Advanced Physical Chemistry

Thermodynamics block

Four and a half weeks, 9x90 minutes

1. Basics of classical thermodynamics
   The concept of heat and temperature and the pressure tensor; the laws of thermodynamics, thought experiments with “perpetuum mobile” concepts; the Carnot cycle for ideal and real systems
2. Axiomatic thermodynamics by Callen
   Comparison of the traditional postulates with Callen’s axioms; change of variables using Legendre transformations; the role of big numbers.
3. Statistical thermodynamics
   Expansion of a charge distribution; the Hamilton equation for a system of mass points; the phase space; the density distribution function of microstates; the partition function; micro-canonical ensemble; molecular chaos; Lyapunov exponents and spectrum; Difference between equilibrium and dissipative systems; Lochsmidt paradox; fluctuation theorem; fractals; ergodic hypothesis and mixing; other ensembles by Laplace transformations; the statistical definition of entropy; relationship between all microstates and the most probable microstates; calculation of phase variables (pressure, temperature, energy) and functionals (entropy term containing functions); fluctuations.
4. Equations of state; the virial equation; liquid-vapor equilibrium by the van der Waals equation; a universality relationship: the rule of corresponding states; the critical point.
5. Mixtures; the Gibbs paradox.
6. Linear Irreversible thermodynamics; the balance equations of hydrodynamics; constitutive equations; non-equilibrium systems far from equilibrium.
7. Structure of solids and liquids; measurements by X-ray or neutron diffraction; (unit cell, Miller indices); liquid crystals, rotator phase, superionic conduction.
8. A quiz to understand some concepts of thermodynamics.

Theoretical Chemistry block

Four and a half weeks, 9x90 minutes

1. (1st lecture) **Angular momentum**: construction of the operators, eigenvalues, eigenfunctions, physical consequences; magnetic moments; spin and spin moments; application to the hydrogen atom.
2. (2nd lecture) **Electronic structure of atoms**: Hamiltonian and the Independent Electron Approximation (IEA), orbitals, orbital energies, electron shells, electronic configuration, Aufbau principle; Angular momentum operators for many electron system; representation of atomic states and the corresponding notation; Hund's rule, spin-orbit interaction, total angular momentum, atoms in magnetic field.
3. (3-4th lectures) **Molecular symmetry, group theory**: symmetry operations, point groups and their properties, representations and the character table, direct-product representation; application in electronic structure and spectroscopy.
4. (5-6th lectures) **Chemical bond**: quantum mechanical definition of chemical bond, approximation: IEA, MO theories, LCAO-MO, Valence Bond theory; diatomic molecules, electronic structure of transition-metal complexes; quantum chemistry of periodic systems, band structure, conduction and isolating bands, semiconductors.
5. (7-8th lectures) **Computational Chemistry**: determinant wave function, energy expression with determinant wave function, short derivation of the Hartree-Fock (HF) method, Hartree-Fock-Roothaan method, interpretation of the HF results (orbitals, density, population analysis, Koopmans theorem), basic elements of the Density Functional Theory (DFT), Hohenberg-Kohn theorems, Kohn-Sham DFT, functionals, hybrid methods; atomic basis sets.
6. (9th lecture) Reserve or applications.

Macromolecular Chemistry block

Three weeks, 6x90 minutes

1. Macromolecules, polymers, copolymers, polymer architectures, isomerism of polymers, molecular weight distributions and their characterization (average molecular weights and polydispersity).
2. Polymer conformations, average end-to-end distance, the ideal chain model (freely jointed chain), short range interactions and the effective segment length, persistence length, radius of gyration, distribution of end-to-end distance for ideal coil.
3. Energy and entropy elastic materials (ideal elastomer), comparison of elastic deformation for energy and entropy elastic materials, force required to extend a Gaussian chain, entropy change of network of Gaussian chains on deformation, modulus of a Gaussian network.
4. Dilute vs. semidilute vs. concentrated polymer solutions, entropy change of mixing for small molecules (solvent) and polymers, enthalpy change of mixing for small molecules (solvent) and polymers (c-parameter), Florry-Huggins theory, phase equilibrium (Gibbs free energy of mixing as a function of polymer solution composition, spinodal, binodal), polymer mixtures.