CHEMISTRY
(Major)
(4th Semester)
Course No.: **CHM-DSC-251**
(Physical Chemistry -II)
Chemical Thermodynamics & Equilibrium
Contact Hours: 60; Credits: 04
Full Marks = 100[End Semester Exam (70) Internal Assessment (30)]
Pass Marks = 40 [End Semester Exam (28) Internal Assessment (12)]

Unit I: Chemical Thermodynamics I

Intensive and extensive variables; state and path functions; exact differentials, zeroth law of thermodynamics.

First law: Concept of heat (*q*), work (*w*), internal energy (*U*), and statement of first law; enthalpy (*H*), relation between heat capacities, calculations of *q*, *w*, *U* and *H* for reversible, irreversible and free expansion of gases (ideal and van der Waals) under isothermal and adiabatic conditions.

Thermochemistry: Heats of reactions: standard states; enthalpy of formation and enthalpy of combustion and its applications; calculation of bond energy, bond dissociation energy and resonance energy from thermochemical data, effect of temperature (Kirchhoff's equations) and pressure on enthalpy of reactions.

Unit II: Chemical Thermodynamics II

Second Law: Limitation of First Law, Concept of entropy, statement of the second law of thermodynamics; mathematical expression of 2^{nd} law, Calculation of entropy change for reversible and irreversible processes, Clausius inequality

Free Energy Functions: Gibbs and Helmholtz energy; variation of S, G, A with T, V, P; Free energy change and spontaneity. Relation between Joule-Thomson coefficient and other thermodynamic parameters; Gibbs-Helmholtz equation; Maxwell relations; thermodynamic equation of state.

Unit III: Phase Equilibrium

Concept of phases, components and degrees of freedom, derivation of Gibbs Phase Rule for nonreactive and reactive systems; Clausius-Clapeyron equation and its applications to solid-liquid, liquid-vapour and solid-vapour equilibria, concept of activity and fugacity, phase diagram for one component systems, with applications (H_2O & CO_2)

Phase diagrams for systems of solid-liquid equilibria involving eutectic mixture (Pb-Ag), congruent (Zn-Mg) and incongruent melting points, solid solutions. Three component systems, water chloroform-acetic acid system, triangular plots.

Unit IV: Chemical Equilibrium

Partial molar quantities, Chemical potential-its physical significance, Gibbs-Duhem equation, of ideal mixtures, change in thermodynamic functions in mixing of ideal gases. Criteria of thermodynamic equilibrium, law of mass action, equilibrium constant, factor effecting equilibrium constant, thermodynamic derivation of relations between the various equilibrium constants *Kp*, *Kc* and *Kx*. *Le Chatelier's Principle* (quantitative treatment); Van't Hoff's Isotherm. Coupling of exoergic and endoergic reactions.

Unit V: Ionic Equilibrium

Strong, moderate and weak electrolytes, degree of ionization, factors affecting degree of ionization, ionization constant and ionic product of water. Ionization of weak acids and bases, pH scale, common ion effect.

Salt hydrolysis-calculation of hydrolysis constant, degree of hydrolysis and pH for different salts. Buffer solutions; derivation of Henderson equation and its applications; buffer capacity, buffer range, buffer action and applications of buffers in analytical chemistry and biochemical processes in the human body.

Qualitative treatment of acid – base titration curves (calculation of pH at various stages). Theory of acid–base indicators; selection of indicators and their limitations.

Reference books

- Puri, Sharma, Pathania; Principles of Physical Chemistry, Vishal Publishing Co.45th Edition (2011)
- Peter, A. & Paula, J. de. Physical Chemistry 9th Ed., OUP (2011).
- Castellan, G. W. Physical Chemistry 4th Ed., Narosa (2004).
- Engel, T. & Reid, P. Physical Chemistry 3rd Ed., Prentice-Hall (2012).
- McQuarrie, D. A. & Simon, J. D. Molecular Thermodynamics, Viva Books Pvt. Ltd.: NewDelhi (2004).
- Assael, M. J.; Goodwin, A. R. H.; Stamatoudis, M.; Wakeham, W. A. & Will, S.

Commonly Asked Questions in Thermodynamics, CRC Press: NY (2011).

- Levine, I. N. Physical Chemistry 6th Ed., Tata Mc Graw Hill (2010).
- Metz, C. R. 2000 Solved Problems in Chemistry, Schaum Series (2006)