CHEM 165 – Introductory Physical Chemistry
Fall 2016, MWF 9:40-10:30 AM, Waterman 427
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Introduction

Chem 165 is the first semester of the year-long course in physical chemistry. During this first semester all aspects of physical chemistry will be covered at an introductory level. In broad strokes, the topics comprise: quantum mechanics, spectroscopy, thermodynamics, and kinetics. (The companion course, Chem 260, covers the same scope of subtopics plus statistical mechanics, but in the depth of treatment takes off where this one ends.)

In physical chemistry, the general objective is to <u>understand the underlying theory of many of the facts and rules you have learned</u> in prior chemistry courses. This, in turn, requires math/physics familiarity, rather than knowledge of chemistry in the form of molecular formulas and their reactions. For example, it is a fact that atomic orbitals are the basis of bonding, but do you know why a p-orbital has a “dumbbell” shape? [This was not plucked out of thin air.] It is also a fact that the energy contained in bonds is the basis for chemical reactions, but do you know why two hydrogen atoms would rather get together to form a molecule than exist apart? [Saying that two orbitals “overlap” is fuzzy, and is not a real answer.] At the thermodynamics end, we know that spontaneity is connected to lowering entropy, but is that always true? (Think of amino acids spontaneously forming DNA.) And how did “entropy get invented anyway? Why do there seem to be two worlds, the macroscopic which we track with thermodynamics vs. the microscopic where quantum mechanics is the coin of the realm? [Statistical treatment of the energy level occupation allows us to calculate macroscopic quantities.]

It is the goal of this course to help you to understand how a study of physical chemistry provides clear answers to the above questions, and in the process, demystify these subjects for you.

Prerequisites

Although your conceptual understanding of the subject matter is more important to me than being able to crank out mathematical calculations, the two cannot be separated. If you don’t have a good grasp of the math or physics underneath the subject material, you may have serious difficulties.

Thus the prerequisites (preferably) or co-requisites for the course are:
(1) Mathematics -- Math 22 for Chemistry majors, and Math 20 for all others not planning to take Advanced Physical Chemistry, and
(2) Physics -- Phys 51 for Chemistry majors, and Phys 11 for all others not planning to take Advanced Physical Chemistry.

If you do have the appropriate background, being a little foggy on the details can certainly be remedied by reviewing your earlier class material, or by stopping by my office to see me.

Minor in Chemistry

If you are enrolled in this course to satisfy the Chemistry minor you must, of course, satisfy the prerequisites. If you do but you feel apprehensive about your math/physics background, I strongly urge you to consider one of the less mathematically challenging courses such as, for example Quantitative Analysis (Chem 121), which is offered this semester, or Chem 131 (Inorganic Chemistry) next semester.

Textbook

For this new course, we will use: "Physical Chemistry for the Chemical Sciences" by Raymond Chang and John Thoman (1st edition). We will cover, in order:

Chapter 10: Quantum mechanics (classical physics, Schrodinger equation, particle in a box)
Chapter 11: Applications to vibration and rotation (infrared, microwave spectroscopy)
Chapter 12: Electron structure (the hydrogen atom, many-electron atoms)
Chapter 13: The chemical bond (potential energy curves, molecular orbital theory)
Chapter 14: Electronic spectroscopy (UV-vis absorption, and luminescence)
Chapter 1: Properties of gases (kinetic theory, van der Waals equation of state)
Chapter 3: First law of thermodynamics (heat, work, enthalpy, and thermochemistry)
Chapter 4: Second law of thermodynamics (entropy, Gibbs free energy)
Chapter 5: Gibbs energy applications (phase equilibria, phase diagrams)
Chapter 6: Solutions (colligative properties, phase diagrams of mixtures)
Chapter 15: Chemical kinetics (experimental rates, reaction order, temperature dependence)

There are 40 lectures in the semester. On average, each of these 11 chapters will take about 3.5 lectures to cover. [A much more detailed description of the topics to be covered is presented as an Appendix to this document.]

While this textbook closely approximates my pedagogic approach, you should understand that for most upper level courses the textbook is an aid, not the "bible". Depending on the material/chapter, various sub-topics will not be covered in class (or the reverse). The rule of thumb to use in this course is that if a concept is not discussed in lecture, you don't need to know the corresponding passage of a chapter unless I assign some reading on your own. Conversely you are responsible for all material discussed in class.

Also, be aware that much of the content may be presented by me differently from the way the author has done a given topic. Having said all this, I want to emphasize that trying to learn the subtleties of physical chemistry just from attending lectures and reviewing my notes is probably not going to cut it. There is real value to reading a textbook with wording that is different from the way the instructor presents it – and it is a good book to reference for any future chemistry topic.

Homework

The content in this course is pretty challenging, and cannot be mastered without blood, sweat, and tears as you review the material and do the homework problems. I will assign homework problems on average once per week. They will be fairly short, usually consisting of one or two problems, and are due promptly at the start of the following lecture. I will collect them at 9:45; if you arrive late, your HW will be late as well. These will be graded as follows:

Perfect or almost perfect, both in content and presentation (3 points)
Contains incorrect work, or was a sloppy presentation (2 points)
Contains incorrect work, and was a sloppy presentation (1 point)
Late submission by start of next lecture (score minus 1 point)
Did not turn in work by start of next lecture (0 points)

I will assign and collect about 11 HW sets. This means that you will be able to garner 33 points for the homework category (given a 1-point base). The score will be tripled to come up to the same weight as one exam. Answers will be posted on Blackboard. It goes without saying, however, that actually doing the problems on your own firms up the knowledge that is in your head.

Work must be turned in on 8½ x 11 inch sheets off a pad of lined paper, and writing is to be only on one side of a sheet. One pad of such paper from the UVM Bookstore or Staples should last you all semester, and costs less than $2.

Exams

We will have three semester exams at approximately equal intervals. From experience, I know that students appreciate not having the one-hour time constraint for their exams. Instead, I will design exams that could be finished in just over an hour but give you two hours, and have them outside of lecture's class times. I have tentatively scheduled them on Thursday evenings from 7 PM till 9 PM. What you are responsible for does not include the previous Wednesday's lecture material. The three exams are spread out as evenly as possible on the following schedule:

Exam 1 — September 29, covering Lecture #1 through Lecture #12 (12)
Exam 2 — October 27, covering Lecture #13 through Lecture #23 (11)
Exam 3 — December 1, covering Lecture #24 through Lecture #35 (11)

If your schedule does not fit with this, I will allow some flexibility in your exam start time on those days. Exams count as 100 points each, for a total of 300 points. In general terms, on exams will appear calculational problems, short-answer questions, longer-answer explanations, and multiple choice questions. Two related issues to keep in mind are that I will not discuss exam material on the day of the exam, and that my standing policy is that no make-up exams will be given. Our final exam is scheduled for December 12, 10:30-12:30. It is comprehensive (cumulative) in nature, and multiple-choice in format, worth 200 points. Please get your travel plans in order right away with this date in mind.

Grade

Your grade for the course will be based on the total number of points you accumulate out of 600, relative to the class average. Thus, there is no meaningful letter grade that can be assigned to any one exam. I can only indicate approximate ranges based on a "curve".

Although I cannot at this time predict the difficulty of the exams and the overall strength of the class, I can say that the average score for the course has usually been around 65%. In a large statistical sample, for this course the average performance falls in the B category. But please note that the average could also be a little lower or higher, depending on the overall performance of the class. This grading scheme is based on the assumption that attendance is perfect, and that students come prepared and are engaged.

Office Hours and Outside Help

My office is Cook A-119. I will be available in my office Monday, Wednesday, and Friday, 10:30-11:30 AM (subject to change). You are welcome to just stop by my office during these times, but it would be even more efficient if you let me know that you will be coming in, and what I can help you with. If these times are not suitable for you, we can also set up an appointment at another, mutually convenient time. I encourage you very strongly to use me to clear up difficulties the material as soon as possible. Obviously, the next lecture will be that much easier to follow.

The only time I will not answer questions is on the day of the exam because I want to discourage "cramming" at the last moments. Also, in addition to the above, you can call me at 656-0273, or use e-mail (*willem.leenstra@uvm.edu*) for quick consultations. You will find that I am exceedingly available. Review sessions may be scheduled if student demand warrants it. Organize it yourselves, and contact me.

Class Notes

My own experience tells me that it is hard to follow the thread of a discussion if you are furiously copying from the blackboard. Instead, I will have available on the web, via Blackboard, copies of my notes after each lecture. This allows you to just listen (or take skeleton notes) and possibly stay engaged easier. If, however, you are the type of student who learns better by taking your own notes, you should of course do so, and then use my notes as a backup.

Blackboard

This course management system will also serve as our course website. On it you will find this Syllabus and also information about exams, homework, as well as your grades.

Responsibilities

Attendance. From the above, it should be very clear that missing a lecture (or spacing out on one) can be extremely detrimental to your continued understanding of the material. Thus, I expect perfect attendance. If you have a valid, serious reason to be absent, you must call me beforehand. It will be up to you to get all the information presented at the missed class.

Preparation. Secondly, I expect you to come prepared for each lecture by having read ahead in the textbook. The lectures won't seem so mysterious if you know what is coming. If I find that the class, in general, is not keeping up with the outside reading, I may "pop" a quiz on you.

Participation. Finally, I expect you to participate in class by being alert and ready to answer questions. I find it personally insulting to see you spacing out, looking off into space, or exhibiting a case of "sleepy eyes". This expectation falls in the rubric of common courtesy or mutual respect. So please make a determined effort to absorb all the information from each lecture.

Appendix: Topics in Detail

Quantum Chemistry

Review of early experiments, and the failure of their classical explanations: (1) black-body radiation resolved by Planck's quantization of oscillator energies; (2) electronic spectroscopy of the hydrogen atom accounted for by Bohr's quantization of angular momentum of electron orbits; (3) photoelectric effect rationalized by Einstein's quantization of light waves into photons, plus the assumption that energy is proportional to frequency.

Wave-particle duality extended to the reverse of (3) above: beams of electrons showing diffraction. Then de Broglie providing a connecting equation spanning these two worlds. Review of why macroscopic entities cannot exhibit quantization. A natural consequence of the wave character of particles is that precise determination of its position is impossible. Heisenberg's uncertainty principle sets down the precise lower limits of the error in position and velocity measurements.

Operator algebra is defined as needed for the basic postulates of quantum mechanics (QM): (1) position and momentum can be cast as operators; (2) the energy eigenvalue equation of Schrodinger, $H\psi=E\psi$, must be obeyed, and is a specific example of the utility of the general eigenvalue equation; (3) the Born interpretation sets the probability density prediction as the square of wavefunction ψ; (4) for non-eigenvalue outcomes of predicted measurement, the expectation value can always be calculated.

The simplest example of quantum mechanics is the particle in the box (pib). An infinite set of wavefunctions are found along with their energies. Squares of wavefunctions are graphed and interpreted, and energy eigenvalues are explored. Extrapolating to the macroscopic world is shown to be futile. Tunneling is introduced for the pib, and the Heisenberg uncertainty principle is applied to the pib results. Credibility of the model is applied to the absorption spectrum of polyenes. Degeneracy as a concept is introduced within the pib model.

The harmonic oscillator (HO) is the next model to be investigated via QM. Wavefunction solutions are asserted, and graphed to allow interpretation of the probability densities. The energy solutions are explored. Tunneling can be illustrated with the HO model as well.

The first chemical system is looked at via QM: the hydrogen atom. The Hamiltonian is developed in Cartesian coordinates but not converted to spherical polar coordinates and therefore the solutions are not found explicitly. The wavefunction results are viewed as a function of radius r. Energy results are seen to coincide with Bohr's results.

The prototype for multi-electron atoms is helium, whose Hamiltonian is developed. By neglecting electron-electron repulsion, a simple solution consisting of the product of one-electron hydrogen-like wavefunctions is obtained. The variational method is discussed as a general method for improving approximate wavefunctions, and is then applied to the helium atom. In lieu of a detailed solution, the lifting of degeneracy of the 2s and 2p orbitals is rationalized with shielding and penetration of the shield. The effect of the intrinsic spin of electrons is introduced.

The prototype for molecular bonding is the hydrogen molecular ion. It is asserted that application of the variational principle leads to the well-known energy level diagram and orbital sketches of second-row diatomics. Bond order and magnetism are explored for these systems. By going to LiH, the concept of hybridization of atomic orbitals comes about naturally without invoking valence bond theory.

Vibrational spectroscopy of real molecules is discussed as an extension of the idealized HO model to that of an anharmonic oscillator. Concepts of selection rules, overtones, and Raman spectroscopy are presented. As well, vibrational spectroscopy provides a convenient model to discuss the Boltzmann population distribution and its effect on energy level populations as seen in so-called hot bands.

Thermodynamics

The ideal gas law is reviewed, and the absolute zero of temperature is shown to be a natural consequence of the law. Deviation from ideality is explored through the van der Waals equation. The modification of the ideal model and its result in a modified equation is a general scientific (and chemistry) principle, and thus a detailed discussion is therefore important as a general subject. The van der Waals interaction is seen to be at the heart of the empirical adjustments to the ideal gas law that need to be made.

The first law of thermodynamics is shown to be no more than an accounting scheme for energy exchange in a chemical system. Details of “work” are explored, comparing reversible and irreversible processes. Its complement “heat” is also looked at via calorimetry techniques. The overall “energy” is an experimentally difficult quantity to measure in a closed-volume (bomb) setup. For the more convenient open-air setup, a new quantity, enthalpy, is defined, which will be used in place of internal energy.

Thermochemistry is introduced as simply algebra applied to cyclic chemical processes. Enthalpies of formation are seen to be just a convenient set of standards through which Hess’s law is used in a more systematic way.

Entropy is introduced phenomenologically (as opposed to starting with the Carnot cycle). Entropy changes for the many different processes that can be traversed in PV or VT space are calculated by the appropriate equations (which have been derived earlier). The tie-in of entropy change to the concept of randomness are demonstrated via three archetypical randomization processes: free expansion, mixing, and heat flow from the hotter to the colder object when they are joined.

Spontaneity of a chemical process is demonstrated to not be controlled by energy lowering only, but also needs to include entropy. But the apparent contradictions that result from considering entropy alone are resolved when considering not only the system, but also the surroundings, i.e., increase in entropy is sought only for the universe, in its totality. The Gibbs free energy is seen to be a convenient construct to keep track of energy/entropy and system/surroundings contributions to overall spontaneity.

Phase equilibria are introduced phenomenologically via PT graphs. Minimization of Gibbs free energy can also be applied to the graphs, and results in an equation that connects pressure changes to temperature changes, the Clausius-Clapeyron equation. Temperature dependence of enthalpy is worked into the equation to account for deviation from ideality.

The special case of liquid-vapor phase changes is of great utility to chemists as it can aid in understanding fractional distillation. Starting with Raoult's law, the equation describing the so-called bubble point line (temperature of the L-V equilibrium as a function of liquid composition) can be derived. By incorporating Dalton's law, the dew point line (temperature of the L-V equilibrium as a function of vapor composition) can also be derived. By switching to pressure as the dependent variable, fractional distillation for an ideal mixture of two components is easily demonstrated.

Non-ideal solutions obey Raoult's law only as a solvent, and follow Henry's law as solutes. Introducing preferentially attractive interactions results in a high-boiling azeotrope; conversely, preferentially repulsive interactions result in a low-boiling azeotrope. Nevertheless, fractional distillations is still demonstrated.

Kinetics

Rates of reactions are visualized as changes in concentrations with time. Their behavior is cast in the form of a "differential" rate law. Experimentally, the rate law can be found by measuring the initial rates as a function of initial concentrations. The order of the kinetics with respect to each of the reactants can be obtained in this manner.

When the differential rate law is integrated, elapsed time can also be used in establishing rate laws. Equations are developed for the cases of first-order, second-order, and zeroth-order kinetics.

Microscopic reversibility and detailed balancing are two concepts that provide the connection between rates of reactions and the equilibrium constant. The temperature dependence of k is expressed via the Arrhenius equation.

Mechanisms of reactions result is specific rate laws. Thus, proposed mechanisms can be ruled out by establishing the rate law of that mechanism, and comparing it to the experimentally determined one. One special case of a catalyzed reaction is ubiquitous in biochemistry: the enzyme-substrate reaction. The rate law governing such a reaction is derived as the so-called Michaelis-Menten equation. Lineweaver and Burk modified that equation slightly, and in the process generated a more easily visualized plot.