

**UNIVERSITY OF MADRAS**  
**B.Sc. DEGREE COURSE IN CHEMISTRY**  
**SYLLABUS WITH EFFECT FROM 2020-2021**

**BCY-DSC09**

**CORE-IX: PHYSICAL CHEMISTRY – I**

**Learning Outcomes**

1. Introduced to concepts of thermodynamics such as equilibrium constant and entropy
2. Learning fundamental concepts about solutions and the basis of separation techniques such as steam distillation and solvent extraction
3. Introduced to phase rule and its application to one component and two component systems
4. Introduced to colligative properties and methods of their determination
5. Introduced to the concept of conductance in electrochemistry

Semester	Subject Title	Total Hours	Credit
V	PHYSICAL CHEMISTRY - I	60	4

**UNIT I: THERMODYNAMICS III (12 hrs)**

Equilibrium constant and free energy change - Thermodynamic derivation of law of mass action - Equilibrium constants in terms of pressure and concentration ( $K_p$  and  $K_c$ ) and their relation - Thermodynamic interpretation of Lechatelier principle (Concentration, temperature, pressure and addition of inert gases). Systems of variable composition - Partial molar quantities - Chemical potential - Variation of chemical potential with T, P and X (mole fraction) - Gibbs-Duhem equation-Duhem-Margules equation.van't Hoff reaction isotherm - van't Hoff's isochore- Clapeyron equation and Clausius- Clapeyron equation - Applications- Nernst heat theorem - Third Law of Thermodynamics - Statement of third law and concept of residual entropy - Evaluation of absolute entropy from heat capacity data- exception to third law (CO, ortho and para hydrogen).

**UNIT II: SOLUTIONS (12hrs)**

Ideal and Non-ideal solutions. Concept of activity and activity coefficients - Completely miscible liquid systems - benzene and toluene.Raoult's law and Henry's law. Deviation from Raoult's law and Henry's law.Azeotropes- HCl-water and Ethanol-water system - Partially miscible liquid systems (Upper and lower CST) - phenol-water, triethylamine-water and Nicotine-water systems. Completely immiscible liquids –principle and applications of steam distillation - Nernst Distribution Law- thermodynamic derivation, application to solvent extraction, limitations of distribution law

**UNIT III: THERMODYNAMICS OF PHASE TRANSITIONS (10 hrs)**

Definition of terms in the phase rule - Derivation and application to one component system water and sulphur - super cooling, sublimation. Two component systems - reduced phase rule - solid-liquid equilibria, simple eutectic (lead-silver), desilverisation of lead –Compound formation with congruent melting point. (Mg-Zn) and incongruent melting point (Na-K).Solid solutions - (Ag- Au) - freezing mixtures - KI-H<sub>2</sub>O system.

**UNIT IV: DILUTE SOLUTIONS AND COLLIGATIVE PROPERTIES (10 hrs)**

Colligative properties - relative lowering of vapour pressure, osmosis - Law of osmotic pressure-isotonic solutions, effect of concentration and temperature on osmotic pressure - thermodynamic derivation of elevation of boiling point and depression in freezing point - determination of molecular masses using the above properties [experimental details not required]- abnormal molecular masses and van't Hoff factor - degree of association and degree of dissociation.

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**UNIT V: ELECTRO CHEMICAL CONDUCTANCE**

**(16 hrs)**

Electrical transport and conductance in metal and in electrolytic solution. Specific conductance and equivalent conductance. Measurement of equivalent conductance. Using Kohlraush's bridge. Arrhenius theory of electrolytic dissociation and its limitations. Weak and strong electrolyte according to Arrhenius theory Ostwald's dilution laws- applications and limitation. Variation of equivalent conductance with concentration. Migration of ion-ionic mobility. Kohlraush's law and its applications. The elementary treatment of the Debye- Hückel Onsager equation for strong electrolytes. Evidence for ionic atmosphere. Wien effect and Debye-Falkenhagen effect. Transport number - Determination by Hittorf method and moving boundary method. Application of conductance measurements- Determination of  $\Lambda_0$  of strong electrolytes. Determination of  $K_a$  of weak acids. Determination of solubility product of a sparingly soluble salt. Conductometric titrations.

**TEXT BOOK**

1. Puri B.R., Sharma L.R., Pathania M.S., Principles of Physical Chemistry, 47<sup>th</sup> ed., Vishal Publishing Co., 2016.
2. Textbook of Physical Chemistry, M V Sangaranarayanan; V Mahadevan, Universities Press Private Limited, Chennai, 2011

**REFERENCE BOOKS**

1. Atkins P.W., Physical Chemistry, 5<sup>th</sup> ed., Oxford Universities Press Private Limited, 1994.
2. Castellan G.V., Physical Chemistry, New Delhi, Orient Longmans.
3. Levine I.N., Physical Chemistry 6<sup>th</sup> ed., 2009.
4. Rajaram J. and Kuriacose J.C., Thermodynamics for students of chemistry 3<sup>rd</sup> ed., Shoban Lal & Co., 2013.
5. Bajpai D.N., Advanced Physical Chemistry, S.Chand Publishing, 2001.
6. Negi A.S. and Anand S.C., A Textbook of Physical Chemistry, John Wiley & Sons Pvt. Ltd., 1986.