# Systematic Physical Chemistry
# A Preparatory Course for the Comprehensive Exam in Physical Chemistry

## *List of topics and suggested materials*

**1. Thermodynamic system. The laws of thermodynamics. The Callen axioms of thermodynamics. Joule's experiments. Energy, heat, work, and entropy. The concept of thermodynamic equilibrium. Reversible, irreversible and adiabatic processes. Carnot cycle, Efficiency.**

Theory: Keszei: Chapters 2, 5.1, 5.2, Appendix A3 (Optional - Atkins: Chapters 1-5)

**2. Thermodynamic equilibrium in composite systems. Fundamental and state functions. Conjugated variables. Energy representation and entropy representation. Definitions and usage of $C_V$, $C_P$, $\kappa_T$, $\kappa_S$, $\alpha$. The absolute value of the entropy of a real gas.**

Theory: Keszei: Chapters 2.2, 3, 4.4.2

**3. The mathematical formalism of thermodynamics. The Euler equation. The Gibbs-Duhem equation. Total derivative of S, U, H, A, and G. Maxwell-relations. Conjugate variables.**

Theory: Keszei: Chapters 2.2, 4

**4. Statistical themodynamics. Interactions between particles (Coulomb's law, Lennard-Jones potential, etc.). Degrees of freedom for the molecular motions (translation, vibration, rotation). Ensembles. Energy distribution and partition function of the microcanonical and canonical ensembles. Molecular partition functions. Connections to macroscopic thermodynamics. Fluctuations.**

Theory: Keszei: Chapter 10.

**5. Phase equilibria. Criteria of phase stability in one-component systems. The phase rule of Gibbs. Phase diagram of one-component systems. Clapeyron's equation, Clausius-Clapeyron equation. Phase diagram of two-component systems. Eutectic composition, eutectoid, peritectic. Critical point. First and second order phase transitions.**

Theory: Keszei: Chapter 7.

**6. Ideal and real mixtures. The chemical potential, its concentration dependence. Raoult's law. Distillation. Fugacity and activity. Colligative properties. Azeotropes. Isotope effects. Joule-Thompson coefficient.**

Theory: Keszei: Chapter 6.

**7. Equation of state for gases. The theorem of corresponding states. The van der Waals and the virial equations. Structure of liquids and solid crystals. Bravais cells. Crystal structure determination methods. Glassy structures and liquid crystals.**

Theory: Keszei: Chapter 4.5, Atkins: Chapters 1, 21, 24.5

**8. Chemical equilibriums in reacting systems. Equilibrium constants of homogeneous reactions, standard reaction quantities and equilibrium constants with respect to different reference states.**

**Equilibrium constants of heterogeneous reactions. The equilibrium constant and its dependence on pressure and temperature. The Gibbs-Helmholtz equation.**

Theory: Keszei: Chapter 8.

**9. Molecular theories of chemical reactions: collision theory and transition state theory. The general form of the rate equations of elementary reactions, their solutions. Mechanism of chemical reactions. The rate equations of complex reactions, their solutions. Integrated rate equations. Quasi-stationary reactions. Chain reactions and explosions. Catalysis and inhibition. Oscillatory reactions and chemical chaos.**

Theory: Atkins: Chapters 25, 26, 27.

**10. Transport processes. Diffusion, heat and electric conduction, viscosity. Connection with the equilibrium of composite systems. The continuity equation of hydrodynamics. The continuity equation of conserved quantities. Cross effects.**

Theory: Keszei: Chapter 11.

**11. Sensors and measuring systems. Calibration and validation of measuring instruments. Fundamentals of process control. Pressure and temperature sensing devices. Methods of concentration measurement with special emphasis on time dependence. Computer-based measurement automation.**

Theory: Richard P. Wayne: Chemical Instrumentation (Oxford Chemistry Primers), Vesztergom Soma's powerpoint file, pdf file

**12. Calorimetric Methods and Instruments. Applications of calorimetry in chemistry. Construction of the phase diagram of a binary system (alloy). Cooling curves. Determination of the heat of solution and the heat of hydration by means of a calorimeter.**

Experimental handouts: Thermal analysis of Sn-Pb alloys, Determination of the enthalpy of solution of anhydrous and hydrous sodium acetate by anisothermal calorimeter, and the enthalpy of melting of ice by isothermal heat flow calorimeter

**13. Vapor-liquid equilibrium. Single component systems: Measurement of vapor pressure of a liquid as a function of temperature. Multicomponent systems: Boiling point diagrams. Distillation principles and processes. Determination of some characteristic parameters of a distillation column. The separation efficiency of distillation columns.**

Theory: Keszei: Chapter 7.8
Exprimental handouts: Static method, Smith-Menzies method, Ramsay-Young method for determining the heat of vaporization of single component systems. Rectification.

**14. Determination of molar mass by vapor density. Investigation of colligative properties. Experimental methods for the determination of activity and activity coefficients. Molar mass and activities from freezing-point depression data.**

Theory: Atkins: Chapters 7.5, 7.6, 7.7
Experimental handouts: Victor-Meyer method, freezing-point depression measurement I, freezing-point depression measurement II (an example from the internet)

**15. Electrochemical systems. Electrode, electrochemical cell. Measurement of the terminal voltage and electromotive force (EMF) of an electrochemical cell, determination of internal resistance. Concentration and temperature dependence of EMF. Calculation of thermodynamic data from electrochemical measurements.**

Theory: Inzelt György's note., Keszei: Chapter 9.2
Experimental handouts: Measurement of the terminal voltage and electromotive force (EMF), temperature dependence of EMF.

**16. Thermodynamics of a single bulk phase containing charged particles. Experimental and theoretical approaches for the study of such systems. Determination of mean activity coefficients from cell measurements, transport processes in electrolyte solutions. Determination of the pH using a hydrogen electrode and a glass electrode. Determination of the ion product for water. Systems of limited solubility.**

Theory: Keszei: Chapter 9.2, Atkins: Chapter 10
Experimental handouts: Mean activity coefficient determination, pH, ionic product for water

**17. Analysis of the chemical kinetics of homogeneous and heterogeneous reactions. Methods for monitoring the progress of chemical reactions. Determination of reaction orders and rate constants. Catalytic and autocatalytic reactions. Promoters and inhibitors. (Kinetics of catalytic decomposition of H2O2. Investigation of the reaction between KMnO4 and oxalic acid by spectrophotometry. Kinetic study of the heterogeneous reaction between CaCO3 and hydrochloric acid.)**

Theory: Keszei Ernő's ppt file on experimental methods in kinetics
Experimental handouts: kinetics of a second order reaction, permanganate-oxalic acid reaction, decomposition of hydrogen-peroxide

**18. Kinetics of electrode processes. Analysis of steady-state and potentiodynamic polarization curves. Voltammetry, the study of electrolysis mechanisms. Conductometric methods and instruments. Experimental methods for determination of transference numbers.**

Experimental handouts: transport number, electrolysis,

**19. Measurement of the viscosity of gases and liquids. The activation energy of viscous flow. Calculation of the mean free path. Methods for the determination of diffusion coefficients.**

Theory: Atkins pp. 818-830. Keszei: Chapter 11.
Experimental handouts: Gases, Höppler, Ostwald methods.

**20. Thermodynamics of surfaces. Experimental methods for the determination of surface tension, and the interpretation of the experiments.**

Theory: Atkins pp. 962-970, Keszei: Chapter 9.1
Experimental handouts: capillary rise, bubble pressure, and stalagmometric method.

**21. Principles of quantum mechanics. Physical quantities and their measurement, state functions, expectation values, Schrödinger equations, stationary states, simultaneous measurement of quantities, and the Heisenberg uncertainty principle.**

Theory: Szalay Péter's notes: 1st part

**22. Quantum mechanical description of the H atom and of many-electron atoms. Hamiltonians, Schrödinger's equation (energy, eigenfunctions), degeneracy, orbital drawings, electron density, electron spin, independent electron model, Pauli principle, Slater determinant, orbitals and their images, orbital energies, Aufbau principle, electron configuration, characterization of states, Hund's rule.**

Theory: Szalay Péter's notes: 2nd part, and 3rd part

**23. Electronic structure of molecules. Hamiltonians, orbitals of H2+, the LCAO-MO approximation, the electronic structure of the hydrogen molecule in the VB and MO picture. Electronic structure of diatomic molecules. Electronic structure of the water molecule within the MO and VB techniques, canonical and localized orbitals, hybrid orbitals.**

Theory: Szalay Péter's notes: 4th part, 5th part and 7th part

**24. Introduction to the theory of chemical structure determination methods. Disciplines of spectroscopic measurements, factors determining the appearance of spectra, distinction of spectroscopic techniques based on energy and characteristic motions. Understanding simple spectra.**

Theory: Császár Attila's notes: Part 1, Szalay Péter's Hungarian notes: Chapter 5.1

**25. Rotational and vibrational spectroscopies. Description of diatomic molecules within the rigid rotor approximation, energy levels and selection rules, rotational tops, applications of rotational spectroscopy. Vibrations of di- and polyatomic molecules, the harmonic oscillator approximation, classical and quantum mechanical description, energy levels, selection rules, internal coordinates, normal coordinates, role of symmetry, applications (IR and Raman spectroscopy).**

Theory: Atkins: Chapter 16, Szalay Péter's Hungarian notes: Chapters 5.2, 5.3, Advanced level - Császár Attila's notes, Part 2, Part 3

**26. Electron and NMR spectroscopies. Rules of UV and visible spectroscopies, selection rules, vibrational fine structure, practical applications, fate of excited states, fluorescence, phosphorescence, basics of photoionization spectroscopy, ESCA. Magnetic properties of nuclei, quantum mechanical description of spin, basics of NMR measurements, qualitative description of spectra, chemical shift, spin-spin coupling, applications.**

Theory: Atkins: Chapters 17 and 18, Szalay Péter's Hungarian notes: Chapters 5.4, 5.5, Advanced level - Császár Attila's notes, Part 4, Part 6, Part 7

**27. Surface energy and its consequences. Interfacial tension and mechanical equilibrium between two phases separated by a curved interface. Equilibrium vapor pressure of liquid drops and bubbles. Size dependent solubility of small particles.**

Theory: Hunter, Chapter 5.

**28. Basics of interfacial thermodynamics. The Gibbs equation and its applications. Surface active and inactive materials. Adsorption isotherms. The state equations of the adsorbed layer.**

Theory: Hunter, Chapters 5 and 6.

**29. Sedimentation, Ostwald ripening, and aggregagtion (or coagulation). The classical DLVO theory of colloidal stability. Cogaulation kinetics. The impact of electrolyte concentration on the coagulation rate of colloidal particles.**

Theory: Hunter, Chapter 9.

**30. Amphihilic molecules, surfactants. The formation of micelles. The hydrophobic interactions. Mixed micelles, solubilization, polymer/surfactant association.**

Theory:

**31. Macromolecular colloids. Polymer solutions. The statistical coil conformation of polymers. Polymergels. Polyelectrolytes.**

Theory:

**32. Basics of rheology. Flow curves and their interrelation to the structure of colloidal systems. Rubber elasticity of polymers.**

Theory: Hunter, Chapter 4.

**Literature:**

Atkins - P. W. Atkins, Physical Chemistry, 5th Edition, Oxford University Press
Hunter - R. J. Hunter, Introduction to Modern Colloid Science, Oxford University Press, 1998
Keszei - E. Keszei. Chemical Thermodynamics, Springer, 2012.