Core IV

Chemical thermodynamics, equilibrium, and Colligative property

Course Objectives:

The learners should be able to apply principles and laws of thermodynamics to reversible and irreversible systems. In addition, they should be able to use spectroscopic data to calculate thermodynamic properties of ideal & real mixtures. In addition, understand the change in thermodynamic properties, equilibrium constants, partial molar quantities, chemical potential. Also able to identify factors affecting equilibrium constant using the principles and techniques of statistical thermodynamics.

Course Outcomes:

By the end of the course, the students will be able to:

- Discuss the laws of thermodynamics and applications to natural phenomena.
- Acquire a strong foundation of partial molar properties, its variation with temp and pressure for different systems and able to apply on the thermodynamics of simple mixtures.
- Inculcate firm foundations in the fundamentals and application of chemical equilibrium, and ΔG derive the relationship between different equilibrium constants.
- Understand the basic concept of Solutions of non-volatile solutes, colligative properties. Calculate various thermodynamic properties (ΔHneutralization, ΔHhydration & Cv) for chemical reactions using calorimeter.

Unit-I: Chemical thermodynamics

Intensive and extensive variables; state and path functions; isolated, closed and open systems; 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 of molecules and ions 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

Carnot cycle, efficiency of heat engine, Carnot theorem; **Second Law:** Concept of entropy; thermodynamic scale of temperature, statement of the second law of thermodynamics; molecular and statistical interpretation of entropy. Calculation of entropy change for reversible and irreversible processes. **Third Law:** Statement of third law, concept of residual entropy, calculation of absolute entropy of molecules. 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, inversion temperature, Gibbs- Helmholtz equation, Maxwell relations, thermodynamic equation of state.

Unit-III: Systems of variable composition

Partial molar quantities, dependence of thermodynamic parameters on composition; Gibbs Duhem equation, chemical potential of ideal mixtures, change in thermodynamic functions in mixing of ideal gases. **Chemical equilibrium**: Criteria of thermodynamic equilibrium, degree of advancement of reaction, chemical equilibria in ideal gases, concept of fugacity. Thermodynamic derivation of relation between Gibbs free energy of reaction and reaction quotient (vant Hoff's reaction). Equilibrium constants and their quantitative dependence on temperature, pressure and concentration. Free energy of mixing and spontaneity; thermodynamic derivation of relations between the various equilibrium constants K_p, K_c and K_x. Le Chatelier principle (quantitative treatment) and its applications.

Unit-IV: Solutions and Colligative Properties

Dilute solutions; lowering of vapour pressure, Raoult's and Henry's Laws and their applications. Thermodynamic derivation using chemical potential to derive relations between the four colligative properties: (i) relative lowering of vapour pressure, (ii) elevation of boiling point, (iii) Depression of freezing point, (iv) osmotic pressure and amount of solute. Applications in calculating molar masses of normal, dissociated and associated solutes in solution.

List of experiments

1. Determination of heat capacity of a calorimeter for different volumes using change of enthalpy data of a known system (method of back calculation of heat capacity of calorimeter from known enthalpy of solution or enthalpy of neutralization).
2. Determination of heat capacity of the calorimeter and enthalpy of neutralization of hydrochloric acid with sodium hydroxide.
3. Calculation of the enthalpy of ionization of ethanoic acid.
4. Determination of heat capacity of the calorimeter and integral enthalpy (endothermic and exothermic) solution of salts.
5. Determination of basicity/proticity of a polyprotic acid by the thermochemical method in terms of the changes of temperatures observed in the graph of temperature versus time for different additions of a base. Also calculate the enthalpy of neutralization of the first step.
6. Determination of enthalpy of hydration of copper sulphate.
7. Determination of heat of solution (ΔH) of oxalic acid/benzoic acid from solubility measurement.

Text Books:

- ✓ *P. W. Atkins& J. de Paula, Elements of Physical Chemistry, Oxford University Press, 6th Ed., 2006.*
- ✓ *D. A. McQuarrie, & J. D Simon. Molecular Thermodynamics Viva Books Pvt. Ltd.: New Delhi 2004.*
- ✓ *K. L. Kapoor, Text Book of Physical Chemistry, Mac Grow Hill, 3rdEdn. 2017*
- ✓ *B. D. Khosla, V. C. Garg, & A. Gulati, Senior Practical Physical Chemistry, R. Chand & Co.: New Delhi 2011.*

Reference Books:

- ✓ *T. Engel & P. Reid, Physical Chemistry 3rd Ed. Pearson 2013.*
- ✓ *S.C. Kheterpal Pradeep's Physical Chemistry, Vol. I & II, Pradeep Publications 2011.*
- ✓ *Puri, Sharma &Pathania, Principles of Physical Chemistry, Vishal Publishing Co, 47th Edn., 2017.*