INTRODUCTION TO MOLECULAR THERMODYNAMICS

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Preface

The premise of this book is a simple one: You don't have to be a mathematical genius to appreciate the essentials of thermodynamics. All you need is a basic understanding of probability—how it can be used to predict the outcome of events and how, especially when dealing with a huge number of events, simple ideas of probability predict outcomes that are for all practical purposes totally certain.

In the first chapter of this book, we show that with just a basic understanding of probability you can understand why it is that chemical reactions approach equilibrium and why the natural unpredictability of random events makes equilibrium a dynamic state, constantly fluctuating, constantly testing the possibilities. You'll see how Le Châtelier's principle—that a disturbed equilibrium will spontaneously adjust to form a new one—is just a natural outcome of this fluctuation. And you will find that these fluctuations seemingly disappear as we go to more and more particles. But that is just an illusion. The fluctuations are always there and, basically, those fluctuations, tiny as they may be, are what allow for chemical reactions to take place at all.

But to understand what's really going on in the world, we have to add the idea of energy: countable energy. In Chapter 2, when we start to consider the simplest chemical system—with just a few particles and just a few "quanta" of energy—we find the most amazing result: The most probable distribution of that energy in a system (the Boltzmann distribution, what we call equilibrium) is easily predictable. Temperature plays a role here, not so much as the cause, but rather as the effect. Temperature, we will see, is simply a way of monitoring the distribution of energy in a system. It's really the energy and how it is distributed that makes all the difference.

The problem with energy is that it's conserved. It gets traded back and forth between a system and its surroundings, but it's a fair trade, and this in itself cannot explain why some chemical reactions occur and some do not. Enter entropy—a measure of the number of ways energy can be distributed. Entropy turns out to be the key to understanding what's going on in real chemical processes. Entropy is not conserved, and that fact alone drives natural processes in the direction we call "forward in time."

It's really quite amazing that just a few simple ideas can go so far. But they do, and that is why we are so excited to be sharing them with you at this introductory level. You are about to take part in an adventure into the inner workings of the molecular world. Be prepared to be amazed; be prepared to be surprised at the simplicity of it all. That's the beauty of molecular thermodynamics.

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January, 2008

To the Instructor

It is a great privilege to share this book with you. We think you will enjoy teaching from this text as much as we do, and we look forward to hearing from you as you do so. We use this book in our first-year program here at St. Olaf College. It isn't an honors program at all—in fact, knowing that the majority of these students will not end up being chemistry majors is actually one of the most exciting aspects of using this book. 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. The trick, we believe, is to have a book that hits the right level. And this book, in our opinion, does exactly that. It may seem at first blush that only students with very strong math backgrounds would thrive using this book, but our experience is that any student willing to put time into the course can do well. The mathematics in this book goes no further than algebra and the manipulation of logarithms—the background anyone taking a first-year chemistry course would have.

For those students who are headed toward being chemistry majors, this experience will prove to be an exciting challenge. They may have had an outstanding high school chemistry experience, but they still may not ever have thought of chemistry in terms of probability and energy the way they will in your class using this book. Time and again we have seen these students get more and more excited as they make their way through our course. The overwhelming reaction we have seen is something like, "Wow, I can't believe this all makes so much sense!" That's our goal, of course, and don't be surprised if you start saying that yourself as you teach it. It does make sense. This book is one single, sensible story. This approach pays big dividends later on in a chemistry major's coursework. In later courses students can use more math and focus on the details—they will already know the story and will be far less likely to lose sight of the forest for the trees.

The word *molecular* in the title of this book emphasizes that we are taking a distinctly chemical approach to thermodynamics. This is not the standard third-year physical chemistry approach, filled with calculus and differential equations. This is not an abstract introduction to the "pure" thermodynamics dear to physicists, which is wholly macroscopic and requires no understanding of the underlying structure of the system or the surroundings. Instead, by emphasizing always the molecular context and using a simple model that involves only as much mathematics as necessary, we offer students insight into the interaction of matter and energy at a level they can fully appreciate. The focus here is on chemical reactions—what makes them go or not go; how we can predict their course. We start with the simplest of reactions, just the isotope exchange between H_2 and D_2, and talk about probability. There are fluctuations in how the molecules are distributed, but the more particles we add, the less we are able to detect those fluctuations. We then add the idea of quantization of energy and find that one distribution that is most probable follows an amazingly simple mathematical law discovered by Boltzmann.

Chapter 3 introduces the four major ways energy is stored in real chemical systems—in the form of electronic, vibrational, rotational, and translational energy. Certainly this is an approximation, but we can use these differences, then, to talk about heat, work, bonding, and the effect of temperature on chemical equilibrium. Entropy is introduced as a way of counting possibilities, and the effect of concentration and pressure on molar entropy falls right out of this understanding. The approach to enthalpy involves focusing on the effect of energy transfer on the distribution of energy in the *surroundings.* Considerations of entropy in both the system and the surroundings lead us to Gibbs energy.

To relate this all to chemical reactions, we use the graphical method developed by Gibbs in the late 1870s, involving graphing Gibbs energy as a function of temperature. Although Gibbs used this method only for describing changes of phase (many such applications are given in Chapter 12), we find that it is also extremely valuable in the context of any sort of situation involving "reactants" and "products." In effect, we are using reaction Gibbs energies as a way of getting at reaction potentials.

In our experience, it takes about 20 days—roughly seven weeks, three days per week—to take this special "behind-the-scenes" look at what makes molecules do what they do. You can take a look at how we do this ourselves by checking the daily notes at *http://www.stolaf.edu/depts/chemistry/imt/days* or the syllabus at *http://www.stolaf.edu/people/hansonr/chem126*. In addition, be aware that there is a whole suite of helpful accessories awaiting you at *http://www.stolaf.edu/depts/chemistry/imt*. Take a look at the "Online Interactive Guide." We use this extensively in class on a daily basis, and students use it on their own, as well.

We encourage you to contact us to ask us more about how we make this work. We have a variety of lab experiences, for example, that cover all aspects of this book. We would be more than happy to share them with you if requested.

Above all, have fun!

To the Student: How to Study Thermodynamics

Learning anything new is a challenge, and this is going to be something 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 there are several pages there you might find useful. The Concept Index page should be of great interest, for sure. We are very excited to offer this page, which provides an on-line overview of many of the chapters. For each chapter, there is a guided tour using slides, extensive commentary, searchable index, additional study questions, occasional animations and "tools," and many solved problems and quizzes.
- There's a *big* table in the back of this book (Appendix A) 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 especially important, it is labeled with a chapter equation reference such as 11.1. Highlight these and work hard not so much to memorize them as to understand what they are trying to tell you.
- As you read, try to say the mathematics to yourself in words (or better, if your roommate can stand it, say it out loud). 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 yet. Slow down, go to Appendix A, 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. You should be able to see the logic.
- Memorize now Hanson's 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. Still, we hope you will take something of this experience with you.

Even with these tips, this may be stressful for some of you. If you experience trouble, please talk it over with your professor or teaching assistant. They know lots of tricks and are probably 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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Well over 1500 students have gone through our program, either here at St. Olaf or at Macalester College. We appreciate all the feedback that has been offered.

Many of the ideas in this book are based on the pioneering work of others, namely Leonard Nash, *Elements of Statistical Thermodynamics* (Addison Wesley, 1968), Richard Dickerson, *Molecular Thermodynamics* (W. A. Benjamin, 1969), and especially William Davies, *Introduction to Chemical Thermodynamics* (Saunders, 1972).

RMH thanks Debbie, Ira, and "Daddy's stuck on the computer" Seth. Your understanding has meant the world to me. Let's go camping!

SG thanks Siri, Max, and especially Hans.

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