



1

Introduction

For good or evil, all physical processes observed in the Universe are subject to the laws and limitations of thermodynamics. Since the fundamental laws of thermodynamics are well understood, it is unnecessary to limit your own understanding of these thermodynamic restrictions.

In this text we lay out the straightforward foundation of thermodynamics, and apply it to systems of interest to engineers and scientists. Aside from considering gases, liquids and their mixtures – traditional problems in engineering thermodynamics – we consider also the thermodynamics of DNA, proteins, polymers, and surfaces. In contrast to the approach adopted by most traditional thermodynamics texts, we begin our exposition with the fundamental postulates of thermodynamics, and rigorously derive all steps. When approximations are necessary, these are made clear. Therefore, the student will not only learn to solve some standard problems, but will also know how to approach a new problem on safe ground before making approximations.

Thermodynamics gives interrelationships between the properties of matter. Often these relationships are non-intuitive. For example, by measuring the volume and heat capacity¹ as functions of temperature and pressure, we can find all other thermodynamic properties of a pure system. Then, we can use relations between different thermodynamic properties to estimate the temperature rise of a fluid when it is expanded in an insulated container, or, we can use such data to predict the boiling point of a liquid. In Chapter 2, we introduce the necessary variables to describe a system in thermodynamic equilibrium. We also discuss several assumptions that are made early on. In that chapter, the natural thermodynamic variables are energy and volume, or, for a surface, energy and area, and for a polymer, energy and length. Subsequently, in Chapter 3, we introduce additional variables that are useful for solving problems when temperature and pressure are controlled. In Chapter 4, we consider phase diagrams for pure substances. In other words, we learn how to predict the temperature or pressure at which a pure liquid will boil, or when a pure vapor will condense.

Rigorously speaking, thermodynamics applies only to systems at equilibrium, that is, systems that are stable at rest, and that are not subject to a temperature gradient or flow. However, for many systems that are out of equilibrium, it is possible to make reasonable approximations and use thermodynamics even during flow, or when the temperature and pressure are changing with time. Such approximations are considered in Chapter 5, so that we may begin to solve problems involving flows and changes.

¹ The heat capacity will be defined in Chapter 2, but roughly means something like the amount of energy necessary to raise the temperature of a substance by one degree.

Chapter 6 introduces statistical mechanics. Statistical mechanics allows us to (1) connect thermodynamics to molecular properties; (2) study small systems, and large systems near critical points, where thermodynamics does not apply; and (3) consider fluctuations in thermodynamic variables. Most of what follows in the book does not require statistical mechanics, although the final section of most remaining chapters will invoke it.

In order to make a strong intuitive connection between molecules and thermodynamics, Chapter 7 discusses many of the important molecular interactions. Chapters 8 and 9 introduce the machinery to solve vapor–liquid equilibrium problems, such as dew-point and bubble-point calculations, in mixtures. We study reactions in Chapter 10. Polymers and surfaces are considered throughout the text, but Chapters 11 and 12 cover these topics in greater detail.

Thermodynamics is an extremely broad field, and no single text can cover all of the topics important to engineering and science. Therefore, it is usually important to revisit thermodynamics repeatedly. In this book we try to give an overview of many important topics in engineering, and a flavor of how these problems are solved. Typically, more advanced models will exist to cover a given topic, but the solution techniques are essentially the same. Let us consider some questions that it is appropriate to ask of the field. These are only representative of the very broad scope of thermodynamics. Many more questions are possible than those presented here.

1.1 RELEVANT QUESTIONS FOR THERMODYNAMICS

1. What is temperature? What does it have to do with “entropy”?
2. Pick up a butane lighter that has a transparent casing. Note that it contains both liquid and gas. These phases are both butane, at the same temperature and pressure. Yet, some of it is liquid and the rest is gas. Why? How can we predict when the substance will be just one phase, and when it will separate into two? (See an example of a region where a model fluid makes two phases – called a phase diagram – in Figure 4.5 on p. 124.)
3. Press the button to open the valve in the lighter, but without striking the flint to start a flame, and measure the temperature of the exiting fluid. It is approximately the temperature of an ice cube. Could we have predicted that?
4. A refrigerator (or air conditioner) makes heat flow from a cold space to a warm one. How does it do that? How much energy must we expect to buy from the utility company to do that?
5. Compress an ideal gas (say air in a balloon) at constant temperature. The balloon pushes back, so it can be used to do work, say lift a book off of the floor. However, it is possible to prove that the compressed and uncompressed gas has the same energy. So, how can it do work? A traveler once said that energy is “the ability to do work.” Was he wrong?
6. Stretch a rubber band and move it quickly to your lips; it feels warm. Let it contract, and it feels cool. Why does a rubber band do that? It is also an experimental fact that a rubber band’s tension at constant length increases with temperature, as can be shown with a hair

- dryer. That is not true for a metal spring. It certainly does not seem obvious that these observations are related – could thermodynamics tell us why?
7. Some pure-component fluids, or mixtures of fluids, refract white light in beautiful, opalescent ways, showing many colors. This thermodynamic point (specific temperature, density, etc.) is called the *critical point*. How do these fluids do that?
 8. Creutzfeldt–Jakob disease was initially transmitted from one surgery patient to another by surgical tools, although the tools had supposedly been sterilized by heat. Many researchers now believe that the disease is not caused by an organism, but by an errant protein called a *prion*. How can a single errant protein out of countless proteins in the brain cause such a degenerative disease?
 9. We have all learned that “like likes like,” e.g., olive oil dissolves in vegetable oil, but not in water. What is the explanation for this?
 10. Contrary to the previous statement, polymers do not easily dissolve in solvents of similar chemical makeup, and do not mix with nearly identical polymers. In fact, Figure 11.3 on p. 369 shows that hydrogenated and deuterated polybutadiene are not miscible, although they are chemically nearly identical! Why?
 11. We learn early on in physics that energy is conserved. Yet, most economic analyses revolve around the cost of energy. If it is always around, why are we so concerned with it?
 12. Mechanical laws would allow the existence of a perpetual-motion device. How do the laws of thermodynamics prohibit its existence?
 13. Air flows into the Ranque–Hilsch vortex tube of Figure 5.3 on p. 159 at room temperature, but exits in a hot stream and a cold stream. Although energy is conserved, it seems like we are getting a free lunch. How is this physically possible? Couldn't we build a perpetual-motion machine from it?
 14. Certain molecules in a gas phase can react only when they are adsorbed on a catalytic surface. If we increase the pressure in the gas phase, how will the amount of adsorption change? How can this experiment be used to estimate surface area in porous materials?
 15. If the pressure “acting” on a substance is increased at constant temperature, will its volume always decrease?
 16. If your equipment tells you that the heat capacity of your new wonder compound is negative, is it time to call the manufacturer for technical support?
 17. We find that the ground water for our drinking supply has been contaminated. How much energy must we expend to remove the contaminant?
 18. What is the best separation we can expect from distillation? What is the minimum amount of energy necessary to achieve this separation?
 19. If we burn one gallon of gasoline, what is the greatest amount of work we can expect to get out?
 20. In primary school, I learned that there were three phases of matter: gas, liquid and solid. This is incorrect. What other kinds of phases are there?
 21. Someone once told me that a fuel cell has a higher theoretical efficiency than an engine. Is that true?
 22. If one uses optical tweezers to pull on a segment of DNA, why does the strand pull back?

23. A helical coil of DNA in a solvent will uncoil and separate into two strands if the temperature is raised. This is *denaturing*. Actually, there is a range of temperatures within which the DNA is partially coiled and attached, and partially separated. What is this temperature range, and how does it change with solvent?

The following chapters should help you answer all of these questions. For the moment, let us review a couple of basic concepts that are important to begin with.

1.2 WORK AND ENERGY

The mathematics background necessary to follow this book is reviewed in Appendix A. We assume that the reader is familiar with the typical units and dimensions of length, mass, and energy. Work and energy play key roles in thermodynamics, so let us review these physical concepts briefly.

Recall that work is defined as force times distance²

$$\text{Work} := \text{Force} \times \text{Distance}. \quad (1.1)$$

If I lift an object of mass m off the floor by a distance l , then the work I have done on the object is the constant force $m\vec{g}$, times the distance l . Hence, $W = m|\vec{g}|l$, where $|\vec{g}|$ is the gravitational constant, and W is work.

We also know that energy is conserved, so the potential energy $E_{\text{potential}}$ of the object must have increased, $\Delta E_{\text{potential}} := E_{\text{potential}}^{\text{final}} - E_{\text{potential}}^{\text{initial}} = m|\vec{g}|l$.

By similar arguments, we can find other forms of energy, such as kinetic energy. For example, if we exert a constant force \vec{F} on a baseball of mass m , neglecting friction with air, the ball will undergo constant acceleration according to Newton's classical mechanics,

$$\vec{F} = m \frac{d\vec{v}}{dt}, \quad (1.2)$$

where \vec{v} is the velocity of the ball, and t is time. During an infinitesimal time dt , the ball is displaced by $\vec{v} dt$. Hence, the infinitesimal change in kinetic energy of the ball E_{kinetic} is the infinitesimal amount of work

$$dE_{\text{kinetic}} = \vec{F} \cdot \vec{v} dt = m \frac{d\vec{v}}{dt} \cdot \vec{v} dt = m\vec{v} \cdot d\vec{v}. \quad (1.3)$$

If we integrate each side from zero initial speed (and zero kinetic energy) to the final speed $|\vec{v}|$, we find

$$E_{\text{kinetic}} = \frac{1}{2} m |\vec{v}|^2. \quad (1.4)$$

We see that, if we know the force and displacement of an object, we can find its change in kinetic energy. You may already be familiar with the result, but notice how it was obtained – from the definition of work and the conservation of energy. Similar ideas will be used in Chapter 2.

² The symbol $:=$ means “is defined as.”

Note that power is the rate at which we do work. Hence, the quantity $\vec{F} \cdot \vec{v}$ is the power exerted on the ball.

EXAMPLE 1.2.1 A piston in a box changes the volume V in the box. How much work does it take to compress the piston by a distance L ?

Solution. Since the pressure P inside the box might be changed by the act of compression, it is best to begin with an infinitesimal compression of the piston. The infinitesimal work (ΔW) is the force times the infinitesimal distance ($\Delta \text{Distance}$, where positive $\Delta \text{Distance}$ means a decrease in volume) the piston moves. However, the force is the pressure times the area A of the piston,

$$\Delta W = PA \Delta \text{Distance} = -P \Delta V, \quad (1.5)$$

where ΔV is the change in volume of the box. Make careful note of the minus sign. If we integrate all of these infinitesimal changes, we obtain

$$W = - \int_{V_0}^{V_f} P dV, \quad (1.6)$$

where V_0 and V_f are the initial and final volumes of the box.

We can test our answer by examining the dimensions. Work has units of energy. The potential energy is given by $m|\vec{g}|l$, so it has units of (mass \times length²/time²), since $|\vec{g}|$ has dimensions of acceleration. The integral on the right side has dimensions of pressure times volume. Pressure is (force/area), or (mass \times length/time²/length²), or (mass/time²/length). Hence, the integral has dimensions (mass \times length²/time²) and our analysis is dimensionally consistent. \square

In the previous example, we found the work done to compress a gas in a box. But what form of energy changed? Is there an additional way to change this form of energy? The answers to these questions are given in Chapter 2.

Exercises

- 1.1.A** By searching other texts, find examples of problems where thermodynamics plays an important role in understanding. Cite your reference(s). (Actually, it would be much more difficult to find a problem where thermodynamics does not apply.)
- 1.1.B** In later chapters (see Section 3.6) we discover that all thermodynamic properties can be reduced to just a few measurable quantities. Two of these quantities are called “the coefficient of thermal expansion,” which is defined by Eqn. (3.60), and “the isothermal compressibility,” Eqn. (3.61). Design simple experiments to measure these two quantities for a substance. Although it has not yet been introduced, assume that temperature is easily measured by a thermocouple, whose probe is a thin wire.

- 1.1.C** Aside from gas, liquid and solid, what other kinds of phases are there? There are actually several kinds of solid phases, so you may choose to name and describe one of these. Please give a reference from which you learned of this phase of matter. The more obscure and bizarre the phase is, the better.
- 1.2.A** If we exert a torque \mathcal{T}_ω on a stirring paddle such that it rotates with angular velocity ω , how much power (work per time) are we exerting on the paddle?
- 1.2.B** What other kinds of energy can you think of? Cite some examples where such forms might be relevant, and specify how they might inter-convert with some other form of energy.
- 1.2.C** How much work does it take to stretch a spring from a length L_0 to L if you know how the tension \mathcal{T} varies with L ? In particular, what if the tension is zero at L_0 , and varies linearly with displacement?
- 1.2.D** A lever arm allows one to exert large forces. In other words, one applies a small force at one end of the arm, and a large force is given by the end nearer the fulcrum. Is work “conserved” in this case? In other words, does the lever arm exert the same work at the short end as it receives at the long end? Show your answer quantitatively.

2

The postulates of thermodynamics

Thermodynamics is the combination of a structure plus an underlying governing equation. Before designing plays in basketball or volleyball, we first need to lay down the rules to the game – or the *structure*. Once the structure is in place, we can design an infinite variety of plays and ways that the game can run. Some of these plays will be more successful than others, but all of them should fit the rules. Of course, in sports you can sometimes get away with breaking the rules, but Mother Nature is not so lax. You might be able to convince your boss to fund construction of a perpetual-motion machine, but the machine will never work.

In this chapter we lay the foundation for the entire structure of thermodynamics. Remarkably, the structure is simple, yet powerfully predictive. The cost for such elegance and power, however, is that we must begin somewhat abstractly. We need to begin with two concepts: energy and entropy. While most of us feel comfortable and are familiar with energy, entropy might be new. However, entropy is no more abstract than energy – perhaps less so – and the approach we take allows us to become as skilled at manipulating the concept of entropy as we are at thinking about energy. Therefore, in order to gain these skills, we consider many examples where an underlying governing equation is specified. For example, we consider the fundamental relations that lead to the ideal-gas law, the van der Waals equation of state, and more sophisticated equations of state that interrelate pressure, volume, and temperature.

Although the postulates are fairly simple, their meaning might be difficult to grasp at first. In fact, most students will need to revisit the postulates many times, perhaps over several years. We recommend that you think about the postulates the way you might vote in Chicago – early and often (or even after you die). Throughout most of the book, however, we will use the postulates only indirectly; in other words, we will derive some important results in this chapter, and then use these results throughout the book. It is therefore important to remember the results derived here and summarized at the end of the chapter.

2.1 THE POSTULATIONAL APPROACH

Where does Newton's law of motion $\vec{F} = (d/dt)(m\vec{v})$ come from? How did Einstein discover $E = mc^2$? These equations were not derived from something – they were guessed in a flash of brilliant insight. We have come to accept them for several reasons. First, because they describe a great many experiments, and were used to predict previously unknown phenomena. Secondly, they are simple and straightforward to comprehend, although perhaps sometimes difficult to implement. Thirdly, and more importantly, we accept these assertions, or *postulates*, of Newton

and Einstein because we have never seen them violated. It is for these reasons that we believe that energy is always conserved.

In this chapter we describe the postulates that make up the theory of thermodynamics. Just like Newton and Einstein, we must be willing to abandon our theory if experiments ever contradict the postulates. The postulates given here are not the most general possible, but are designed to be easily understood, and applicable to most systems of interest to engineers and scientists. In a few sections we briefly consider generalizations. The approach in this chapter is essentially that of Callen [21]. Hence, the same restrictions apply – namely, the system must be isotropic, homogeneous, and large enough for us to neglect surface effects if we are talking about the bulk, or that we may neglect edge effects if we are talking about surfaces, and there must be no external forces.

In what follows we make five fundamental postulates. The first postulate (first law) posits the existence of an additional form of energy called “internal energy,” which, along with kinetic, potential, electromagnetic, and other energies, obeys a conservation principle. The second postulate assumes that every system has equilibrium states that are determined by a few macroscopic variables. The third postulate introduces a quantity called “entropy” on which internal energy depends. The fourth postulate (the second law) and the fifth (Nernst) postulate prescribe properties of entropy. The rest of thermodynamics follows from these straightforward ideas which have far-reaching consequences.

2.2 THE FIRST LAW: ENERGY CONSERVATION

What is the definition of energy? Despite using the word and the concept nearly every day, most engineers and scientists stop short when asked this question. Nonetheless, we still find the concept very useful. Consider a few simple thought experiments about energy. (1) How much energy does this book have if you hold it above your head before letting it drop to the floor? You might answer that it has potential energy $m|\vec{g}|l$, where $|\vec{g}|$ is the gravitational constant, and l is the height of the book above the floor. (2) If the book is flying with speed $|\vec{v}|$ while it is at height l above the floor, is its energy $m|\vec{g}|l + \frac{1}{2}m|\vec{v}|^2$? (3) What if I place an ice cube on the book? We note that the ice melts, and we assume (correctly) that heat was transferred from the book to the ice.

What do these experiments tell us? First, we notice that the energy we ascribed to the book changed depending on the situation. That is because the situations made us think about several different *degrees of freedom* or variables that we used to define the book’s energy. When we held the book over our head, we instinctively thought of position, and then calculated the potential energy of the book. When we pictured the book flying, we then thought of position and velocity, and added the kinetic energy. When the ice melted on the book, we thought about concepts like temperature, heat, or maybe internal energy.¹

Note that, before we can talk about energy accurately, it is important to *specify the system*, and to *specify what variables we are using*. In our first example the system is the book,

¹ Our postulates will allow us to distinguish clearly among internal energy, heat, and temperature.

and the position of the book is the variable. The other important point is the first law, or first postulate.

Postulate I (the first law). Macroscopic systems possess an *internal energy* U that is subject to a conservation principle and is extensive.

An **extensive variable** is one that is linearly dependent on system size, and, conversely, an **intensive variable** is one that is independent of system size.² From a statistical-mechanical, or atomistic, point of view, we do not need this postulate, since we know that atoms store energy. We also know that all forms of energy obey a conservation principle. However, we choose to make this starting point clear in our framework by expressing it as a postulate.

This internal energy is somehow transferred from the book to the ice in our thought experiment. Internal energy has properties just like other forms of energy in that it can be exchanged between different systems, converted to and from other forms of energy, or used to extract work. By “conservation principle,” we mean that, if we add up all of the forms of energy in an isolated system, the sum total of those energies is constant, although one form might have increased while another decreased, say some kinetic energy became internal energy. It is worthwhile to quote extensively from Callen [21, p. 11].

The development of the principle of conservation of energy has been one of the most significant achievements in the evolution of physics. The present form of the principle was not discovered in one magnificent stroke of insight but was slowly and laboriously developed over two and a half centuries. The first recognition of a conservation principle repeatedly failed, but in each case it was found possible to revive it by the addition of a new mathematical term – a “new kind of energy.” Thus consideration of charged systems necessitated the addition of the Coulomb *interaction energy* ($Q_1 Q_2 / r$) and eventually of the energy of the electromagnetic field. In 1905 Einstein extended the principle to the relativistic region, adding such terms as the relativistic rest-mass energy. In the 1930s Enrico Fermi postulated the existence of a new particle called the *neutrino* solely for the purpose of retaining the energy conservation principle in nuclear reactions ...

Where is internal energy stored? Although it is not necessary to introduce atoms and molecules into the classical theory of thermodynamics, we might be bothered by this question. The answer might be in the vibrations of the atoms (kinetic energy) and the spring-like forces between atoms (potential energy), or in the energies in the subatomic particles. So why do we call it “internal energy” instead of kinetic plus potential energy, for example? Recall our thought experiments above, where we found that the variables used to describe our system are essential to define energy. If we knew the precise positions and velocities of all the atoms in the book, we could, in principle, calculate all $\sim 10^{23}$ kinetic and potential energies of the book, and we would not need to think about internal energy. However, that approach is not just impractical, but, it turns out, not even necessary. We can carry out meaningful calculations of internal energy by using just a few variables that are introduced in Postulate III.

² A precise mathematical definition will be given shortly, in Postulate III.

2.3 DEFINITION OF HEAT

If we do work on a system, then its energy must be increased. However, we often observe that, after we have done work on a system, its internal energy returns to its original state, although the system has done no work on its environment. For example, push the book across the table, then wait a few minutes. Although you performed work on the book, it has the same initial and final potential, kinetic, and internal energies. The reason why the internal energy of a system can change without work is that energy can also be transferred in the form of **heat**.

Since the internal energy of a system may be changed either by work or by heat transfer, and we have postulated that energy is conserved, we can define the heat transfer to, or from, a system as

$$\delta Q := dU - \delta W. \quad (2.1)$$

It is worthwhile to commit this equation to memory, or, better yet: $dU = \delta Q + \delta W$. In this notation, work is positive when done on the system, and heat is positive when transferred to the system. We write the differentials for heat and work using δ instead of d because they are **imperfect differentials**.

Perfect differentials are not dependent upon the path taken from the “initial” to the “final” states – they depend only on the initial and final values of the independent variables.

Imperfect differentials δ have two important properties that distinguish them from perfect differentials d . First, imperfect differentials do depend upon the path. For example, if we set this book on the floor and push it a short distance $d\vec{x}$ away using force \vec{F} and then the same distance $-d\vec{x}$ back to its original position using force $-\vec{F}$, then the sum (perfect) differential for its position is zero – exactly the same as if we had left the book sitting there: $d\vec{x}_{\text{tot}} = d\vec{x}_1 + d\vec{x}_2 = d\vec{x} + (-d\vec{x}) = 0$. However, the work done on the book was positive in both moves, so the sum (imperfect) differential of the work is positive, even though the book ended up where it began: $\delta W_{\text{tot}} = \vec{F}_1 \cdot d\vec{x}_1 + \vec{F}_2 \cdot d\vec{x}_2 = \vec{F} \cdot d\vec{x} + (-\vec{F}) \cdot (-d\vec{x}) = 2\vec{F} \cdot d\vec{x}$.

Secondly, if we integrate a perfect differential, we obtain a difference between final and initial states. For example, if we integrate $d\vec{x}$ from \vec{x}_0 to \vec{x}_1 , we obtain the difference $\Delta\vec{x} = \vec{x}_1 - \vec{x}_0$. When we integrate δW , for example, we simply obtain the total work in the path W , not a difference.

In order to control, and therefore measure, the internal energy of a system, we need to control both the heat flow and the work done on the system. This manipulation is accomplished primarily through control of the *walls* of a system. The following definitions establish ideal conditions that we may approach approximately in real situations.

An **adiabatic wall** is one that does not allow heat to flow through it. In real situations this is approximated by heavily insulated walls. On the other hand, a **diathermal wall** is one that permits heat to flow through it freely. In addition, we often assume that the wall has a sufficiently