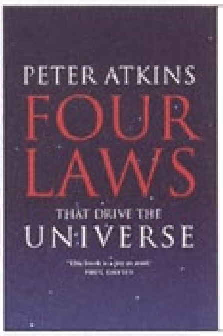
THERMODYNAMICS FOR EVERYONE

Easy-to-read book **EXPLAINS THE CONCEPTS** behind the equations

REVIEWED BY LAURENCE LAVELLE

FOR THOSE READERS who like short book reviews, let me assist you. "Four Laws That Drive the Universe," by Peter Atkins is an outstanding introduction to thermodynamics. This brief book converts introductory thermodynamics, which is often an abstract topic of mathematical equations, into prose that is easy to read and logical, explains the concepts behind the equations, and develops the equations. This book will be an asset to all students and instructors of thermodynamics. It will also be of interest to a general audience that wants to find out more about the inner workings of the world around them.



FOUR LAWS THAT DRIVE THE UNIVERSE, *by Peter Atkins, Oxford University Press, 2007, 128 pages, $19.95 hardcover (ISBN: 978-0199232369)*

For those readers seeking a more detailed review of Atkins' work, read on. This elegant and highly insightful book is written for a wide audience with an interest in understanding temperature, heat flow, work, energy, entropy, and efficient engines. These topics are what scientists and students of science call thermodynamics, which includes four well-known laws of thermodynamics. Throughout "Four Laws That Drive the Universe," the approach is to develop a strong conceptual foundation with as few equations as possible.

This book sets the standard on how to communicate complex scientific material. It shows that it is possible to develop conceptual foundations with prose that develops scientific equations with greater depth and understanding than the usually sterile scientific text that often merely states equations and all their technical formalities. Readers will also appreciate the helpful topic, symbol, and unit indexes at the back of the book. Most calculations are explained, but some readers may want to see all numbers used to calculate an answer, and the occasional British colloquialism may confuse some non-U.K. readers.

Chapter 1, "The Zeroth Law," discusses a property—temperature—and how it arises by considering systems at thermal equilibrium. For those wondering why it is called the zeroth law, the book explains that two previous laws called the first and second laws of thermodynamics were already well established. However, chapter 1 does far more than discuss temperature and thermal equilibrium. It effectively covers all the fundamental tools of thermodynamics: open, closed, and isolated systems; extensive and intensive properties; mechanical equilibrium; diathermic and adiabatic systems; temperature scales (Celsius, Fahrenheit, Kelvin); the difference between classical and statistical thermodynamics; energy distributions; Boltzmann distribution; and the temperature-dependent distribution of molecular speeds. All are covered with stunning clarity and ease, with several historical comments that facilitate their understanding. This chapter also contains brief gems, such as the conceptual basis of how a thermometer works. However, the section advocating expressing temperature in units of inverse joules needs additional discussion, or it may not be appropriate for an introductory thermodynamics text.

Chapter 2, "The First Law," discusses the conservation of energy by emphasizing the practical relationship between work and

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EXOTHERMIC Wood burning is an example of thermodynamics in a natural system.

energy. Here, the reader needs to pay attention to the efficiently worded sentences. For example, pages 25–27 describe adiabatic systems (no heat transfer, or $q = 0$) where work (w) done brings about a change in the system. Because the internal energy (U) of this closed system has changed, the relationship between w and U must be $w = U$. The same systems are then discussed on page 28 but this time with no insulation ($q \neq 0$), and the reader discovers that more work is needed to bring about the same change in internal energy because the noninsulated system loses energy in the form of heat. What is being conceptually developed here is the equation $w + q = U$ without explicit use of equations. My summary of this process is more formal than the book's. This conceptual pathway to introductory thermodynamics is refreshing and, with the many excellent figures used throughout the book, visually powerful. Equations such as $w + q = U$ are easily stated, as many textbooks covering thermodynamics do. However, this book is different in that it gives the reader a sense of what it is like to develop an equation.

Chapter 2 also introduces and explains fundamental concepts such as internal energy, state functions, the thermodynamic and molecular nature of heat and work, reversible processes, enthalpy, heat capacities, and the fluctuation-dissipation theorem (which I would have liked more on) with an insightful discussion on the molecular origin of heat capacity. The last page of chapter 2 mentions Noether's theorem, which states that there is a relationship between a conservation law (for example, the conservation of energy) and symmetry (for example, uniform time). In other words, the first law of thermodynamics (conservation of energy) is a consequence of uniform time. I hope Atkins will write further on this topic.

In chapter 2 the use of C_P (heat capacity at constant pressure) and C_V (heat capacity at constant volume) could have more readily distinguished which heat capacity is being referred to, and a couple of examples of C_P and C_V values would have been informative. Also, I did not see the practical statement in this chapter that enthalpy is q_P, and I'm not sure experimentalists, including biochemists, will appreciate some of the enthalpy comments. For example, enthalpy is described as a property contrived to do the bookkeeping of expansion work. Perhaps enthalpy, when it is introduced, should be described as the heat released or taken up under conditions of constant pressure, which makes it more convenient to study (no high pressures) and is of practical importance when studying natural systems such as wood burning and biochemical reactions.

Chapter 3, "The Second Law," discusses entropy with a foundation that includes a clear and detailed discussion of heat transfer, thermal efficiency of heat engines, and the thermodynamic meaning of a spontaneous process. Approximately midchapter, the reader is ready to understand entropy and is given several numerical examples. It is also made clear that even though a system or its surroundings may individually undergo an entropy decrease, there cannot be a net or total entropy decrease.

ALSO DISCUSSED is the fact that an engine without a cold sink cannot produce work. Or, perhaps more important, as is made clear to the reader, for a heat engine to do work, heat must flow from hot to cold, and in doing so, there is a net entropy increase. Additional examples of increasing entropy (isothermal expansion of a gas and heating a gas), described in classical and statistical terms, lead smoothly to a discussion of absolute entropy and why residual entropy accounts for differences, when they occur, between thermodynamic entropy and statistical entropy. Several descriptive and quantitative examples of residual entropy nicely support the section.

The last two sections of this chapter

further emphasize that for work to be done there must be a net increase in entropy. This principle is illustrated by discussion and calculations using refrigerators and heat pumps as examples, as well as a brief mention of combustion and biological systems. This chapter, like the others, has nuggets of information that stand alone yet flow along as an integral part of the main theme. For example, as part of the foundation leading up to entropy, page 59 mentions the practical convenience of using water's triple point (coexistence of solid, liquid, and water vapor) as a reference point. It is a fundamental property of water and independent of parameters.

Given the global importance of our impact on the environment, chapter 3 may leave some readers wanting more on the relative efficiencies of solar, wind, wood, coal, gas, oil, and nuclear energies, as well as more discussion on why a device—for example, a heat pump—can be more efficient than another, say an electric heater.

Chapter 4, "Free Energy," discusses the availability of work, and the wonderful opening paragraph sets the tone for what I found to be the most enjoyable chapter. The way in which temperature, internal energy, and entropy are combined and discussed to generate new expressions of free energy (Helmholtz and Gibbs) is exquisite. Most books present the first three laws of thermodynamics as one unit and free energies as a separate unit. This treatment, unfortunately, results in students thinking that free-energy equations have little to do with the fundamental laws of thermodynamics. This chapter will be a wonderful asset to students and instructors, especially those in life and physical sciences courses with a biophysical emphasis. This brief chapter is so conceptually strong and clear that it alone may provide enough of a thermodynamic background for instructors who need to focus on free energies as part of a broader (nonthermodynamic) syllabus.

IN ADDITION to deriving free-energy relationships by discussion, the main point of the chapter is that the Helmholtz and Gibbs free-energy equations conveniently allow one to focus on only the system of interest and to determine whether that system is capable of doing work.

Given the importance of Gibbs free-energy changes (ΔG) to the chemical, biochemical, biophysical, and life sciences in general, more ΔG examples would be of interest to a larger audience. Also, the last section discusses why systems change spontaneously when $\Delta G < 0$, change nonspontaneously when $\Delta G > 0$, and will not change when $\Delta G = 0$, when the system has reached equilibrium. For the novice reader it will take some effort to realize that a negative ΔG is what drives a system to do useful work. Given that the title of the book is "Four Laws That Drive the Universe," nonequilibrium, or $\Delta G \neq 0$, is an important part of what this book is about. Students and those with little background in thermodynamics will need assistance in making this link. Having said that, the section in chapter 4 discussing phase changes with respect to Gibbs energy is wonderful, as is the last section on the relationship between systems reaching equilibrium and ΔG.

Chapter 5, "The Third Law," discusses the difficulty of cooling a system to absolute zero, or $T = 0$. The first half of this chapter goes into detail, including examples of why $T = 0$ cannot be reached. Without intending to spoil the excellent story by giving away the punch line, I should point out that $T = 0$ has not been experimentally observed because the entropies of substances converge to a common value as T approaches 0. Read the book for more detail and pay extra attention to figure 20.

The second half of chapter 5 discusses negative absolute temperatures, and although creative and thought-provoking, it left me cold, perhaps even negatively cold (double pun intended). I am not sure whether this section belongs in an introduction to thermodynamics. But perhaps it will spark the imagination of some young student.

In closing, this exceptional book explaining thermodynamics was written by a master author of more than 50 books who makes reading a pleasure. Even though this short book can be read in a day, I encourage all readers to spend much time reading and rereading it as your time, like mine, with this book will be greatly rewarded.

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