Subject Code : CCN4B12

CORE COURSE XII – PHYSICAL CHEMISTRY III

Unit I

Quantum Chemistry – III

Need for approximation methods – Variation method (Statement, proof, secular equation, application to hydrogen and helium atom) – perturbation method for non degenerate systems (first order correction to eigenvalue and eigenfunction, application to helium atom).

Angular momentum in many electron system (spin orbit interactions, L-S and j-j coupling schemes) – elementary idea of Hartree – Fock self consistent field method.

MO and VB treatment of hydrogen molecule (electron density, forces and their role in chemical binding) - hybridization, solving wave equation for sp, sp^2 and sp^3 hybrid orbitals – Huckel's molecular orbital theory and its application to ethylene and butadiene (charge density, n bond order and free valence)

Unit II

Molecular Spectroscopy III: NMR: Spin and applied magnetic field – Larmor precession – relaxation precession – PMR chemical shift – spin-spin coupling (AX and A_2 spin systems in terms of spin Hamiltonian and spin product functions) – Fourier Transformation NMR – multiple pulse nmr (effects of pulses, the rotating frame of reference, free induction decay FID, multiple pulse spin-spin and spin-lattice relaxation, inversion recovery) – ^{13}C nmr – chemical exchange – evaluation of thermodynamic parameters in simple system.

ESR Spectroscopy: basic principles, zero field splitting and Kramer's degeneracy, factors affecting the g value – presentation of spectra – hyperfine splitting – isotopic and ansisotropic hyperfine coupling constants, spin Hamiltonian, spin densities and McConnell relationship, measurement technique and applications.

Unit III

Quantum statistics: Bose-Einstein (BE) distribution function – Femi-Dirac(FD) distribution function – comparison of them with Maxwell-Boltzmann statistics - Application of BE statistics to photon gas, superfluidity of liquid helium – application of FD statistics to electron gas and thermionic emission.

Heat capacities of solids – Einstein and Debye's treatments – concept of negative Kelvin temperature.

Non-equilibrium thermodynamics: Thermodynamics of irreversible processes – Entropy production and entropy flow in open system – Onsagar theory – phenomenological relations – Onsager reciprocal relations – steady state conditions – L12 = L21 wrt (i) thermoelectricity, (ii) electrokinetic effect (iii) thermomolecular pressure difference (iv) transference number method.

Unit IV

Ionics: Transport of ions in solution – Debye – Huckel theory – radius of ionic atmosphere and its calculation – Debye-Hucket-Onsagar equation modifications – asymmetry and electrophoretic effects – evidences for ionic atmosphere – Debye – Falkenhegen and Wien's effects – extension to Debye-Hucket-Onsagar theory.

Activity of ions in solution – Experimental determination – Debye – Huckel limiting law (derivation, verification and modification) – activity coefficient at higher concentration – Bjerrum model.

Electrode – Electrolyte equilibrium – Nernst equation – and its limitation - equilibrium electrode potentials – classification of electrodes – concentration cells – liquid junction potentials – thermodynamic quantities from EMF data.
Electrochemical energy – Storage systems – primary and secondary batteries – fuel cells.

Unit V

Electrokinetic phenomena: Theories of electrical double layer – Electrical double layer potential – theory of multiple layers at electrode electrolyte interface – double layaer capacity – ectrokinetic phenomena (zeta potential, electro osmosis, sedimentation potential)

Processes at the electrodes – the rate of charge transfer – current density – Butler – Volmer equation – Tafel equation-

Principles of Electro deposition of metals: electrochemical corrosion – construction and use of pourbaix and Evans diagram and prevention of corrosion – electrochemical oxidation and reduction.
Polorography and cyclic voltametry: Principles and applications.

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