SUBJECT 3, Chemistry 3: Physical

Aims: The first-year physical chemistry course lays foundations in the key areas of quantum mechanics, physics, thermodynamics and reaction kinetics, upon which the whole of modern physical chemistry is based.

States of matter and equilibrium Thermodynamics


Electrochemistry


States of Matter

Microscopic view of structure and motion in the three states; radial distribution function. Density, mechanical properties, diffusion and viscosity, degrees of freedom, equipartition and heat capacity. Intermediate states of matter: liquid crystals, gels, glasses. Intermolecular forces and pair potentials. Gas imperfection, van der Waals equation, virial expansion. Relationship between potential energy curve and the virial coefficients/internal energy. Single component phase diagrams (e.g., H2O, CO2, He); phase coexistence and stability, triple point, critical point, multiple solid phases.

Quantum Mechanics and Spectroscopy

Quantum theory of atoms and molecules


Kinetics


Reaction kinetics

Rates of reactions. Order and molecularity. Rate laws and their determination. Experimental measurement of reaction rates. Sequential and reversible reactions, pre-equilibrium, the steady state approximation: applications to unimolecular reactions (Lindemann) and enzyme catalysis. Temperature dependence of reaction rates: Arrhenius Equation, activation energies, elementary collision theory.
Syllabus for Part IA 2017-18 (Year 2)

PHYSICAL CHEMISTRY

The Examination will consist of questions relating to the lecture courses given in the second year, together with all the first year material:

Quantum Theory

Operators: basic notions and properties; linear operators, eigenvalue equations; degeneracy; expansion in a complete set. Postulates of QM and deductions there from; expectation values and the meaning of measurement in QM; the time-dependent Schrödinger equation; stationary states and the time-independent Schrödinger equation. Commutators: definition, evaluation, properties. Physical significance of commutators; complementary observables, simultaneous dispersion-free measurement and the uncertainty principle (weak and strong). Bra-ket notation; definition and properties of Hermitian operators. One-body problems: the free particle (wave-particle duality; commutation and measurement; peculiarities). The particle in a d-dimensional box (quantization via boundary conditions; zero-point energy; the correspondence principle; degeneracy). Rotational motion: angular momentum; angular momentum operators, commutation relations and their significance; particle on a ring; particle on a sphere and eigenfunctions of $L^2$; the rigid rotor. The H-atom. The simple harmonic oscillator: wavefunctions, energy levels and properties. The variational principle. The existence of electron spin. Spin functions for a single electron. Spin functions for two electrons; singlet and triplet states. The Pauli principle, antisymmetric wavefunctions, Slater determinants Introduction to atomic spectra. He atom: variational calculation of ground state $1s^2$; orbital approximation. $1s^12s^1$ configuration; singlets and triplets. Atomic states: LS coupling; treatment of spin-orbit coupling. The Zeeman effect in atoms (magnetic fields), g-factors. The Stark effect (electric fields).

Liquids and Solutions


Statistical Mechanics

Systems of independent particles. Aims of statistical mechanics. Distribution of molecules over molecular quantum states: microstates, configurations and the weight of a configuration. The most probable configuration and derivation of Boltzmann distribution for independent molecules. Definition and significance of molecular partition function, q. Factorization of q into translational,
rotational etc. components; calculation of $q_{\text{trans}}$ and $q_{\text{elec}}$. Determination of internal energy, $E$, and specific heat, $C_v$, from $q$; application to monatomic gas.

Limitations of Maxwell-Boltzmann statistics. Mean values of observables; applications to bulk magnetization, paramagnetic susceptibility and derivation of Curie Law. Interacting particles. Concept of an ensemble. The canonical ensemble and the canonical distribution. The canonical partition function, $Q$, its physical significance and determination of internal energy from $Q$. Entropy in statistical mechanics, and its relation to $Q$. Determination of enthalpy, Helmholtz free energy, Gibbs free energy and chemical potential from $Q$. Independent particles II. Reduction of $Q$ for special case of independent molecules: the relation of $Q$ to $q$ for (i) independent distinguishable and (ii) independent Indistinguishable particles. Summary of thermodynamic functions for independent particles expressed in terms of $q$; separability of thermodynamic functions into contributions from different modes. Calculation of molecular partition function and selected applications. $q_{\text{trans}}$, $q_{\text{elec}}$ and the statistical thermodynamics of a monatomic gas; molar entropies and the Sackur-Tetrode equation. Rotational contribution to $q$ for heteronuclear molecules; the high temperature limit and characteristic rotational temperature, $\text{rot}$. Rotational contributions to $S$ and $C_v$. The effects of nuclear spin: symmetry numbers and $q_{\text{rot}}$ for homonuclear diatomics and other symmetrical molecules. Applications to rotational spectroscopy. Vibrational partition functions, $q_{\text{vib}}$, for diatomic molecules and polyatomics. Chemical equilibrium. Statistical mechanical result for the equilibrium constant $K$ of a general chemical reaction. Calculating the equilibrium constant and selected examples: dissociation reactions, isotope exchange reactions, thermal ionization equilibria. Transition state theory – the derivations. Concept of the transition state and the reaction coordinate. Transition state theory in terms of separable motion. The quasi equilibrium hypothesis. Derivation of the explicit expression for $k(T)$ in terms of partition functions.

**Atomic and Molecular Spectroscopy**

General aspects of Spectroscopy: Energy levels of molecules; Born-Oppenheimer separation; the photon; interaction of radiation with matter; absorption; emission; transition moments; Einstein Coefficients, selection rules. Atomic Spectroscopy: Revision of H-atom; wavefunctions; atomic orbitals; selection rules; Grotrian diagrams; Many electron atoms; Alkali metal (and pseudo-1-electron) atoms; Penetration and shielding; The quantum defect; Selection rules and spectra; Determination of ionisation energies; Russell Saunders coupling; Atomic term symbols; The Helium atom; Singlet and triplet states; configurations, terms and levels; Hund’s rules; electron correlation; Effects of external fields – Zeeman interactions; spin-orbit coupling; Molecular Spectroscopy (General) Molecular Rotational Spectroscopy; Rotors and their symmetry; revision of rigid rotor; moments of inertia; isotope effects; centrifugal distortion; selection rules; Stark effect; Complications of nuclear spin statistics. Molecular Vibrational Spectroscopy; Revision of harmonic oscillator and selection rules; Anharmonicity; normal vs local modes; symmetry considerations; vibration rotation spectroscopy. Molecular electronic spectroscopy; Potential energy curves/surfaces; Description of diatomic (linear) molecules; Classification of electronic states; Electronic selection rules; Franck-Condon Principle;
Valence


Rate Processes