Course: Discipline Specific Core 8

Semester	**4**
Paper Number	**HCHCR4082T (60 MARKS) & HCHCR4082P (40 MARKS)**
Paper Title	**CORE COURSE 8: PHYSICAL CHEMISTRY**
No. of Credits	**Theory-04, Practicals-02**
Theory/Composite	Composite
No. of periods assigned	Th: 4 Pr: 3
Name of Faculty member(s)	Dr. Asish K. Nag Dr. Rina Ghosh Dr. Indranil Chakraborty
Course description/objective	***Theory:*** **Applications of thermodynamics**: Concept of ideal solutions and formulation of Raoult's and Henry's laws. From this, the effect of a solute on certain thermodynamic properties of the solution will be discussed. Application to phase equilibria governed by the famous phase rule of Gibbs, which shows the extent to which various parameters can be varied with preservation of the equilibrium between phases. Application to systems of gradually increasing complexity with the help of phase diagrams. **Electrical Properties** Electrical properties are the starting point of molecular interactions. Small imbalances of charge distributions in molecules confer upon them certain properties which will be dealt with in detail. Ion-ion interactions are very important in governing properties of electrolyte solutions and these will be dealt with separately under ionic equilibria. The concept of activity will be introduced and its importance in the departure from ideality will be discussed in detail. The principles of thermodynamics developed earlier has been applied to the description of the thermodynamic properties of reactions that take place in electrochemical cells in which, progress of the reaction drives electrons through an external circuit. Thermodynamic arguments can be used to derive an expression for the electrical potential of such cells and the potential can be related to their composition. The definition of standard potentials is important in this context, in order to predict the equilibrium constants. **Quantum Mechanics** Quantum mechanical application for quantisation of rotational motion will be discussed. The corresponding equation for a particle in s spherically symmetric Coulomb potential and the possible solutions will be analysed. The treatment will be extended to hydrogenlike systems. ***Practical:*** 1. Experimental method of determining the solubility product of sparingly soluble salts and examining the dependence on ionic strength of the medium. 2. Performing redox titrations by constructing appropriate cells and noting the change in emf. Students will use this principle to determine i) formal potential and ii) solubility product. 3. Observation of the primary kinetic salt effect on a reaction involving ions. Development of the concept of dependence of the rate constant on ionic strength of the medium. 4. Performing pH-metric titration to note the nature of dependence of pH on the volume of titrant (base). Determination of pKa of weak monobasic and dibasic acids by this method.
Syllabus	Annexure Core Course: 8
Texts	

<table>
<tr><td>Reading/Reference Lists</td><td>Theory:

1. Castellan, G. W. Physical Chemistry, Narosa
Atkins, P. W. & Paula, J. de Atkins', Physical Chemistry, Oxford University Press
McQuarrie, D. A. & Simons, J. D. Physical Chemistry: A Molecular Approach, Viva Press
Levine, I. N. Physical Chemistry, Tata McGraw-Hill
Moore, W. J. Physical Chemistry, Orient Longman
Mortimer, R. G. Physical Chemistry, Elsevier
Engel, T. & Reid, P. Physical Chemistry, Pearson
Levine, I. N. Quantum Chemistry, PHI
Atkins, P. W. & Friedman, Molecular Quantum Mechanics, Oxford
Engel, T. & Reid, P. Physical Chemistry, Pearson
Klotz, I.M., Rosenberg, R. M. Chemical Thermodynamics:Basic Concepts and Methods Wiley
Rastogi, R. P. & Misra, R.R. An Introduction to Chemical Thermodynamics, Vikas
Glasstone, S. An Introduction to Electrochemistry, East-West Press

Practical:

1. Viswanathan, B., Raghavan, P.S. Practical Physical Chemistry Viva Books (2009)
Mendham, J., A. I. Vogel's Quantitative Chemical Analysis 6th Ed., Pearson
Harris, D. C. Quantitative Chemical Analysis. 6th Ed., Freeman (2007)
Palit, S.R., De, S. K. Practical Physical Chemistry Science Book Agency
University Hand Book of Undergraduate Chemistry Experiments, edited by Mukherjee, G. N., University of Calcutta
Levitt, B. P. edited Findlay's Practical Physical Chemistry Longman Group Ltd.
Gurtu, J. N., Kapoor, R., Advanced Experimental Chemistry S. Chand & Co. Ltd.
</td></tr>
<tr><td>Evaluation</td><td><table>
<tr><td>Theory: 60 marks</td><td>Practical: 40 marks
(Continuous Assessment)</td></tr>
<tr><td>CIA: 10
End-Sem: 50</td><td>Internal Assessment Exams: 30
Viva (End Sem): 8
Attendance: 2</td></tr>
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<tr><td>Paper Structure for the End Sem Theory Exam (50 marks)</td><td>6 (SIX) Questions (each of 10 marks) will be set and the students will have to answer any 5 (FIVE).
Each of the Questions (10 marks) will consist of 2 or 3 parts (of 2/ 3/ 4/ 5)</td></tr>
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Annexure Core Course (CC): 8

(Credits: Theory-04, Practicals-02)

<u>CHEMISTRY -C VIII: PHYSICAL CHEMISTRY-III</u>

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures

a) Application of Thermodynamics – II **(20 lectures)**

<u>Colligative properties</u>: Vapour pressure of solution; Ideal solutions, ideally diluted solutions and colligative properties; Raoult's law; 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; Abnormal colligative properties

<u>Phase rule</u>: Definitions of phase, component and degrees of freedom; Phase rule and its derivations; Definition of phase diagram; Phase diagram for water, CO_2, Sulphur

First order phase transition and Clapeyron equation; Clausius-Clapeyron equation - derivation and use; Liquid vapour equilibrium for two component systems; Phenol-water system

Three component systems, water-chloroform-acetic acid system, triangular plots

<u>Binary solutions</u>: Ideal solution at fixed temperature and pressure; Principle of fractional distillation; Duhem-Margules equation; Henry's law; Konowaloff's rule; Positive and negative deviations from ideal behavior; Azeotropic solution; Liquid-liquid phase diagram using phenol- water system; Solid-liquid phase diagram; Eutectic mixture

b) Electrical Properties of molecules **(20 Lectures)**

<u>Ionic equilibria</u>: Chemical potential of an ion in solution; Activity and activity coefficients of ions in solution; Debye-Huckel limiting law-brief qualitative description of the postulates involved, qualitative idea of the model, the equation (without derivation) for ion-ion atmosphere interaction potential. Estimation of activity coefficient for electrolytes using Debye-Huckel limiting law; Derivation of mean ionic activity coefficient from the expression of ion-atmosphere interaction potential; Applications of the equation and its limitations

<u>Electromotive Force</u>: Quantitative aspects of Faraday's laws of electrolysis, rules of oxidation/reduction of ions based on half-cell potentials, applications of electrolysis in metallurgy and industry; Chemical cells, reversible and irreversible cells with examples; Electromotive force of a cell and its measurement, Nernst equation; Standard electrode (reduction) potential and its application to different kinds of half-

cells. Application of EMF measurements in determining (i) free energy, enthalpy and entropy of a cell reaction, (ii) equilibrium constants, and (iii) pH values, using hydrogen, quinone-hydroquinone, glass and SbO/Sb_2O_3 electrodes

Concentration cells with and without transference, liquid junction potential; determination ofactivity coefficients and transference numbers; Qualitative discussion of potentiometric titrations (acid-base, redox, precipitation)

Dipole moment and polarizability: Polarizability of atoms and molecules, dielectric constant and polarisation, molar polarisation for polar and non-polar molecules; Clausius-Mosotti equation and Debye equation (both without derivation) and their application; Determination of dipole moments

c) Quantum Chemistry **(20 Lectures)**

Angular momentum: Commutation rules, quantization of square of total angular momentum and z-component; Rigid rotator model of rotation of diatomic molecule; Schrödinger equation, transformation to spherical polar coordinates; Separation of variables. Spherical harmonics; Discussion of solution

Qualitative treatment of hydrogen atom and hydrogen-like ions: Setting up of Schrödinger equation in spherical polar coordinates, radial part, quantization of energy (only final energy expression); Average and most probable distances of electron from nucleus; Setting up of Schrödinger equation for many-electron atoms (He, Li)

LCAO and HF-SCF: Covalent bonding, valence bond and molecular orbital approaches, LCAO-MO treatment of H_2^+; Bonding and antibonding orbitals; Qualitative extension to H_2; Comparison of LCAO-MO and VB treatments of H_2 and their limitations; Hartree-Fock method development, SCF and configuration interaction (only basics)

Core Course – X (LAB)

(60 Lectures)

Experiment 1: Determination of solubility of sparingly soluble salt in water, in electrolyte with common ions and in neutral electrolyte (using common indicator)

Experiment 2: Potentiometric titration of Mohr's salt solution against standard $K_2Cr_2O_7$ solution

Experiment 3: Determination of K_{sp} for AgCl by potentiometric titration of $AgNO_3$ solution against standard KCl solution

Experiment 4: Effect of ionic strength on the rate of Persulphate – Iodide reaction

Experiment 5: Determination if indicator constant of BCG indicator by colourimetric method.

Experiment 6: pH-metric titration of acid (mono- and di-basic) against strong base