Committee on Professional Training

Physical Chemistry Supplement

Context

Physical chemistry provides the fundamental concepts and organizing principles that underlie all aspects of chemistry and related fields. It develops rigorous and detailed explanations of central, unifying concepts in chemistry and contains mathematical models that provide quantitative predictions. Physical chemistry contains the mathematical underpinning to concepts applied in analytical, inorganic, organic, and biochemistry courses, as well as more advanced topics in chemistry. Physical chemistry techniques and explanations are used for atomic, molecular, nanoscale, mesoscale, and macroscopic materials.

Conceptual Topics

Physical chemistry should emphasize the connection between microscopic models and macroscopic phenomena and the transition from atomic scale to macroscopic scale materials, from both a theoretical and an experimental perspective. Courses should develop both qualitative and quantitative models of physical properties and chemical change, and students should critically apply these models to deepen their understanding of chemical phenomena. Problem solving is a key activity in learning physical chemistry. Physical chemistry courses typically require at least two semesters of calculus and two semesters of physics. Previous experience with multivariable techniques is highly desirable, and exposure to differential equations and linear algebra is very useful as well. In addition, prior chemistry courses may provide preparation for the principal areas of coverage in physical chemistry.

The core treatment of physical chemistry will typically address each of the major concepts listed in bold below. However, a two-semester course cannot cover all of the topics listed for each concept, and a one-semester course will require an even more judicious choice of topics and coverage. A broad survey of the concepts and in-depth treatment of selected topics is a common and effective approach. Because physical chemistry concepts underlie the descriptions of many phenomena, it is especially useful to include examples of current scientific interest, make connections to others areas in chemistry, and study interdisciplinary applications of physical chemistry.

- **Thermodynamics and equilibria**. Standard functions (enthalpy, entropy, Gibbs energy, etc.) and applications. Microscopic point of view especially for entropy. Chemical potential applied to chemical and phase equilibria. Non-ideal systems; standard states; activities; Debye-Huckel limiting law. Gibbs phase rule; phase equilibria; single and multi-component phase diagrams. Thermodynamics of electrochemical cells. Thermodynamics of elastomers and coil-type molecules.

- **Chemical kinetics.** Differential and integral expressions with emphasis on single-step and multi-–stepphenomena of various orders. Relaxation processes. Microscopic reversibility. Derivation of rate laws from chemical mechanisms. Steady-state approximation. Chain reactions and polymerization. Collision theory; absolute rate theory; transition state theory. Isotope effect. Enzyme kinetics. Molecular reaction dynamics including molecular beams, trajectories, and lasers. Reactions on surfaces. Photochemistry.

- **Quantum mechanics**. Postulates and formulation of Schrodinger equations. Operators and matrix elements. Particle-in-a-box. Simple harmonic oscillator. Rigid rotor; angular momentum. Hydrogen atom; hydrogenic wave functions. Spin; Pauli principle. Approximate methods. Helium atom. Hydrogen molecule ion; hydrogen molecule, Diatomic molecules. LCAO method. Computational chemistry. Quantum chemistry applications.

- **Spectroscopy** (often interspersed with quantum mechanics to provide immediate applications). Light-matter interaction; dipole selection rules. Rotational spectra of linear molecules. Vibrational spectra. Term symbols. Electronic spectra of atoms and molecules. Magnetic spectroscopy. Raman spectroscopy; multiphoton selection rules. Lasers.

- **Statistical thermodynamics** (often associated with thermodynamics). Ensembles. Maxwell-Boltzmann distributions. Standard thermodynamic functions expressed in partition functions. Partition function expressions for atoms, rigid rotors, harmonic oscillators. Einstein crystal; Debye crystal.

- **Interdisciplinary applications**. Atmospheric, biophysical, materials, and/or quantum chemistry.

Practical Topics

The physical chemistry laboratory gives students experience in connecting quantitative models with observed chemical phenomena using physical chemistry concepts. The pedagogical goal is for students to understand the qualitative assumptions and limitations of models and the quantitative ability of the models to predict observed chemical phenomena.

Students must understand how to record good measurements, decide whether their measurements are valid, and estimate the errors in their primary experimental variables. This entails understanding the principles and use of electronic instrumentation for making measurements, as well as developing laboratory problem-solving experience with these instruments. Hands-on experience with modern instrumentation for measurement of physical properties and chemical change is essential. The opportunity for students to design aspects of their own experiments is quite valuable in learning about making measurements. During their data analysis, students must develop the ability to propagate experimental measurement uncertainties into uncertainties in calculated chemical quantities. A detailed error analysis is an important feature of physical chemistry laboratory reports.

Computers should assist in the collection, analysis, and graphing of data, as well as in the writing of reports. It is important that students gain experience with spreadsheet programs and linear least-squares fitting for data analysis. Computational tools such as Mathematica, MATLAB, or Mathcad are useful for helping students connect models to observed phenomena, and experiments using modern computational techniques (quantum calculations, molecular modeling) play an important role.

A sample list follows from which a set of experiments in physical chemistry might be selected. Within the physical chemistry area itself, as well as in an integrated laboratory, it is common for individual experiments to combine several aspects of experimental methods and theoretical concepts.

- **Thermodynamics.** Heat of combustion; enthalpy of reaction in solution. Thermodynamic functions from the temperature dependence of an equilibrium constant or the emf. Study of a system in which activity coefficients play a prominent role. Synthesis and characterization of solid state or polymeric materials.

- **Phase Equilibria**. Solid-liquid phase diagram. Liquid-vapor phase diagram.

- **Kinetic Theory**. Thermal conductivity of gases. Diffusion in solution. Knudsen effusion. Viscosity of gases.

- **Kinetics.** Relaxation study (first-order kinetics), possibly using lasers. Kinetic analysis of a complex reaction. Enzyme study.

- **Computational chemistry.** Molecular orbital theory. Calculation of structure and spectral properties

- **Spectroscopy.** Analysis of a vibration-rotation spectrum; isotope effects, e.g., HCl/DCl. Analysis of a polyatomic vibrational spectrum, e.g., SO_2. Analysis of an electronic-vibration spectrum, e.g., I_2. Analysis of electronic spectra, e.g., conjugated polyene dyes. Atomic spectroscopy. Raman spectroscopy. NMR analysis of spin-spin coupling in a non-first-order case. Laser applications.

- **Other.** Micelle formation

Illustrative Modes of Coverage

A common and traditional approach for teaching physical chemistry is a two-semester lecture and laboratory course taught in the third year. The laboratory program may accompany the lectures, be a separate course, or be an intensive single-semester course. The physical chemistry laboratory experience may also be integrated into a broader laboratory experience. These examples are not proscriptive, and creativity in the pedagogy and teaching of physical chemistry concepts is encouraged.

A one-semester course provides both opportunities and challenges for introducing students to the topics of physical chemistry within the context of a degree track. Often these courses provide a broad survey of the concepts and in-depth treatment of selected topics. The challenge of designing a one-semester course in physical chemistry is to determine the important principles that govern the physical and chemical behavior of matter within the context of the course emphasis. For example, a one-semester class for students who are pursuing a biochemistry track might focus on quantum chemistry, thermodynamics, and kinetics with examples from biochemistry used to illustrate these concepts. An environmental degree track could use examples based on analyzing field measurements or the kinetics of air pollutants.

Given the amount of material and time constraints of a one-semester class, some of the important topics in physical chemistry could be moved into other courses. For example discussions of enzyme kinetics could be incorporated into a course in biochemistry, kinetic modeling into an in-depth course in atmospheric chemistry, molecular orbital theory into physical organic or physical inorganic chemistry, and non-ideal solutions and electrochemistry into analytical chemistry. The choice of topics and coverage is at the discretion of the instructor and department; and discussion is encouraged within the department to ensure that important topics are not overlooked.

Independent of the focus of a one-semester physical chemistry course, students should be exposed to both microscopic and macroscopic aspects of physical chemistry, the relationship between these two approaches, and the use of quantitative models for understanding and predicting chemical phenomena of both large and small molecules. Discussion within and among departments is encouraged as the chemistry community works to develop one-semester physical chemistry courses that provide students with the necessary background and training to pursue a career in the chemical sciences.

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