

PAPER – IV, PHYSICAL CHEMISTRY

UNIT-I

Thermodynamics–I: Classical thermodynamics - Brief review of first and second laws of thermodynamics - Entropy change in reversible and irreversible processes - Entropy of mixing of ideal gases - Entropy and disorder - Free energy functions – Gibbs - Helmholtz equation - Maxwell partial relations - Conditions of equilibrium and spontaneity - Free energy changes in chemical reactions: Van't Hoff reaction isotherm - Van't Hoff equation - Clausius Clapeyron equation - partial molar quantities - Chemical potential - Gibbs-Duhem equation - partial molar volume - determination of partial molar quantities - Fugacity - Determination of fugacity - Thermodynamic derivation of Raoult's law.

UNIT II

Surface Phenomena and Phase Equilibria: Surface tension - capillary action - pressure difference - across curved surface (Young - Laplace equation) - Vapour pressure of small droplets (Kelvin equation) - Gibbs-Adsorption equation - BET equation - Estimation of surface area - catalytic activity of surfaces – ESCA , X- ray fluorescence and Auger electron spectroscopy.

UNIT III

Surface Active Agents: Classification of surface active agents - Micellisation - critical Micelle concentration (CMC) - factors affecting the CMC of surfactants, microemulsions – reverse micelles - Hydrophobic interaction.

UNIT-IV

Electrochemistry-I: Electrochemical cells - Measurement of EMF - Nernst equation - Equilibrium constant from EMF Data - pH and EMF data - concentration cells with and without transference - Liquid junction potential and its determination - Activity and activity coefficients - Determination by EMF Method - Determination of solubility product from EMF measurements. Debye Huckel limiting law and its verification. Effect of dilution on equivalent conductance of electrolytes - Anomalous behaviour of strong electrolytes. Debye Huckel-Onsager equation - verification and limitations - Bjerrum treatment of electrolytes - conductometric titrations.

UNIT-V

Chemical Kinetics: Methods of deriving rate laws - complex reactions - Rate expressions for opposing, parallel and consecutive reactions involving unimolecular steps. Theories of reaction rates - collision theory - Steric factor - Activated complex theory - Thermodynamic aspects - Unimolecular reactions - Lindemann's theory - Lindemann-Hinshelwood theory. Reactions in solutions - Influence of solvent - Primary and secondary salt effects - Elementary account of linear free energy relationships - Hammett - Taft equation - Chain reactions - Rate laws of $H_2 - Br_2$, photochemical reaction of $H_2 - Cl_2$ Decomposition of acetaldehyde and ethane - Rice-Hertzfeld mechanism.

REFERENCES:

1. Physical Chemistry P.W.Atkins, ELBS
2. Chemical Kinetics - K.J.Laidler, McGraw Hill Pub.
3. Text Book of Physical Chemistry. Samuel Glasstone, Mcmillan Pub.
4. Physical Chemistry, G.W.Castellan. Narosa Publishing House
5. Thermodynamic for Chemists. Samuel Glasstone
6. Electrochemistry, Samuel Glasstone, Affiliated East West
7. Physical Chemistty, W.J.Moore, Prentice Hall
8. Atomic structure and chemical bond. Manas chanda. Tata McGraw Hill Company Limited.