Systematic 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, κ_T, κ_S, α. 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. 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.

5. 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.

6. 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

7. 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.

8. 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

9. 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

10. 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.

11. 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)

12. 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.

13. 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.

Theory: Atkins: Chapters 25, 26, 27.

14. 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.

15. 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 H_2O_2. Investigation of the reaction between $KMnO_4$ and oxalic acid by spectrophotometry. Kinetic study of the heterogeneous reaction between $CaCO_3$ 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

16. 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.

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.