353 CH 82 Chemical Thermodynamics **9 credits**

Course Objectives:
To describe the concepts of thermodynamics and their applications.

Learning Outcomes:
By the end of the course the students are expected to be able to:

- Describe the concepts of chemical thermodynamics.
- Apply thermodynamic principles to solve practical problems in physical and chemical systems.

Pre-Requisite:
800 CH 44, Advanced Chemistry II, Form VI Chemistry or Equivalent

Content

Unit I: Introduction
Systems, states and state functions, Definitions of concepts, Energy, The concept of temperature and the Zeroth or Fourth law of thermodynamics. Measurement of temperature and Pressure.
Equation of States for Gases Concept of ideal gas: Gas laws, Kinetic theory of gases – postulates and derivation. Deviation from ideal behavior, van der Walls equation of state – derivation. Real gases. Fundamental equations.
First Law of Thermodynamics and its Applications:
First law of thermodynamics: Exact differentials, Energy, heat and work. Applications to ideal gases: Heat capacities, relation between C_P and C_V. Isothermal processes: Change in internal energy, heat absorbed, work done-w(rev) and w(irrev). Adiabatic processes: Change in internal energy, work done. Applications to real(van der Walls) gases. Joule - Thomson experiment. Joule - Thomson coefficient and its significance, inversion temperatures. Variation of enthalpy change of reaction with temperature.

Unit II: Thermochemistry
Measurements of heats of reaction. Thermochemical equations. Additivity of enthalpy changes. Calculation of changes in internal energy from the enthalpy change, standard states and standard heats of formation - Heat of combustion; integral heat of solution and dilution, heat of neutralization, heat of hydration; heat of transition - Bond energy and heat of reaction.

Unit III: Entropy, Second Law of Thermodynamics and Third Law of Thermodynamics:
Second law of thermodynamics: Limitations of first law and the need for the second law.Formulation of the second law of thermodynamics on the basis of Carnot cycle. Criteria of spontaneity. Changes in S, G and A as criteria for spontaneous process, dS, dG and dA –exact differentials. Entropy calculations for reversible and irreversible changes. Evaluation of dG and dS for the mixing. Thermodynamic principle of the working of a refrigerator. **Third Law of Thermodynamics:** Entropy and disorder. Third law of thermodynamics. Nernst heat theorem-Planck and Lewis Randall formulation of third law. Absolute values of entropies of solids, liquids and gases. Evaluation of the standard entropy of oxygen, on the basis of heat capacity. Exceptions to third law of thermodynamics.

Unit IV: Gibbs Energy and Helmholtz Energy. The Chemical Equilibrium

The Gibbs energy and The Helmholtz energy, Gibbs energy of formation, Gibbs energy of reaction, Pressure dependence of Gibbs energy and equilibrium, Temperature dependence of Gibbs energy, Real gases-Pressure dependence of Gibbs energy, Fugacity. The Maxwell relations.

Thermodynamics of Equilibrium Processes: Law of mass action. Various forms of equilibriumconstants. Relationships between K_P and K_C; properties of equilibrium constants. Vant Hoff isotherm derivation of thermodynamic equilibrium constant, and its relationship with free energy changes under standard conditions. Vant Hoff isochore. Le-Chatelier-Braun principle: Formation of ammonia. - Application of law of mass action and Le-Chatelier- Braun principle to homogeneous gaseous reactions: dissociation of nitrogen tetroxide and ammonia. **Thermodynamic Properties of Open Systems and Homogeneous Mixture** Partial molar volume, Graphical interpretation of partial molar quantities, Partial molar enthalpy, Internal energy and Gibbs energy of an open system, The chemical potential, Partial molar entropy, Thermodynamic properties of a mixture of two ideal gases. Significance of changes of standard states.

Unit V: Colligative Properties and Phase Equilibria

Colligative Properties of Solutions: Ideal solutions: Vapour pressure - Composition diagrams of solutions. Raoult's law, positive and negative deviations from the law. Principles of fractional distillation. Binary systems. Vapour pressure composition diagrams. Azeotropic mixtures, Partially miscible binary systems. Steam distillation. Solubility of gases in liquids; Henry's law and its relationship with Raoult's law. Thermodynamics derivation of Vapour pressure lowering, freezing point depression, boiling point elevation and osmotic pressure as functions of the composition of the solute. Distribution law: thermodynamic derivation, limitation of the law, application in studying association, dissociation and solvation. Extraction with solvents; efficiency of extraction.

Phase Equilibria and Phase Diagrams Gibbs Phase Rule: Concepts of phase, component and number of degrees of freedom – derivation. Clapeyron and Clausius-Clapeyron equations and their applications to equilibria in phase transitions(solid – liquid, liquid – vapour, solid – vapour). One-component system: Phase diagrams: Water and sulphur systems. Two component system: (i) Simple eutectic: Lead-silver system, (ii) Formation of compound with congruent melting point: Ferric chloride –water system. Three component systems: General account of graphical representation of three component systems, examples of three component systems having one, two partially miscible pairs. Activity coefficients for binary liquid-vapour phase diagrams. Distillation of a mixture of two miscible liquids. Condensed binary systems. Ternary systems.

Delivery: 60 hours of lectures, 15 hours Independent study, 15 hours Assignments. **Assessment:** Coursework 40%; final examination 60%.

Suggested Readings:

1. S.H. Maron and J.B. Lando, 2006, "Fundamentals of Physical Chemistry", Macmillan Limited, New York.

2. B.R. Puri and L.R. Sharma, 2002, "Principles of Physical Chemistry", Shoban Lal Nagin Chand and Co. 3rd edition.
3. P.W. Atkins, 2001, "Physical Chemistry", 7^{th} Edition, Oxford University Press.
4. S.K. Dogra and S. Dogra, 2006, "Physical Chemistry Through Problems", New Age international,4^{th} edition.
5. Gilbert. W. Castellan, 2005, "Physical Chemistry", Narosa publishing House, 3rd Edition.
6. Irving M. Klotz and Robert M. Rosenberg, 2004, "Chemical Thermodynamics", John Wiley and sons, Inc.
7. J. Rajaram and J.C. Kuriacose, 2006, "Thermodynamics", Shoban Lal Nagin Chand and Co.
8. K. L. Kapoor, 2004, "A Textbook of Physical Chemistry (Volume 2 and 3)", Macmillan, India Ltd.