Course: Discipline Specific Core 14

Semester	**6**
Paper Number	**HCHCR6142T (60 MARKS) & HCHCR6142P (40 MARKS)**
Paper Title	**CORE COURSE 14: 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:*** **Molecular Spectroscopy** After eigenstates and eigenvalues have been obtained from quantum mechanical recipes, transitions between the energy levels resulting from interaction with electromagnetic radiation, become very important. Students will be exposed to selection rules governing transitions, unravelling of molecular parameters, explanation of intensity patterns and ratios, presence of isotopes etc. The focus will be on rotational and vibrational excitation of the molecules, coupling between these motions and Raman Spectra. **Photochemistry** Emphasis will be on the decay of electronically excited states of molecules. In this context, quantum yield is a very important parameter which will be discussed in detail. The absorption and emission process will be probed along with other non-radiative process. The information gained from such studies will be discussed with specific examples. **Surface Phenomena** Study of surfaces is a very important aspect of any comprehensive understanding of chemical reaction dynamics. In solids, the extent to which a surface is covered and variation of the extent of coverage with pressure and temperature is an aspect to be investigated. In liquids, presence of a surface tension requires as rather involved approach from the thermodynamic point of view. Colloids, forming a micro heterogeneous phase deserve a separate treatment in terms of stability and coagulation, scattering power, double layered potential and various electrokinetic phenomena. Soft colloidal systems will also be dealt with in sufficient detail. ***Practical:*** 1. To measure the surface tension of liquids and solutions and to have an idea of the surface excess. 2. Measuring optical densities – Verifying the Lambert Beer's law and determining the extinction coefficient – studying the λ dependence of the latter. 3. Introducing Spectrophotometry – Performing certain spectrophotometric experiments such as determination of CMC of a surfactant, isosbestic points, change of OD with time in kinetic experiments.
Syllabus	Annexure Core Course: 14
Texts	
Reading/Reference Lists	**Theory:** 1. Castellan, G. W. Physical Chemistry, Narosa 2. Levine, I. N. Physical Chemistry, Tata McGraw-Hill

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<tr>
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<td>
3. Atkins, P. W. & Paula, J. de Atkin’s, Physical Chemistry, Oxford University Press
4. Physical Chemistry Glasstone
5. McQuarrie, D. A. & Simons, J. D. Physical Chemistry: A Molecular Approach, Viva Press
6. Mortimer, R. G. Physical Chemistry, Elsevier
7. Laidler, K. J. Chemical Kinetics, Pearson
8. Banwell, C. N. Fundamentals of Molecular Spectroscopy, Tata-McGraw-Hill
9. Barrow, G. M. Molecular Spectroscopy, McGraw-Hill
10. Hollas, J.M. Modern Spectroscopy, Wiley India
11. McHale, J. L. Molecular Spectroscopy, Pearson Education
12. Wayne, C. E. & Wayne, R. P. Photochemistry, OUP
13. Brown, J. M. Molecular Spectroscopy, OUP
14. Levine, I. N. Quantum Chemistry, PHI
15. Atkins, P. W. Molecular Quantum Mechanics, Oxford
16. Heimz and Rajagopalan
17. Adamson surface chemistry
18. Rohatgi Mukherjee
19. Vemulapalli

Practical:

1. 1. Viswanathan, B., Raghavan, P.S. Practical Physical Chemistry Viva Books (2009)
2. Mendham, J., A. I. Vogel’s Quantitative Chemical Analysis 6th Ed., Pearson
3. Harris, D. C. Quantitative Chemical Analysis. 6th Ed., Freeman (2007)
4. Palit, S.R., De, S. K. Practical Physical Chemistry Science Book Agency
5. University Hand Book of Undergraduate Chemistry Experiments, edited by Mukherjee, G. N., University of Calcutta
6. Levitt, B. P. edited Findlay’s Practical Physical Chemistry Longman Group Ltd.
7. Gurtu, J. N., Kapoor, R., Advanced Experimental Chemistry S. Chand & Co. Ltd.
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<td>Evaluation</td>
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<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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<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>
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Annexure Core Course (CC): 14

(Credits: Theory-04, Practicals-02)

CHEMISTRY –CC 14: PHYSICAL CHEMISTRY

(Credits: Theory-04, Practicals-02)

Theory: 60 Lectures

a) Molecular Spectroscopy (20 Lectures)

Interaction of electromagnetic radiation with molecules and various types of spectra; Born-Oppenheimer approximation

Rotation spectroscopy: Legendre polynomials as representatives of rotational status. Overlap integral & TMI for the former. Section rules for rotational spectra. Intensities of spectral lines, determination of bond lengths of diatomic and linear triatomic molecules, isotopic substitution. Non rigid rotor – effect on energy levels. Spacing between lines in a non rigid rotor.

Vibrational spectroscopy: Hermite polynomials represent vibrational state of a molecule. Overlap integral and transition moment integral of the Hermites. Selection rule for Vibrational spectroscopy. Classical equation of vibration, computation of force constant, amplitude of diatomic molecular vibrations, anharmonicity, Morse potential, dissociation energies, fundamental frequencies, overtones, hot bands, degrees of freedom for polyatomic molecules, modes of vibration, concept of group frequencies; Diatomic vibrating rotator, P, Q, R branches, contour spectra under low resolution. Determination of molecular parameters.

Raman spectroscopy: Qualitative treatment of Rotational Raman effect; Effect of nuclear spin, Vibrational Raman spectra, Stokes and anti-Stokes lines; their intensity difference, rule of mutual exclusion, structure elucidation from IR and Raman spectra.

Nuclear Magnetic Resonance (NMR) spectroscopy: Principles of NMR spectroscopy, Larmor precession, chemical shift and low resolution spectra, different scales, spin-spin coupling and high resolution spectra, interpretation of PMR spectra of organic molecules

Electron Spin Resonance (ESR) spectroscopy: Its principle, hyperfine structure, ESR of simple radicals

b) Photochemistry (20 Lectures)

Lambert-Beer's law: Characteristics of electromagnetic radiation, Lambert-Beer's law and its limitations, physical significance of absorption coefficients; Laws of photochemistry, Stark-Einstein law of photochemical equivalence quantum yield, actinometry, examples of low and high quantum yields

Photochemical Processes: Potential energy curves (diatomic molecules), Frank-Condon principle and vibrational structure of electronic spectra; Bond dissociation and principle of determination of dissociation energy (ground state); Decay of excited states by radiative and non-radiative paths; Pre-dissociation; Fluorescence and phosphorescence, Jablonskii diagram; mirror image relationship between absorption and fluorescence spectra. Excimer and exciplex formation. Way to get phosphorescence alone.

Rate of Photochemical processes: Photochemical equilibrium and the differential rate of photochemical reactions, Photostationary state; HI decomposition, H_2-Br_2 reaction, dimerisation of anthracene; photosensitised reactions, quenching; Role of photochemical reactions in biochemical processes, photostationary states, chemiluminescence

c) Surface phenomena (20 Lectures)

Surface tension and energy: Surface tension, surface energy, excess pressure, capillary rise and surface tension; Work of cohesion and adhesion, spreading of liquid over other surface; Vapour pressure over curved surface; Temperature dependence of surface tension. Excess pressure; variation of ST with temperature.

Adsorption: Physical and chemical adsorption; Freundlich and Langmuir adsorption isotherms; multilayer adsorption and BET isotherm (no derivation required); Gibbs adsorption isotherm and surface excess; Heterogenous catalysis (single reactant); Zero order and fractional order reactions;

Colloids: Lyophobic and lyophilic sols, Origin of charge and stability of lyophobic colloids, Coagulation and Schultz-Hardy rule, Zeta potential and Stern double layer (qualitative idea), Tyndall effect; Electrokinetic phenomena (qualitative idea only); Determination of Avogadro number by Perrin's method; Stability of colloids and zeta potential; Micelle formation. Soft colloidal systems; surfactants, micelles, cmc & its variation; thermodynamics of micellization.

Core Course – XIV (LAB)

(60 Lectures)

Experiment 1: Determination of surface tension of a liquid using Stalagmometer

Experiment 2: Determination of CMC from surface tension measurements

Experiment 3: Verification of Beer and Lambert's Law for $KMnO_4$ and $K_2Cr_2O_7$ solution

Experiment 4: Study of kinetics of $K_2S_2O_8$ + KI reaction, spectrophotometrically

Experiment 5: Determination of pH of unknown buffer, spectrophotometrically

Experiment 6: Spectrophotometric determination of CMC