

Physical Chemistry: Important Concepts

What is physical chemistry?

At its most basic level, it is the theoretical and experimental foundation for the field of chemistry (and, by extension, much of biology). Using the concepts of physical chemistry, one can, in principle, predict the outcome of any chemical transformation or reaction. Physical chemistry has many connections to each of the other branches of chemistry, including biochemistry. Physical chemistry also has strong connections to physics, and many topics within physical chemistry are discussed (often from a different vantage point) in physics courses. In general, physical chemistry is the most mathematical branch of chemistry, although the math really isn't too bad.

Physical chemistry can be broken down into a few broad areas:

- Bulk (classical) thermodynamics and equilibrium
- Statistical thermodynamics
- Atomic and molecular structure
- Kinetics

Physical chemistry can also be subdivided based on size of the sample being studied. One can start with the smallest chemical entity, the atom, and discuss its structure and properties. The next size up, molecules, can also be discussed in terms of structure of individual molecules and interactions between molecules. Discussions of this sort involve isolated atoms or molecules or small numbers of interacting molecules. On the other hand, classical thermodynamics deals with larger amounts: on the order of a mole of a substance. In fact, classical thermo does not depend on the existence of atoms! Clearly, this is a very different regime. However, there are important connections between very small numbers of atoms and the bulk substance. One of these connections is statistical thermodynamics, which deals with the behavior of larger groups of individual entities (such as atoms) in a probabilistic sense. Another important connection is kinetics, which includes the very important 'detail,' time. One can study the kinetics of a bulk reaction to propose a mechanism (i.e., the sum of individual atomic or molecular transformations) for the reaction, thus yielding crucial information about what is happening on the nanoscale.

Starting small and working up is one way to approach physical chemistry. Using this framework, an outline of topics (four micro, two bridge, four macro) follows.

I. Atomic Structure

- A. Introduction: quantum mechanics
 - i. Failures of classical physics
 - ii. Particles and waves
 - iii. Schrodinger equation
 - iv. Operators
 - v. Translation: particle in a box
 - a. One dimensional
 - b. Three dimensional

- c. Tunneling
 - vi. Vibration
 - vii. Rotation
 - viii. Spin
 - B. H atom
 - i. Schrodinger equation in spherical coordinates
 - ii. r , Θ , and Φ
 - iii. Radial distribution function
 - iv. Values of r
 - v. Orbitals
 - vi. Selection rules
 - C. Multielectron atoms
 - i. Orbitals
 - ii. Atomic states
 - a. M_L
 - b. M_S
 - iii. Term symbols
 - iv. Hund's Rules
 - a. Ground state
 - b. Spin-orbit coupling
 - c. Excited states
 - v. He atom
 - a. Pauli exclusion principle
 - vi. Other multielectron atoms
 - a. Aufbau principle
- II. Bonding
 - A. Introduction
 - B. H_2^{1+}
 - i. Exact calculation of Ψ and E
 - ii. Approximate methods
 - C. H_2
 - i. Valence bond method
 - ii. Molecular orbital method
 - D. Other homonuclear diatomic molecules
 - E. Heteronuclear molecules
 - F. Huckel approximation
 - i. Variation method
 - ii. Overlap integral
 - iii. Secular equation and determinant
 - iv. Bond order, charges, HOMO, LUMO
- III. Molecular Structure
 - A. Symmetry and group theory
 - i. Introduction
 - ii. Symmetry operations
 - a. Definitions
 - b. Examples

- iii. Point groups
 - a. Flow chart
 - b. Examples
- iv. Character tables and representations
 - a. Operating on an orbital or vector
 - b. Development of a character table
 - c. Information in a character table
 - d. Irreducible representations
 - e. Reducible representations and reduction formula
 - f. Examples
- v. Bonding
 - a. Symmetry of orbitals
 - i. Central atom
 - ii. Non-central atoms: SALCs
- vi. Selection rules
- vii. Relationship to molecular properties
 - a. Dipole moment
 - b. Optical activity
- B. Spectroscopy
 - i. Introduction
 - ii. Rotational
 - a. Rotors
 - b. Tops
 - iii. Vibrational
 - a. Harmonic oscillator
 - b. Other factors
 - c. Normal modes
 - d. Infrared
 - i. Selection rules
 - ii. Relationship to group theory
 - iii. Examples
 - e. Raman
 - i. Rayleigh and Stokes lines
 - ii. Selection rules
 - iii. Relationship to group theory
 - iv. Other spectroscopy with Raman
 - iv. Rotation-vibration
 - v. Electronic (UV-vis)
 - a. Diatomic molecules
 - b. Polyatomic molecules
 - i. Laporte selection rule
 - ii. Spin selection rule
 - c. Internal conversion
 - d. Intersystem crossing
 - e. Lasers

- vi. Photoelectron
 - a. Energy expression
 - b. Molecular orbital energies
 - c. Types, uses, and examples
 - vii. Nuclear magnetic resonance (NMR)
 - a. Magnetic fields
 - b. Selection rule
 - c. Local fields
 - d. Chemical exchange
 - e. Nuclear Overhauser effect
 - viii. Electron paramagnetic resonance (EPR, aka ESR)
 - a. Selection rules
 - b. Coupling constants
 - c. Comparisons and contrasts with NMR
- IV. Intermolecular Interactions
- A. Introduction
 - B. Types of interactions
 - i. Dipole-related
 - ii. Hydrogen bonding
 - iii. Repulsive
 - iv. Total interaction
 - C. Solids
 - i. Types of forces
 - ii. X-ray diffraction
 - D. Surfaces
 - i. Surface energy
 - ii. Coverage and UHV environments
 - iii. Physisorption
 - iv. Chemisorption
 - v. Surface tension and capillary action
 - E. Colloids
 - F. Other aggregates
- V. Kinetics
- A. Introduction
 - i. Rate laws
 - ii. Relationship to balanced chemical equation
 - iii. Experimental quantities
 - B. Integrated rate laws
 - i. First order
 - ii. Second order
 - iii. Zero order
 - iv. Other orders
 - C. Methods
 - i. Differential
 - ii. Initial rates
 - iii. Isolation

- D. Temperature dependence
 - i. Arrhenius approach
 - ii. Transition state theory
 - iii. Collision theory
- E. Mechanisms
 - i. Steady state approximation
 - ii. Pre-equilibrium
 - iii. Rate determining step
 - iv. Potential energy surfaces
- F. Catalysis
- VI. Statistical Thermodynamics
 - A. Introduction
 - i. Definitions
 - ii. Brief overview of bulk thermodynamics
 - B. Boltzmann distribution
 - C. Partition function
 - D. Relationship to thermal energy
 - i. q_{trans}
 - ii. q_{rot}
 - iii. q_{vib}
 - iv. C_v
 - E. Relationship to entropy
 - i. S_{trans}
 - ii. S_{rot}
 - iii. S_{vib}
 - F. Free energy and equilibrium constant
- VII. Gases
 - A. Introduction
 - B. Ideal
 - i. Boyle
 - ii. Charles
 - iii. Avogadro
 - iv. Putting it together
 - C. Mixtures
 - i. Mole fraction
 - ii. Pressures
 - D. Kinetic theory
 - i. Pressure
 - ii. Speed distribution functions
 - a. Root mean square speed
 - b. Average kinetic energy
 - c. Average speed and velocity
 - iii. Collision frequency
 - iv. Mean free path
 - E. Real
 - i. Plots

- ii. Boyle temperature
 - iii. Van der Waals equation
 - a. a and b parameters
 - b. Critical point
 - iv. Other equations of state
- VIII. Bulk thermodynamics
- A. Introduction and Zeroth Law
 - B. First Law
 - i. System and surroundings
 - ii. Heat, work and energy
 - iii. Law of conservation of energy
 - a. Relationship to system and surroundings
 - b. Relationship to heat and work
 - c. First Law
 - iv. Cyclic processes and state functions
 - v. Work
 - a. Equations
 - b. External pressure
 - vi. Heat
 - a. Heat capacities
 - b. Relationships to energy and enthalpy
 - vii. Enthalpy
 - a. Definition
 - b. Phase changes
 - c. Reactions
 - d. Consequences of state functions
 - viii. Heat capacities
 - a. $C_p - C_v$
 - b. Ideal gases
 - c. Ideal monatomic gases
 - d. Solids
 - ix. Adiabatic processes
 - a. Definition
 - b. Reversibility
 - c. Irreversibility
 - C. Second and Third Laws
 - i. Entropy
 - ii. Carnot cycle
 - a. Form
 - b. Details and definitions
 - c. Heat pumps, heat engines, and refrigerators
 - iii. Fundamental equation
 - a. Form
 - b. Ideal gas with no extra work
 - iv. More definitions
 - v. Phase changes

- a. Entropies
 - b. Trouton's rule
 - vi. Second Law
 - a. Form
 - b. Details
 - c. Implications
 - vii. Third Law
 - a. Definition
 - b. Implications
 - viii. Entropy revisited
 - D. Gibbs free energy
 - i. Definition
 - ii. Entropy, work, and Helmholtz free energy
 - iii. Pressure
 - iv. Phase changes
 - E. Chemical Potential
- IX. Mixtures and Phase Diagrams
- A. Single component phase diagrams
 - i. Plots
 - ii. Clapeyron equation
 - iii. Clausius-Clapeyron equation
 - iv. First and second order transitions
 - B. Mixing
 - i. Gases
 - a. Gibbs free energy
 - b. Entropy
 - c. Enthalpy
 - d. Volume
 - ii. Liquids
 - a. General
 - b. Ideal solutions
 - c. Nonideal solutions
 - iii. Raoult's law
 - iv. Henry's law
 - v. Activities
 - C. Colligative properties
 - i. Vapor pressure lowering
 - a. Consequences
 - ii. Osmotic pressure
 - D. Multi component phase diagrams
 - i. Phase rule
 - ii. Two component solid-liquid mixtures
 - a. General information
 - b. Eutectics
 - c. Lever law
 - d. Cooling curves

- e. Compounds
 - iii. Two component liquid-liquid mixtures
 - a. Immiscibility
 - b. Partial miscibility
 - c. Critical temperatures
 - iv. Two component liquid-vapor mixtures
 - a. Pressure-composition diagrams
 - i. Ideal
 - ii. Positive deviation
 - iii. Negative deviation
 - b. Boiling point-composition diagrams
 - i. Ideal
 - ii. Positive deviation
 - iii. Negative deviation
 - iv. Azeotropes
 - v. Three component mixtures
 - a. General information
 - b. Solubilities
- X. Equilibrium
- A. Introduction: spontaneity
 - B. Role of G
 - i. Behavior of G
 - ii. Mixing
 - C. Chemical potential and activity
 - D. Different K values
 - E. Dependence of K on environment

Other topics in physical chemistry:

- Equilibrium and dynamic electrochemistry
- Physical chemistry of polymers and biomolecules
- More complete treatment of solids
- Motion in solutions and general diffusion
- Kinetics of complex reactions
- More about applications and modern physical chemistry research