of Acid - base and enzyme catalysis- Mechanism (lock and key, induced fit), Michaelis-Menton equation (no derivation) - Heterogenouscatalysis

Adsorption - Difference between absorption and adsorption - Chemical and physical adsorption and their general characteristics- distinction between them Different types of isotherms - Freundlich and Langmuir. Adsorption isotherms and their limitations - BET theory (no derivation)

UNITIII: PHOTOCHEMISTRY

(10 hrs)

Photo physical processes - Jablonski diagram - Laws of photo chemistry - Lambert - Beer, Grotthus- Draper and Stark -Einstein. Quantum efficiency. Fluorescence and Phosphorescence. Photo chemical reactions - rate law - Kinetics of H_2-Cl_2 and H_2-I_2 reactions, comparison between thermal and photochemical reactions.

UNIT IV: GROUPTHEORY and COMPUTATIONAL CHEMISTRY (10 hrs)

Symmetry elements and symmetry operation symmetry operation of H_2O molecule, Illustration of mathematical rules for the group using symmetry operations of H_2O

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molecule. Construction of multiplication table, for H₂O molecule. Point group - Definition Elements (symmetry operations) of the following point groups C_n (C₂, C₃), C_{nv} (C_{2v}, C_{3v}) and C_{nh}(C_{2h}, C_{3h})

Introduction to computational chemistry – Optimization of structure – Z-matrix, Use of software for computing structures - eg. Avogadro

UNIT V: ELECTROCHEMICAL CELLS (20 hrs)

Electrolytic & Galvanic cells - Reversible and irreversible cells. Conventional representation of electrochemical cells. Electromotive force of a cell and its measurement computation of E.M.F. calculation of thermodynamic quantities of cell reactions ($\Delta G, \Delta H, \Delta S$ and K_{eq}). Application of Gibbs Helmholtz equation. Calculation of E.M.F. Types of reversible electrodes - Gas/metal ion- metal/metal ion; metal/insoluble salt/anion and Redox electrodes. Electrode reactions - Nernst equation - Derivation of cell E.M.F. and single electrode potential - standard hydrogen electrode - reference electrodes (Calomel electrode)- standard electrodes reduction potentials – sign convention - Electrochemical series and its significance. Concentration cell with and without transport. Liquid junction potential. Application of EMF concentration cells. Valency of ion, solubility product and activity co-efficient. Potentiometric titrations. Determination of pH using Hydrogen, quinhydrone and glass electrodes. Determination of pK_a of acids by potentiometric method. Fuel cells - Corrosion - general and electrochemical theory - passivity - prevention of corrosion.

TEXT BOOKS

1. Puri B.R., Sharma L.R. and Pathania M.S., Principles of Physical Chemistry, 47th ed., Vishal Publishing Company, 2016.
2. Sharma K.K. and Sharma L.K., A Text Book of Physical Chemistry, 6th ed., S Chand, 2016.
3. Group Theory In Chemistry: Bonding and Molecular Spectroscopy, Asok K Mukherjee, Bankim Chandra Ghosh, Universities Press Private Limited, Chennai, 2018
4. Problems and Solutions: Physical Chemistry, C Kalidas and M V Sangaranarayanan, Universities Press Private Limited, Chennai, 2020
5. Simple Approach to Group Theory in Chemistry, A, S Swarnalakshmi; T Saroja; R M Ezhilarasi, Universities Press Private Limited, Chennai, 2008
6. Chemical and Electrochemical Energy Systems, R Narayan; B Viswanathan, Universities Press Private Limited, Chennai, 1998

Books for References

1. Maron S.H. and Lando J.B. Fundamentals of Physical Chemistry, Macmillan.
2. Glasstone S. and Lewis. D., Elements of Physical Chemistry, Macmillan
3. Kheterpal S.C. Pradeep Physical Chemistry, Volume I & II, Pradeep Publications Jalandhur, 2004.
4. Jain D.V.S. and Jainhar S.P., Physical Chemistry, Principles and Problems, Tata McGraw Hill, New Delhi, 1988.
5. Bajpai D.N., Advanced Physical Chemistry, S Chand Publishing, 2001.
6. Negi A.S. and Anand S.C., A Textbook of Physical Chemistry, John Wiley & Sons Pvt. Ltd., 1986.