

CHE-HC-2026: PHYSICAL CHEMISTRY II

(Credits: Theory-04, Lab-02)

Theory: 60 Lectures

Course Objective: *In this course the chemical thermodynamics, chemical equilibrium, solutions and colligative properties will be taught to the students. Another unit of this course is systems of variable compositions.*

Learning Outcome: *In this course the students are expected to learn laws of thermodynamics, thermochemistry, thermodynamic functions, relations between thermodynamic properties, Gibbs Helmholtz equation, Maxwell relations etc. Moreover the students are expected to learn partial molar quantities, chemical equilibrium, solutions and colligative properties. After completion of this course, the students will be able to understand the chemical systems from thermodynamic point of view.*

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. Law of equipartition of energy, degrees of freedom and molecular basis of heat capacities.

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. Adiabatic flame temperature, explosion temperature.

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 ; spontaneous process-enthalpy change, entropy change and free energy change considerations. Relation between Joule-Thomson coefficient and other thermodynamic parameters; inversion temperature; Gibbs-Helmholtz equation; Maxwell relations; thermodynamic equation of state.

(36 Lectures)

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.

(8 Lectures)

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. Coupling of exoergic and endoergic reactions. 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); equilibrium between ideal gases and a pure condensed phase.

(8 Lectures)

Solutions and Colligative Properties:

Dilute solutions; lowering of vapour pressure, Raoult's and Henry's Laws and their applications. Excess thermodynamic functions.

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.

(8 Lectures)

Recommended Books

1. Peter, A. & Paula, J. de. *Physical Chemistry 9th Ed.*, Oxford University Press (2011).
2. Castellan, G. W. *Physical Chemistry 4th Ed.*, Narosa (2004).
3. Engel, T. & Reid, P. *Physical Chemistry 3rd Ed.*, Prentice-Hall (2012).
4. McQuarrie, D. A. & Simon, J. D. *Molecular Thermodynamics* Viva Books Pvt. Ltd.: New Delhi (2004).
5. Assael, M. J.; Goodwin, A. R. H.; Stamatoudis, M.; Wakeham, W. A. & Will, S. *Commonly Asked Questions in Thermodynamics*. CRC Press: NY (2011).
6. Levine, I. N. *Physical Chemistry 6th Ed.*, Tata Mc Graw Hill (2010).
7. Metz, C.R. *2000 solved problems in chemistry*, Schaum Series (2006)
8. Puri, B. R.; Sharma, L. R.; Pathania, M. S. *Principles of Physical Chemistry*, Vishal Publishing Co.; 47th Ed. (2017)
9. Kapoor, K. L. *A Textbook of Physical Chemistry (Volume 2)* McGraw Hill Education; Sixth edition (2019)

LAB**60 Lectures****Thermochemistry**

(a) 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).

(b) Determination of heat capacity of the calorimeter and enthalpy of neutralization of hydrochloric acid with sodium hydroxide.

(c) Calculation of the enthalpy of ionization of ethanoic acid.

(d) Determination of heat capacity of the calorimeter and integral enthalpy (endothermic and exothermic) solution of salts.

(e) 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.

(f) Determination of enthalpy of hydration of copper sulphate.

(g) Study of the solubility of benzoic acid in water and determination of ΔH .

Any other experiment carried out in the class.

Recommended Books

1. Khosla, B. D.; Garg, V. C. & Gulati, A., *Senior Practical Physical Chemistry*, R. Chand & Co.: New Delhi (2011).
 2. Athawale, V. D. & Mathur, P. *Experimental Physical Chemistry* New Age International: New Delhi (2001).
-