Physical Chemistry Supplement

Context

Physical chemistry provides the fundamental concepts and organizing principles that are applied in 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.

Conceptual Topics

Physical chemistry should emphasize the connection between microscopic models and macroscopic phenomena. Courses should develop both qualitative and quantitative models of physical properties and chemical change, and students should critically apply them to deepen their understanding of chemical phenomenon. Problem solving is a key activity in learning physical chemistry. The physical chemistry course typically requires 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 principle 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 a 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, etc.) and applications. Microscopic point of view especially for entropy. Gibbs chemical potential applied to chemical and phase equilibria. Non-ideal systems; standard states; activities; Debye-Huckel limiting law. Gibbs phase rule; phase equilibria; phase diagrams. Thermodynamics of electrochemical cells.

- **Kinetic theory of gases.** Maxwell-Boltzmann distribution. Collision frequency; effusion rate. Equipartition of energy; heat capacity. Transport processes; diffusion coefficient; viscosity.

- **Chemical kinetics**. Differential and integral expressions with emphasis on multi-step as well as single-step first-order phenomena. Relaxation processes. Microscopic reversibility. Expressing mechanisms in rate laws. Steady state approximation. Collision theory; absolute rate theory; transition state theory. Isotope effect. Molecular reaction dynamics including molecular beams, trajectories, and lasers.

- **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 and kinetic theory). Ensembles. 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 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.

- **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.

- **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.

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 separate courses, 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. 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.