Physical Chemistry 158b – Chemical Thermodynamics and Kinetics

Course information: Spring 2007 Semester, Dr. Malkiat S. Johal, extension 74253, malkiat.johal@pomona.edu. Required textbook: D. A. McQuarrie and J. D. Simon, *Physical Chemistry: A Molecular Approach*, University Science Books, 1997 (ISBN: 0-935702-99-7).

Office Hours: Monday, Wednesday, Friday 1:00pm to 3:00 pm, or by appointment.

COURSE CONTENT

Unit 1: Partial Differentiation and Equations of State

Week 1/2: Chapter 16; MathChapters G and H. Review of partial differentiation. The properties of gases. Two-parameter and cubic equations of state. Second viral coefficients and intermolecular potentials. Law of corresponding states. Van der Waals constants in terms of molecular parameters. There will be a mid-term exam on the Wednesday of Week 3, testing all the material from Chapter 16 and MathChapter H. The exam will last approximately 1 hour and will be closed book.

Unit 2: Introduction to Molecular Thermodynamics and the Laws of Thermodynamics

Week 2: Chapter 17 and 18; MathChapter B and I. Review of the energy levels of atoms and molecules. Introduction to the Boltzmann distribution law and partition functions. Use of partition functions to obtain the average ensemble energy and heat capacity for a number atomic and molecular systems. Expression for pressure in terms of the partition function. The relationship between system partition functions (Q) and molecular partition functions (q). The molecular partition function expressed as a product of partition functions for each degree of freedom. The translational, rotational and vibrational partition functions.

Week 3: Chapter 19; MathChapter J. The First Law of Thermodynamics. Internal energy, heat and work and their molecular interpretation. Fundamental thermodynamic processes e.g. reversible adiabatic expansion of gases. Enthalpy changes for chemical reactions. The temperature dependence of enthalpy. The concept of entropy.

Week 4: Chapter 20 and 21. Entropy and the Second Law of Thermodynamics. The importance of devising a reversible process to calculate entropy changes. Statistical description of entropy ($S = k_B \mathrm{In}\Omega$), and entropy in terms of a partition function. Entropy and the Third Law of Thermodynamics. Absolute entropies, standard entropies, calorimetric entropies, and spectroscopic entropies.

Week 5: Chapter 22. Helmholtz and Gibbs Energies and the prediction of the direction of a spontaneous process for a system at both constant pressure and volume. Maxwell relations. The Gibbs-Helmholtz equation. Fugacity as a measure of the

nonideality of a gas. The Unit will end with a summary. There will be a mid-term exam on the Friday, testing all the material from Chapter 16 to Chapter 22. The exam will last approximately 1 hour and will be closed book.

Unit 3: Solution Thermodynamics

Week 6: Chapter 24. Liquid-liquid solutions. We will examine partial molar quantities and the Gibbs-Duhem equation. Ideal solutions and Raoult's law. The concept of chemical potential and activity. Gibbs energy of mixing of a binary solution.

Week 7: Chapter 25. Solid-liquid solutions. Raoult's law and Henry's law standard states. Colligative properties. Electrolyte solutions. Debye-Hückel theory and the mean-spherical approximation.

Week 8: Regular solution theory. There will be a mid-term exam on the Friday, testing all the material from Chapter 24 and Chapter 25, including handouts on regular solution theory. The exam will last approximately 1 hour and will be closed book

Week 9: Spring break, no classes.

Unit 4: Physical and Chemical Equilbria

Week 10: Chapter 23. Phase equilbria. Phase diagrams of pure substances. The Clausius-Clapeyron equation. Two dimensional phase diagrams and pressure-area isotherms. Chemical equilibrium.

Week 11: Chapter 26. Chemical equilibrium continued. The Van't Hoff equation. Equilibrium constant and standard Gibbs energies of formation. Equilibrium constants in terms of partition functions. The use of activities in solubility calculations. No classes on Friday: Cesar Chavez Day (staff and instructional holiday—observed).

Week 12: Chapter 28. There will be a mid-term exam on the Monday, testing all the material from Chapter 23 and Chapter 26. The exam will last approximately 1 hour and will be closed book. Chemical kinetics and rate laws. Effect of temperature on the rate constant. Transition state theory.

Unit 5: Chemical Kinetics and Reaction Mechanisms

Week 13: Chapter 29. Reaction mechanisms. Reversible reactions, consecutive, and parallel reactions. The steady-state approximation. Chains reactions, the Lindmann mechanisms, and enzyme catalysis. Explosions.

Week 14: Final. Exact time and place to be announced. We will review the entire course. We will revisit difficult topics and go through a large number of practice

problems. The final exam will be cumulative and cover questions from all Units (equal weighting.) The closed book final examination will last approximately 2 hours. One 8.5” × 11” sheet is allowed for reference to equations and physical constants.

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