CHEM 251
Physical Chemistry I
Chemical Thermodynamics

Fall Term, 2000-2001

Textbook: R. J. Silbey & R. A. Alberty, "Physical Chemistry", Third Ed., John Wiley & Sons, Inc., New York, 2001.

Supplements: (1) P. W. Atkins, "Physical Chemistry", 6th Ed., Freeman, 1998.
(2) M. W. Hanna, "Quantum Mechanics in Chemistry", 3rd Ed., Addison-Wesley, 1981.

Chapters & topics covered:

Chapt. 1, Introduction; Zeroth Law & Equations of State
Chapt. 2, First Law
Chapt. 3, Second and Third Laws
Chapt. 4. Fundamental Equations
Chapt. 5. Chemical Equilibrium
Chapt. 6. Phase Equilibria
Chapt. 7. Electrochemical Euilibria
Chapt. 8. Ionic Equilibria

Exams & quizzes:

There will be two hour exams and a final exam. Ten minute quizzes will be given at irregular intervals during the term. Ten minute quizzes are each counted as one-fifth of an hour exam, and the final is equivalent to two hour exams. The final exam will be a comprehensive exam covering the entire term while emphasizing material not covered by earlier exams. Exams and quizzes will be expected to cover any material covered in the course, including lectures, reading and homework assignments.

Supplementary material:

Students are encouraged to supplement the textbook reading in the library where copies of several good physical chemistry textbooks and other sources may be found. Homework problems will be assigned as necessary in order to test understanding and to illustrate new principles.

Instructor:

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First homework assignment:

1.1-1.4, 1.6-1.9, 1.3, 1.16, 1.19, 1.22-1.24

Gases-equations of state (~four lectures)

Extensive-intensive properties. Ideal gas law. Van der Waals equation of state (weak intermolecular forces). Compressibility factor. Boyle temperature. Kinetic theory introduction (velocity space, collisions with a wall [Knudsen flow], avg. kinetic energy).

First Law of Thermodynamics (~seven lectures)

Temperature. Equipartition of energies. Work and heat. Statement of first law. Pressure-volume work, reversible, irreversible, isothermal and adiabatic. Enthalpy. State functions. Thermochemistry. Heat capacities. Molecular basis of heat capacities. Temperature dependence of ΔH.

Second and Third Laws of Thermodynamics (~nine lectures)

Carnot cycle. What is entropy? Entropy and spontaneous processes. Statement of second law. $\Delta S_{universe}$ as a criterion for direction of reaction or process. Entropy changes for isothermal (reversible and irreversible) expansion or compression. Temperature dependence of entropy. Entropy as disorder. Molecular interpretations of entropy. Trouton's rule.

Evaluation of absolute entropies. Third law. Free energy. Free energy change and direction of reaction. Free energy change with P and T. Free energy and equilibrium. Van't Hoff isotherm. Determination of free energy changes. Temperature dependence of free energy and equilibrium. Van't Hoff isochore.

NOTE: The timing and coverage may be adjusted, as necessary, as the term progresses.

--JGK

Homework Assignments

"The greatest stumbling block that can be erected in the path of learning physical chemistry is the notion that memorizing equations is a sensible way to proceed. Memory should be reserved for the fundamentals and important definitions. Equations are meant to be understood, not to be memorized."—Gilbert Castellan, University of Maryland, 1971

Equations express a mathematical relationship between physical quantities. The various terms and algebraic signs have a physical meaning. Look at them carefully! Rearrange each equation in order to gain a different perspective.

The methods that are used to attack a problem are important. Problems are important only to the extent that they illustrate particular methods, stimulate thinking, or aid in the understanding of fundamental principles. Never attempt to memorize the solution to a particular problem! The algebra and calculus are mathematical tools to apply after the fundamental relations have been established. In working and solving problems, these tools are essential. It requires practice and, sometimes, perseverance to learn how to write a mathematical equation based on the conditions described in a word problem.

In working or solving problems, the student should develop a systematic approach. Be sure to read the question or statement of the problem carefully, making notes of essential conditions or values of variables. Note the quantities that are needed and the questions that are asked. Pay particular attention to units. In setting up equations, always take the time to check the units—often this will show whether or not a variable has been overlooked, a step is missing, or some other mistake has occurred. If a numerical answer is called for, be sure to show the units and give the correct number of significant figures. A common error made by students is to begin rounding off numbers before the calculation is completed. This leads to large errors in the final calculation and is wrong. With computers and calculators readily available, there is no need to round off or approximate numbers prematurely.

On exams, quizzes, or other papers to be graded, write clearly and highlight your answer by drawing a square around it so that the instructor can follow what you have done. Often, partial credit will be given if a multi-step calculation is required and only part of it is incorrect, and the instructor can see that you understand the remaining parts or principles.

Students need to practice by working as many problems and exercises as possible. Answers to exercises and selected problems are given near the back of the textbook. When you think that you understand a particular principle, try to make up your own question or problem using that principle, and then work it.

Finally, all students are encouraged to use their computers as much as possible in this course. A good spreadsheet program, such as Excel, is very effective for working problems and plotting graphs. Maple is a good choice for doing symbolic mathematics problems as well as for ordinary math problems. It can be very helpful to see different relationships plotted graphically and to sharpen the understanding of physical observations or evaluate data.