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