

Bachelors with Chemistry as Major

5th Semester

Title of the course: Selected Topics in Physical Chemistry

Course Code: CHM522J2

Credits: Theory-4, Lab-2

Theory (4 credits: 60 Hours)

Max. Marks: 100, Min Marks: 36

Course Objectives:

- To make students to learn the applied aspects of thermodynamics.
- To introduce the basic concepts of phase equilibria and learn how to sketch and read the phase diagrams of one and two component systems.
- To introduce some basic physico-chemical aspects of, solid-liquid, liquid-liquid and liquid-air interface .
- To introduce the qualitative and quantitative aspects of photochemistry

Learning outcomes:

- Students shall learn to derive some important equations of thermodynamics and understand the implications of these equations.
- Students shall be able to make use of thermodynamic relations for the thermochemical estimations
- Students will understand the basic concepts of Phase transformations and Phase rule
- Students shall be able to sketch and read the phase diagrams of one and two component systems
- Understand some basic concepts of surface chemistry, thermodynamic implications of equilibrium across solid/liquid, solid-gas and liquid-air interfaces, like adsorption.
- To understand the basic aspects of interactions of light with matter and laws of photochemistry.

Unit-I: Applications of Thermodynamics

(15 hours)

The first law of thermodynamics: Joule's law, Joule-Thomson coefficient and inversion temperature. Temperature dependence of enthalpy, Kirchhoff's equation. Bond dissociation energy and its calculation from thermo-chemical data with applications.

The second law of thermodynamics: Variation of A and G with Temperature, pressure and Composition, Gibbs-Helmholtz equation, Entropy change in physical processes, ideal gas expansion and entropy of mixing of ideal gases, Gibb's paradox, Maxwell's relations and thermodynamic equations of state.

Third law of thermodynamics: The molecular interpretation of entropy, The calorimetric measurement of entropy, residual entropy.

Thermodynamics of multicomponent systems: Chemical potential, temperature and pressure dependence.

Unit-II: Phase equilibria

(15 hours)

Phase Equilibria the basics: Meaning of the terms: phase, component and degree of freedom, statement and derivation of Gibbs phase rule. Reaction isotherm and reaction isochore, Clapeyron equation and Clausius-Clapeyron equation, applications.

Phase diagrams of one-component systems (water and sulphur) and two-component systems involving eutectics, congruent and incongruent melting points (lead-silver, $\text{FeCl}_3\text{-H}_2\text{O}$ and Na-K only).

Partially miscible liquids: Lower and upper consolute temperatures, (examples of phenol-water, trimethylamine-water, nicotine-water systems).

Unit-III: Surface Chemistry

(15 hours)

Liquid Surface: Surface tension, the pressure difference across curved surfaces (Laplace equation), the vapor pressure of droplets (Kelvin equation), and Capillary condensation. Thermodynamics of Interfaces: Surface excess, surface tension and thermodynamic parameters, Gibbs adsorption isotherm.

Surfactants: Introduction, types, *cmc* and micellization, vesicles and bilayers

Solid surfaces: Adsorption at solid surfaces, adsorption models; Langmuir adsorption isotherm, BET adsorption isotherm and its use in estimation of surface area. Adsorption on porous solids.

Solid liquid interface: Contact angle, young's equation, wetting, Wetting as contact angle phenomena.

Unit-IV: Photochemistry

(15 hours)

Interaction of radiation with matter, the difference between thermal and photochemical processes. Laws of photochemistry: Lambert-Beer Law, Grothus-Drapper law, and Stark-Einstein law. Jablonski diagram depicting various processes occurring in the excited state, qualitative description of fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing), quantum yield, photosensitized reactions, energy transfer processes (simple examples).

Kinetics of photochemical reactions: Photochemical decomposition of hydrogen iodide. Hydrogen-chlorine and hydrogen-bromine reactions, Comparison with thermal decomposition reactions.

References:

1. Principles of Physical Chemistry; Puri, Sharma and Pathania; S. Nagin Chand & Co; 2011.
2. The Elements of Physical Chemistry; Atkins, P. W.; Oxford University Press.
3. Physical Chemistry; Barrow, G. M.; 5thed.; McGraw-Hill; International Student edition; 1992.
4. Physical Chemistry; Alberty, R. A.; Wiley Eastern Ltd.
5. Essentials of Physical Chemistry; Kapoor, K. L.; Vols. III & IV; 2nded.; Macmillan India Ltd; 2005.
6. Physical Chemistry through Problems; Dogra, S. K.; Wiley Eastern Ltd; 1991.
7. University General Chemistry; Rao, C. N. R.; MacMillan.
8. Elements of Physical Chemistry, Peter Atkins and Julio de Paula, 7th Edition, Oxford University Press, 2016.
9. Physical Chemistry, Concepts and Models, Volume II, Nabakumar Bera, Subhasree Ghosh, Paulami Ghosh, Techno world.
10. Physical Chemistry, Concepts and Models, Volume III, Nabakumar Bera, Subhasree Ghosh, Paulami Ghosh, Techno world.
11. Atkins' Physical Chemistry, Peter Atkins, Julio de Paula & James Keeler, 11th Edition, Oxford University Press, 2018.
12. An Introduction to Chemical Thermodynamics, R. P. Rastogi and R. R. Misra, 6th Edition, Vikas Publishing House Pvt. Ltd. 2018.
13. Chemical Thermodynamics, Classical, Statistical, and Irreversible, Pearson, 2013.

1. Determine solubility of benzoic acid at different temperatures and calculate ΔH of dissolution.
2. To study the adsorption of acetic acid on activated charcoal and verify the Freundlich and Langmuir isotherms
3. Estimation of the cmc of a surfactant (SDS/CTAB) by conductometry
4. Estimation of the surface excess of a surfactant by using a Stalagmometer
5. Determination of the transition temperature of a solid.
6. Estimate the upper consolute temperature of Phenol-Water system
7. To determine the Refractive Index of a given liquid and calculation of specific and molar refractivity.
8. Determination of concentration of binary mixture by measurement of refractive Index
9. To determine the specific rotation of the given optically active compound.
10. Estimation of the concentration of an optically active compound by using polarimetry
11. To verify the Lambert Beer's Law using $\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$ solution and determination of unknown concentration.
12. Determine the concentration of HCl against 0.1 N NaOH spectrophotometrically.

Books Recommended:

1. Vogel's; text book of Quantitative Inorganic Analysis (revised); Bassett, J.; Denney, R.C.; Jeffery, G. H and Mendham, J.; 6th ed.; ELBS; 2007.
2. Experimental Inorganic Chemistry; Palmer, W.G.; Cambridge.
3. Analytical Chemistry; Christian, G. D.; 6th ed.; Wiley; 2008.
4. Practical Physical Chemistry; Khosla, B. D.; Garg, V. C. & Gulati, A.; R. Chand & Co.; 2011.
5. Selected Experiments in Physical Chemistry; Mukherjee N.G. & Ghosh, J.N.; S. Chand & Sons.
6. Experiments in Physical Chemistry; Das, R. C, and Behra, B.; Tata McGraw Hill.
7. Advanced Practical Physical Chemistry; Yadav, J.B.; 20thed.; Goel Publishing House, 2001.