Syllabus for Prelims 2017-18 (Year 1)

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

Le Chatelier's principle. Equations of state. Systems and surroundings. Work and heat. First law. Internal energy. State functions. Expansion work. Reversible and irreversible changes. Heat capacity and enthalpy. Thermochemistry. Standard states. Standard enthalpy changes (transition, reaction, formation). Kirchhoff law. Second law. Direction of change. Entropy. Condition of equilibrium. Entropy changes of phase transition. Temperature and pressure dependence of entropy. Third law. Statistical interpretation. Free energy. A and G. Available work. Temperature and pressure dependence of Gibbs energy. Phase equilibria. Clapeyron and Clausius-Clapeyron equations. One-component phase diagrams. Chemical equilibrium. Thermodynamics of mixtures. Chemical potential. Entropy and enthalpy of mixing. Extent of reaction. Reaction quotient. Condition for equilibrium, equilibrium constant and its temperature dependence; relation to standard Gibbs function.

Electrochemistry

The metal/solution interface. Electrochemical potential. Equilibrium Nernstian electrochemistry. Activity and activity coefficients and their determination. Nernst equation. Cells and half cells. Reference electrodes. Reversibility and irreversibility of cells. Relation of standard potentials to thermodynamic quantities. Conductivity of ionic solutions - liquid junction potentials. Measurement of standard electrode potentials.

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., H_2O, CO_2, He); phase coexistence and stability, triple point, critical point, multiple solid phases.

Quantum Mechanics and Spectroscopy

The physical basis of Chemistry: Electromagnetism Coulomb's Law, electrostatic forces and fields. Electric energy and potential. Electric dipole moment. Electric current, resistance and conductivity. Magnetic forces – the Lorentz force. Magnetic fields and the Biot-Savart law. Magnetic dipoles and magnetic materials. Waves, the E.M. spectrum. Superposition and diffraction. Refraction (Snell's Law).

Quantum theory of atoms and molecules

Quantum theory. Failures of classical physics. Quantization of electromagnetic radiation. Wave-particle duality. The de Broglie relation. The Schrödinger equation. Solution for particle in a one-dimensional square well and results for an n- dimensional square well; particle on a ring and the rigid rotor; simple harmonic oscillator; hydrogen atom. Born interpretation. Correspondence principle. Zero point energy. Quantum Tunnelling. Eigenvalue equations. Position, momentum and Hamiltonian operators. Expectation values, uncertainty principle. Atomic spectra: one-electron atoms and alkali metals. Orbitals, energy levels and quantum numbers. Radial and angular distributions. Term and level symbols. Spin- orbit coupling. Penetration and shielding. Selection rules and spectra. Structure of many-electron atoms and the Aufbau principle.

Kinetics

The physical basis of chemistry: Classical mechanics and properties of gases Newton's Laws of motion: forces, momentum and acceleration. Work, and kinetic and potential energy. Rotations: angular momentum and moments of inertia. Vibrations: simple harmonic motion. Properties of gases: the perfect gas equation. Kinetic theory of gases, origin of pressure, Maxwell-Boltzmann distribution. Molecular motions and equipartition. Collisions between molecules, mean free path, collision frequency, effusion, diffusion.

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. $1s^1 2s^1$ 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

Ideal solutions: entropy of mixing, zero enthalpy of mixing, Raoult's law, ideal solubility, depression of freezing point, osmotic pressure. Regular solutions: the effects of non-zero interactions, non-zero enthalpy of mixing, Henry's law, vapour pressure, phase separation. Polymer solutions: polymer dimensions in solution (theta and good solvents, radius of gyration), Flory-Huggins model, entropy and enthalpy of mixing, osmotic pressure. Electrolyte solutions: activity coefficients of ions in solution, Debye-Hückel (D-H) theory, Debye-length, ionic strength, application of D-H to solubility and dissociation. Surface of liquids and solutions: surface tension, Laplace's law, the Kelvin equation, the Gibbs dividing surface and the Gibbs adsorption equation.

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_{trans} and $q_{elec.}$ 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_{trans}, q_{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, $_{rot}$. Rotational contributions to S and C_v. The effects of nuclear spin: symmetry numbers and q_{rot} for homonuclear diatomics and other symmetrical molecules. Applications to rotational spectroscopy. Vibrational partition functions, $q_{vib,}$ 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;

Band heads; Dissociation energies; Birge-Sponer extrapolation; Predissociation. Raman and Rayleigh Scattering; rotational and vibrational transitions; selection rules; mutual exclusion in centrosymmetric molecules; Raman vs. IR

Valence

Born-Oppenheimer Approximation. Bonding in H_2^+ (LCAO approximation). Many-electrons - the Orbital Approximation. Deficiencies of the orbital approximation. binding of He_2 , splitting of degenerate configurations, dissociation of H_2. Application of Variation Principle to find LCAOs - the Secular Equations. Simplification due to symmetry and electronegativity differences. Examination of energy levels of diatomic molecules. Splitting into terms (O_2) and levels (NO). Electronic and Photoelectron Spectra of Molecules. Franck-Condon Effects. Selection Rules. Examination of vibrational and rotational structure. Band heads. Birge-Sponer extrapolation. Predissociation. Radiationless transitions. Polyatomics - Hückel simplifications of the secular equations. Use of symmetry. Properties from the wavefunction - bond- order, electron density, dipole moments, spectral properties, organic reactivity.

Rate Processes

Simple collision theory. Collision frequency and collision cross section. Reaction cross section and steric factor. Potential energy surfaces. Classical motion over PES's. Link between reaction cross sections and rate constants. Transition state theory. Comparison with simple collision theory. Calculation of rate constants. Estimation of pre-exponential factors. Temperature dependence of rate constants. Kinetic isotope effects. Quantum mechanical tunnelling. Non- Arrhenius behaviour. Thermodynamic formulation of TST. Liquid-phase kinetics. Comparison of liquid-phase and gas-phase reactions. Encounter pairs, cage effect, and geminate recombination. Wavelength and viscosity dependence of photodissociation, radical scavenging, kinetics of I_2 photodissociation, cluster reactions, spin effects. Diffusion controlled reactions. Smoluchowski theory. Stokes-Einstein relation. Effects of solvent viscosity and temperature, reactions between ions, spin effects. Activation controlled reactions. Gibbs energy of reaction, effect of electrostatic interactions, influence of solvent permittivity, entropy and volume of activation, electrostriction, influence of pressure and ionic strength. Electron transfer reactions. Marcus theory. Gibbs energy and reorganization energy. Marcus inverted region. Homogeneous and heterogeneous electron transfers. Interfacial kinetics. Electric potential and its effect on interfacial reaction rates. Butler-Volmer equation. Transfer coefficients. Overpotential. Tafel relations. Voltammetry.