UNIVERSITY OF CALICUT

M.Sc. CHEMISTRY (CSS PATTERN) - SEMESTER I

CH1CO4 – THERMODYNAMICS, KINETICS AND CATALYSIS

(3 Credits, 54hrs)

Unit 1: Thermodynamics (9hrs)

Review of First and Second law of thermodynamics, Third law of thermodynamics, Need for third law, Nernst heat theorem, Apparent exceptions to third law, Applications of Third law, Determination of Absolute entropies, Residual entropy.

Thermodynamics of Solutions: Partial molar quantities, Chemocal potentioal, Variation of chemical potential with temperature and pressure, Partial molar volume and its determination, Gibbs-Duhem equation, Thermodynamics of ideal and real gases and gaseous mixtures, Fugacities of gases and their determinations, Activity, Activity coefficient, standard state of substance (for solute and solvents), Duhem-Margules equation and its applications. Thermodynamics of ideal solutions, Deduction of the laws of Raoult's ebullioscopy, cryoscopy, and osmotic pressure. Non ideal solutions, Deviations from Raoult's law, Excess functions- excess free energy, excess entropy, excess enthalpy, excess volume.

Unit 2: Thermodynamics of Irreversible Processes (9 hrs).

Simple examples of irreversible processes, general theory of non –equilibrium processes, entropy production, the phenomenological relations, Onsager reciprocal relations, application to the theory of diffusion, thermal diffusion, thermo-osmosis and thermo-molecular pressure difference, electro-kinetic effects, the Glansdorf -Pregogine equation.

Unit 3: Chemical Kinetics (9 hrs)

Kinetics of reactions involving reactive atoms and free radicals - Rice - Herzfeld mechanism and steady state approximation in the kinetics of organic gas phase decompositions (acetaldehyde & ethane); Kinetics of chain reactions – branching chain and explosion limits (H_2-O_2 reaction as an example); Kinetics of fast reactions-relaxation methods, molecular beams, flash photolysis; Solution kinetics: Factors affecting reaction rates in solution, Effect of solvent and ionic strength (primary salt effect) on the rate constant, secondary salt effects.

Unit 4: Molecular Reaction Dynamics (9 hrs)

Reactive encounters: Collision theory, diffusion controlled reactions, the material balance equation, Activated Complex theory – the Eyring equation, thermodynamic aspects of ACT; Comparison of collision and activated complex theories; The dynamics of molecular collisions – Molecular beams, principle of crossed-molecular beams; Potential energy surfaces - attractive and repulsive surfaces, London equation, Statistical distribution of molecular energies; Theories of unimolecular reactions - Lindemann's theory, Hinshelwood's modification, Rice -Ramsperger and Kassel (RRK) model.

Unit 5: Surface Chemistry (9 hrs)

Adsorption: Adsorption isotherms, Langmuir's unimolecular theory of adsorption, BET equation, derivation, determination of surface area of adsorbents, heat of adsorption and its determination; Experimental methods for studying surfaces – SEM, TEM, and ESCA

Unit 6: Catalysis (9hrs)

Homogeneous catalysis – mechanism -Arrhenius intermediates and van't Hoff intermediates - acid base catalysis – specific and general acid catalysis – enzyme catalysis- Michaelis-Menten Mechanism- Auto catalysis - oscillating reactions – mechanisms of oscillating reactions (Lotko -Volterra, brusselator and oregonator) Heterogenous catalysis –adsorption and catalysis- unimolecular surface reactions – bimolecular surface reaction –Langmuir-Hinshelwood echanism and Eley-Rideal mechanism – illustration using the reaction 2CO + O2 . 2CO2

References:

1. *P. Atkins & J. De Paula, Atkins's Physical Chemistry, 10/e, OUP, 2014*.
2. Keith J. Laidler, *Chemical Kinetics 3rd edn*., Pearson Education, 1987(Indian reprint 2008).
3. Steinfeld, Francisco and Hase, *Chemical Kinetics and Dynamics 2 nd edition,* Prentice Hall International . Inc
4. Santhosh K. Upadhyay, *Chemical Kinetics and Reaction Dynamics,* Springer, 2006.
5. Richard I. Masel, *Chemical Kinetics and Catalysis* , Wiley Interscience, 2001.
6. K.J.Laidler, J.H.Meiser and B. C. Sanctuary, *Physical Chemistry,* Houghton Mifflin Company, New York, 2003.
7. A.W. Adamson, *Physical Chemistry of surfaces* , 4th edition, Interscience, New York, 1982.

8. G. K. Vemulapalli, *Physical Chemistry*, Printice Hall of India.
9. M.K. Adam, *The Physics and Chemistry of surfaces* , Dover Publications
10. S. Glasstone, *Thermodynamics for chemists,* East-West 1973.
11. Rajaram and Kuriokose, *Thermodynamics*, East-West 1986
12. Pigoggine, *An introduction to Thermodynamics of irreversible processes* , Interscience
13. B.G. Kyle, *Chemical and Process Thermodyna mics*, 2nd Edn, Prentice Hall of India