Introduction to Molecular Thermodynamics

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Cover: The "Ivy Mike" test of the first Hydrogen bomb (1952)
http://www.enviroweb.org/enviroissues/nuketesting/atmosphr

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Many thanks to those who took the time to give valuable feedback based on the first draft, including Jeff Dahlseid, Paul Fischer, John Giannini, George Hardgrove, Paul Jackson, Gary Miessler, Wes Pearson, Gary Spessard, Don Tarr, Mary Walczak, Anne Walter, and John Walters. It is a privilege to have such wonderful colleagues. Very special thanks go to Beth Abdella for test driving the first draft with only a week's notice. Way to go, Beth! RMH thanks Debbie, Ira, and "Daddy's stuck on the computer" Seth. Your understanding has meant the world to me. Let's go camping! Over 100 students, listed below, provided much valuable critique. Their help has made this a much better draft. Good job!

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To the Reader:

It is truly a great privilege to share this with you. For over twenty years, St. Olaf College has had a unique second semester of first-year chemistry. We have set our standard introductory chemistry textbook aside for about seven weeks to take a really close "behind-the-scenes" look at what makes molecules do what they do. We have done this for three reasons. First, our second semester of first-year chemistry at St. Olaf College is designed to fill part of a department accreditation requirement for a first semester of physical chemistry. Second, we firmly believe that it is possible for first-year students to learn the basics of physical chemistry at a level appropriate to a first-year course. Third, we are convinced that having these discussions with *first-year* students, many of whom will never take another chemistry course, is one of the greatest services we can provide those students. The trick, we believe, is to have an understanding faculty and the right tools.

To make this work, the tool we chose was an outstanding textbook by William Davies entitled *Introduction to Chemical Thermodynamics: A Non-Calculus Approach.* This textbook, long since out of print, has been critical to our success all these many years. The focus on intuition and the logical progression of ideas cannot be beat. To a large extent, the approach used by Davies has been used in this text as well.

However, over the years it has gotten harder and harder to teach from this textbook. Besides being out of print, "Davies" (as it is affectionately referred to around here) uses outdated conventions—*E* for internal energy instead of *U*; calories instead of Joules, –*w* instead of +*w*, extensive rearrangement of natural log terms when using the "ln" key on a calculator works just fine, the almost complete lack of real-world examples. The list goes on and on. Each year it has gotten more difficult to integrate this book into a modern teaching style.

Having returned from a wonderfully relaxing vacation in Colorado, during the last week of 1998, I decided something had to be done. I made a list of all the revisions needed and discussed these with colleagues George Hardgrove, Beth Abdella, Mary Walczak, and Susan Green. We all agreed that the time had come. None of us, mind you, thought it would mean a new book! Alas, being the one having interim off for once, I set to work. After two days I threw in the towel and gave up. It was just too hard a job sifting through all the various issues and trying to come up with solutions that fit 3 inches of space here, 2 there. Then something magical happened. The words just flowed, and my fingers couldn't stop typing.

The result of this adventure was a first draft, which was well received, despite its hasty production, by 198 students and three faculty during the Spring of 1999. A second draft followed in the Spring of 2000. This second draft incorporated suggestions made in over 400 chapter reviews written by students at the end of that first semester of use. We were very pleased to see that, mostly, students found the casual style welcome and much more readable than what they were used to in first-year texts. In almost every case, we were able to respond creatively and positively to these mostly constructive suggestions. The second draft was better organize and better cross-referenced, and it included almost 100 more pages of text, 200 homework problems, and an almost completely new set of figures. Appendix I was as HUGE success, and it was expanded to include cross references to chapter sections. Major revisions in that second draft included an expanded section in Chapter 3 focusing on chemical reactions, moving of the discussion of the pressure effect on entropy forward two chapters, refocusing the chapter on pressure effect on free energy as a discussion of the equilibrium constant, a complete rewrite of Chapter 12 (phase changes), and a new appendix showing data for the vaporization of water.

Primarily, this third draft adds an index and corrects several minor typographical errors. The job isn't finished yet. We are aware of the immensity of Chapter 3, in particular, and are very interested in any and all suggestions as to how it can be made more manageable. We have heard the feedback that the worked problems in the chapters, integrated as they are with the text, are not always easy to find when it comes to homework time. We continue to strive for the best possible book. Please let us know how to improve it!

Bob Hanson, January 3, 2003
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How to Study Thermodynamics

Learning anything new is a challenge, and this is going to be something *really* new. Sometimes we professors forget how hard it is for students to remember all those new ideas. It's stressful. What's obvious for us is almost certainly *not* obvious for you. Here are a few tips that might relieve some of the stress:

- Check the web site ***http://www.stolaf.edu/depts/chemistry/imt*** as anything new will be posted there. Many of the figures from the book can be found there in animation. Several simulations and calculations you can use to check homework problems are also on the site.

- There's a BIG table in the back of this book (Appendix I) with all the many constants and symbols in alphabetical order. Refer to it when you forget what a symbol means.

- Equations are concise mathematical sentences. When you find an equation in the text that is important, it has a caption on the right such as "Eqn. 11.1" Highlight these and work hard not so much to memorize them (since a good calculator can remember them for you), but instead to understand what they are trying to tell you.

- As you read, try to say the mathematics to yourself (or better , if your roommate can stand it, out loud) in words, not in symbols. For example, "$\Delta U = q + w$" should be pronounced, "The change in internal energy is the sum of the heat put in plus the work put in." If you find you *can't* do that, it's a flag that you probably don't understand it. Slow down, go to Appendix I, and check what those symbols mean.

- Read slowly, and take notes as you read. You can't do this stuff by looking at a homework problem and then figuring out where in the book is a good example just like it. Not here. No way. Forget that. Try to follow the progression of ideas in the chapter. If it's written well, you should be able to see the logic. If you can't follow it, IT'S NOT WRITTEN WELL ENOUGH. LET US KNOW SO WE CAN FIX IT!!!

- Memorize now the *Zeroth Law of Thermodynamics*: Learning requires work.

- Remember, no course lasts forever. Years from now, when you've gotten your dream job, you'll forget you ever read this.

Even with these tips, this may be stressful for some of you. If you experience trouble, *please* talk it over with your professor. We know lots of tricks and are more than happy to sit down with you and go over any problems you have with this material. The payoff to studying molecular thermodynamics will be a good sound understanding of what's happening around you and how you can (or cannot) control it. Good luck to you!

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