Name of the Programme: M. Sc -I (Physical Chemistry)

Course Code: CHP-503 **Title of the course:** Chemical Kinetics and Thermodynamics

Number of Credits: 04

Effective from AY: 2022-23

Prerequisites for the course:	Students should have studied physical chemistry courses at M.Sc. Chemistry in semester I	
Course Objective:	1. To introduce concepts of reaction kinetics and thermodynamics 2. To provide fundamental knowledge of theories that govern chemical reactions 3. To introduce newer classes of reaction types and their kinetics 4. To introduce latest developments in the advance instrumental techniques and methods for monitoring reaction kinetics and dynamics.	
Content	**1. Theories of reaction rates** a. Generalized kinetic theory and extended collision theory. Concept of collisional number, collisional frequency factor, collisional and reactive cross section, steric factor, microscopic rate constant. Assumptions and limitations of collision theory. b. Conventional transition state theory, equilibrium hypothesis and derivation of reaction rates. Thermodynamic formulation of transition state theory. Arrhenius temperature dependent and independent activation energy and its significance. Assumptions and limitations of transition state theory. Lindemann-Hinshelwood theory of thermal unimolecular reactions.	No of hours 10
	2. Elementary reactions in solutions Collisional kinetics in solution, effect of solvent polarity, solvent cohesion energy, and ion-dipole and dipole-dipole reactions on reaction rates.	3
	3. Kinetics of Homogeneous reactions Homogeneous kinetics, enzymatic reactions and Michaelis-Menten, Lineweaver-Burk and Eadie Analysis, Autocatalytic reactions.	5
	4. Composite reactions Types of composite mechanisms, kinetics of parallel and consecutive reactions. Introduction to shock tube method and its use in combustion analysis.	3
	5. Fast Reactions Photochemical fast reactions, Pulsed laser photolysis, and its use in monitoring fast reactions.	3
	6. Reversible, Irreversible and Oscillatory reactions. a. Kinetics of reversible reactions and graphical analysis b. Oscillatory reactions, Voltera-Lotka hypothesis of oscillatory reactions. The significance of bi-stability in the Briggs-Rauscher Reaction and Belousov-Zhabotinskii reaction.	4
	7. Reaction Dynamics	2

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<tr><td rowspan="3"></td><td>Introduction to potential energy surfaces, description of H_2O and HF potential energy surface diagrams.</td><td></td></tr>
<tr><td>8. Equilibrium Thermodynamics
a. Important terminologies in Thermodynamics; Thermodynamics state functions; work & heat; work expansion; Mathematical interlude Exact and inexact differentials. Cyclic rule; partial derivatives.
b. Heat change at constant pressure, volume; relationship between Qp & Qv; Heat capacities Cp, Cv; Concept of Entropy, entropy change for an ideal gas at different conditions; Entropy of mixing of ideal gas and the Gibbs paradox; Physical significance of entropy.
c. Work function and free energy function; Variation of free energy with temperature and pressure; Maxwell relations; Thermodynamic equations of state; Gibbs-Helmholtz equation.
d. Thermodynamics of open systems, partial molar properties; chemical potential, variation of chemical potential with temperature and pressure; Gibbs-Duhem equation; Duhem-Margules equation; applications of chemical potential; thermodynamic derivation of phase rule.</td><td>17</td></tr>
<tr><td>9. Non-Equilibrium thermodynamics
a. Concept of internal entropy and spontaneity of a process in relation to free energy. Chemical affinity and extent of a reaction. Phenomenological Laws and Onsager's Reciprocal Relations; Conservation of Mass and energy in closed and open system.
b. Postulates of non-equilibrium thermodynamics.
Entropy production in heat flow.
Entropy production of chemical reactions and
Entropy production/entropy flow in open system.
c. Principle of microscopic reversibility and the Onsager reciprocal relations; Validity of Onsager’s equation and its verification; Application of Irreversible Thermodynamics to Biological Systems; Application to thermo-electric and electrokinetic phenomena.</td><td>13</td></tr>
<tr><td>Pedagogy</td><td colspan="2">Mainly lectures and tutorials. Seminars / term papers /assignments / presentations / self-study or a combination of some of these can also be used. ICT mode should be preferred. Sessions should be interactive in nature to enable peer group learning.</td></tr>
<tr><td>References / Readings</td><td colspan="2">1. K. J. Laidler, Chemical Kinetics, 3rd Ed.; Pearson Education, 1987; (printed in India by Anand Sons, 2004).
2. P.W. Atkins and J. De. Paulo, Atkins’ Physical Chemistry, 8th Ed. Oxford University Press, 2007.
3. J. I. Steinfeld, J. S. Francisco and W. L. Hase, Chemical Kinetics and Dynamics, 2nd Ed.; Prentice Hall, 1999.
4. D. K. Chakrabarty and B. Viswanathan, Heterogeneous Catalysis, New Age International Publishers, 2008.</td></tr>
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	5. S. K. Scott, Oscillations, waves and Chaos in chemical kinetics, Oxford Science Publications, 1994. 6. T. S. Briggs, and W. C. Rauscher, An oscillating iodine clock, J. Chem. Educ., 1973. 7. G. W. Castellan, Physical Chemistry, 3rd Ed.; University of Maryland, Addison-Wesley Publishing Company, 1983. 8. E. N. Yeremin, Fundamentals of Chemical Thermodynamics Firebird Publications, 1978. 9. D. A. McQuarrie & John D. Simon, Physical Chemistry: A molecular approach, Viva Books Pvt. Ltd., New Delhi, 2019. 10. S. R. De Groot, Non-equilibrium thermodynamics, Dover Publications, 2011. 11. A. Kleidon, R.D. Lorenz (Eds.), Non-equilibrium thermodynamics and the production of entropy: life, earth, and beyond, Springer Berlin Heidelberg New York, 2005. 12. J. Rajaram, J. C. Kuriacose, S. N. & Co., Thermodynamics for students of Chemistry, Classical, Statistical and Irreversible, Jalandhar, 1996. 13. P. W. Atkins & J. De. Paulo, Atkins' Physical Chemistry, 8th Ed.; Oxford Univ. Press, 2007.
Course outcomes:	1. Students should be in a position to understand and explain various concepts in chemical kinetics and thermodynamics. 2. Students should be in a position to apply these concepts during the lab course in experimental physical chemistry. 3. Students will able to explain the concept of equilibrium and non-equilibrium thermodynamics. 4. Students will able to explain the elementary reactions in solutions.