

# 1

## What is thermodynamics?

### 1.1 Introduction

Thermodynamics is the branch of science that deals with relative energy levels and transfers of energy between systems and between different states of matter. Because these subjects arise in virtually every other branch of science, thermodynamics is one of the cornerstones of scientific training. Various scientific specialties place varying degrees of emphasis on the subject areas covered by thermodynamics – a text on thermodynamics for physicists can look quite different from one for chemists, or one for mechanical engineers. For chemists, biologists, geologists, and environmental scientists of various types, the thermodynamics of chemical reactions is of course a central concern, and that is the emphasis to be found in this book. Let us start by considering a few simple reactions and the questions that arise in doing this.

### 1.2 What is the problem?

#### 1.2.1 Some simple chemical reactions

A chemical reaction involves the rearrangement of atoms from one structure or configuration to another, normally accompanied by an energy change. Let's consider some simple examples.

- Take an ice cube from the freezer of your refrigerator and place it in a cup on the counter. After a few minutes, the ice begins to melt, and it soon is completely changed to water. When the water has warmed up to room temperature, no further change can be observed, even if you watch for hours. If you put the water back in the freezer, it changes back to ice within a few minutes, and again there is no further change. Evidently, this substance ( $\text{H}_2\text{O}$ ) has at least two different forms, and it will change spontaneously from one to the other depending on its surroundings.
- Take an egg from the refrigerator and fry it on the stove, then cool to room temperature. Again, all change seems now to have stopped – the reaction is complete. However, putting the fried egg back in the refrigerator will not change it back into a raw egg. This change seems not to be reversible. What is different in this case?

## What is thermodynamics?

- Put a teaspoonful of salt into a cup of water. The salt, which is made up of a great many tiny fragments of the mineral halite (NaCl), quickly disappears into the water. It is still there, of course, in some dissolved form, because the water now tastes salty, but why did it dissolve? And is there any way to reverse this reaction?

Eventually, of course, we run out of experiments that can be performed in the kitchen. Consider two more reactions:

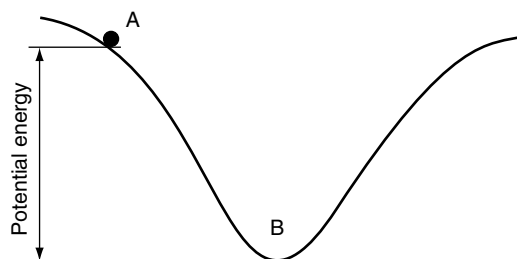
- On a museum shelf, you see a beautiful clear diamond and a piece of black graphite side by side. You know that these two specimens have exactly the same chemical composition (pure carbon, C), and that experiments at very high pressures and temperatures have succeeded in changing graphite into diamond. But how is it that these two different forms of carbon can exist side by side for years, while the two different forms of H<sub>2</sub>O cannot?
- When a stick of dynamite explodes, a spectacular chemical reaction takes place. The solid material of the dynamite changes very rapidly into a mixture of gases, plus some leftover solids, and the sudden expansion of the gases gives the dynamite its destructive power. The reaction would seem to be nonreversible, but the fact that energy is obviously released may furnish a clue to understanding our other examples, where energy changes were not obvious.

These reactions illustrate many of the problems addressed by chemical thermodynamics. You may have used ice in your drinks for years without realizing that there was a problem, but it is actually a profound and very difficult one. It can be stated this way: What controls the changes (reactions) that we observe taking place in substances? Why do they occur? And why can some reactions go in the forward and backward directions (i.e., ice→water or water→ice) while others can only go in one direction (i.e., raw egg→fried egg)? Scientists puzzled over these questions during most of the nineteenth century before the answers became clear. Having the answers is important; they furnish the ability to control the power of chemical reactions for human uses, and thus form one of the cornerstones of modern science.

### 1.3 A mechanical analogy

Wondering why things happen the way they do goes back much further than the nineteenth century and includes many things other than chemical reactions. Some of these things are much simpler than chemical reactions, and we might look to these for analogies, or hints, as to how to explain what is happening.

A simple mechanical analogy would be a ball rolling in a valley, as in Figure 1.1. Balls have always been observed to roll down hills. In physical terms, this is “explained” by saying that mechanical systems have a tendency to change so as to reduce their *potential energy* to a minimum. In the case of the ball on the surface, the potential energy (for a ball of given mass) is determined by the height of the ball above the lowest valley, or some other

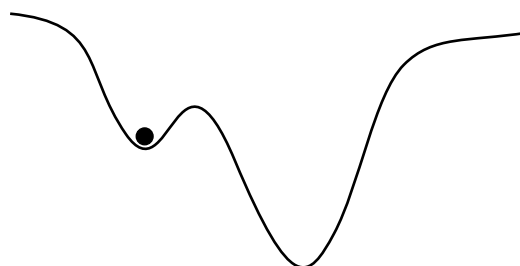


**Figure 1.1** A mechanical analogy for a chemical system – a ball on a slope. The ball will spontaneously roll into the valley.

reference plane. It follows that the ball will spontaneously roll downhill, losing potential energy as it goes, to the lowest point it can reach. Thus it will always come to rest (equilibrium) at the bottom of a valley. However, if there is more than one valley, it may get stuck in a valley that is not the lowest available, as shown in Figure 1.2. This is discussed more fully in Chapter 2.

It was discovered quite early that most chemical reactions are accompanied by an energy transfer either to or from the reacting substances. In other words, chemical reactions usually either liberate heat or absorb heat. This is most easily seen in the case of the exploding dynamite, or when you strike a match, but in fact the freezing water is also a heat-liberating reaction. It was quite natural, then, by analogy with mechanical systems, to think that various substances contained various quantities of some kind of energy, and that reactions would occur if substances could rearrange themselves (react) so as to *lower* their energy content. According to this view, ice would have less of this energy (per gram, or per mole) than has water in the freezer, so water changes spontaneously to ice, and the salt in dissolved form would have less of this energy than solid salt, so salt dissolves in water. In the case of the diamond and graphite, perhaps the story is basically the same, but carbon is somehow “stuck” in the diamond structure.

Of course, chemical systems are not mechanical systems, and analogies can be misleading. You would be making a possibly fatal mistake if you believed that the energy of a stick of dynamite could be measured by how far above the ground it was. Nevertheless, the analogy is useful. Perhaps chemical systems will react such as to lower (in fact, minimize) their *chemical* energy, although sometimes, like diamond, they may get stuck in a valley higher than another



**Figure 1.2** The ball has rolled into a valley, but there is a deeper valley.

### Mechanics versus thermodynamics

Generally speaking, there are two main problems in learning thermodynamics. One, of course, is to learn the details of the specialized procedures in one's discipline, which in our case involves chemical reactions, activities, fugacities, equilibrium constants, and so on. The other, either more or less important depending on your point of view, is to understand thermodynamics as a whole – what is it, what do the variables mean, and how does it relate to other branches of science? In this book, the first four chapters deal mostly with this latter problem, and the rest of the book with the details.

At several points in these first few chapters we will make reference to classical mechanics, the science which deals with the motions of bodies and the forces causing those motions. This is an attempt to put thermodynamics into a broader perspective; to make analogies with possibly more familiar situations. Balls rolling in valleys and swinging pendulums are actually a special case in mechanics, known as dissipative systems. That is, dynamic systems in which energy is gradually dissipated (generally due to friction), and in which the moving body comes to rest in an equilibrium position.

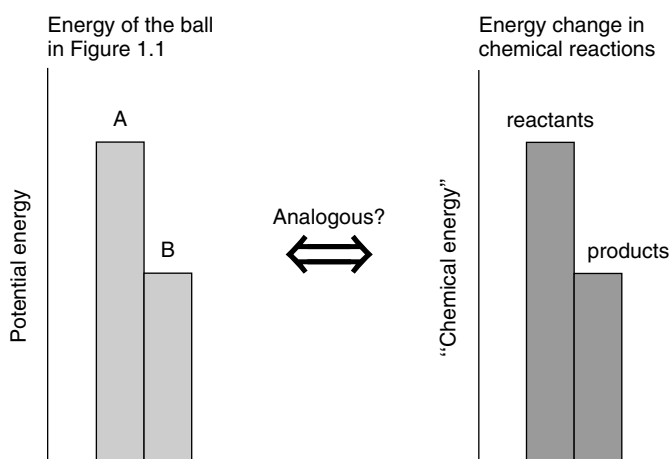
In mechanics, the motion of the body and its trajectory in a three-dimensional valley might be considered, and the dissipated kinetic energy is simply lost from the system. The energy “loss” is dissipated as heat, but mechanics knows nothing about this. The potential energy change is independent of all this, as in Figure 1.1. Thermodynamics, on the other hand, knows nothing about kinetic energy and trajectories, but is concerned with energy changes between two different equilibrium states. In Figure 1.2 the two states are shown as valleys at different elevations, and the energy is potential energy; in thermodynamics the two states might be calcite and aragonite, and the energy is in a different form.

nearby valley. We will see that this is in fact the case. The analogy *is* useful. The problem lies in discovering just what kind of energy is being minimized. What is this *chemical energy*?

### 1.3.1 Chemical energy

We mentioned above that an early idea was that it is the *heat* energy content of systems that is minimized in chemical systems, that is, reactions will occur if heat is liberated. This is another way of saying that the heat content of the *products* is less than the heat content of the *reactants* of a reaction, so that the reaction liberates heat (Figure 1.3)

This view of things was common in the nineteenth century, and a great deal of effort was expended in measuring the flow of heat in chemical reactions.



**Figure 1.3** Mechanical processes always act so as to lower the potential energy content of the mechanical system. Perhaps, by analogy, chemical systems have some sort of “chemical energy” that is lowered during chemical reactions.

However, we don’t even have to leave our kitchen to realize that this cannot be entirely correct. The melting of ice is obviously a reaction in which heat is *absorbed*, not liberated, which is why it is useful in cooling drinks. Therefore, despite the appealing simplicity of the “heat content” argument for explaining why chemical reactions occur, it cannot be the whole story. Nevertheless, the idea that some kind of “chemical energy” is liberated in reactions, or that “chemical energy” is minimized in systems at rest (equilibrium) is a powerful one. Perhaps heat is not the only energy involved. What other factors might there be? Not too many, we hope!

### 1.3.2 Plus something else?

Another very important clue we must pay attention to is the fact that some chemical reactions are able to take place with no energy change at all. For example, when gases mix together at low pressures, virtually no heat energy is liberated *or* absorbed. The situation is similar for a drop of ink spreading in a glass of water. These are spontaneous processes<sup>1</sup> characterized by a *mixing* process, rather than by a reorganization of atomic structures like graphite→diamond, or raw egg→fried egg. Our “chemical energy” term will have to take account of observations like these.

At this point, we might become discouraged, and conclude that our idea that some sort of chemical energy is being reduced in all reactions must be wrong – there seem to be too many exceptions. It certainly was a puzzle for a long time. But we have the benefit of hindsight, and because we now know that this concept of decreasing chemical energy of some kind is in fact the correct answer, we will continue to pursue this line of thought.

<sup>1</sup> We are using the terms *reaction* and *process* more or less synonymously here. Later on (§2.6) we will make a distinction.

### 1.4 Limitations of the thermodynamic model

This book outlines the essential elements of a first understanding of chemical thermodynamics, especially as applied to natural systems. However, it is useful at the start to have some idea of the scope of our objective – just how useful is this subject, and what are its limitations? It is at the same time very powerful and very limited. With the concepts described here, you can predict the equilibrium state for most chemical systems, and therefore the direction and amount of reaction that should occur, including the composition of all phases when reaction has stopped. The operative word here is “should.” Our model consists of comparing equilibrium states, one with another, and determining which is more stable under the circumstances. We will not consider how fast the reaction will proceed, or how to tell if it will proceed at all. Many reactions that “should” occur do not occur, for various reasons. We will also say very little about what “actually” happens during these reactions – the specific interactions of ions and molecules that result in the new arrangements or structures that are more stable. In other words, our model will say virtually nothing about *why* one arrangement is more stable than another or has less “chemical energy,” just that it does, and how to determine that it does.

These are serious limitations. Obviously, we will often need to know not only if a reaction *should* occur but *if* it occurs, and at what rate. A great deal of effort has also been directed toward understanding the structures of crystals and solutions, and of what happens during reactions, shedding much light on why things happen the way they do. However, these fields of study are not completely independent. The subject of this book is really a prerequisite for any more advanced understanding of chemical reactions, which is why every chemist, environmental scientist, biochemist, geochemist, soil scientist, and the like, must be familiar with it.

But in a sense, the limitations of our subject are also a source of its strength. The concepts and procedures described here are so firmly established partly because they are independent of our understanding of *why* they work. The laws of thermodynamics are distillations from our experience, not explanations, and that goes for all the deductions from these laws, such as are described in this book. As a scientist dealing with problems in the real world, you need to know the subject described here. You need to know other things as well, but this subject is so fundamental that virtually every scientist has it in some form in his tool kit.

### 1.5 Summary

The fundamental problem addressed here is why things (specifically, chemical reactions) happen the way they do. Why does ice melt and water freeze? Why does graphite turn into diamond, or vice versa? Taking a cue from the study of simple mechanical systems, such as a ball rolling in a valley, we propose

that these reactions happen if some kind of energy is being reduced, much as the ball rolls in order to reduce its potential energy. However, we quickly find that this cannot be the whole story – some reactions occur with *no* decrease in energy. We also note that whatever kind of energy is being reduced (we call it “chemical energy”), it is not simply heat energy.

For a given ball and valley (Figure 1.1), we need to know only one parameter to determine the potential energy of the ball (its height above the base level, or bottom of the valley). In our “chemical energy” analogy, we know that there must be *at least* one other parameter, to take care of those reactions that have no energy change. Determining the parameters of our “chemical energy” analogy is at the heart of chemical thermodynamics.

## 2

# Defining our terms

### 2.1 Something is missing

We mentioned in Chapter 1 that an early idea for understanding chemical reactions held that spontaneous reactions would always be accompanied by the loss of energy, because the reactants were at a higher energy level than the products, and they wanted to go “downhill.” This energy was usually thought to be in the form of heat, but this idea received a setback when it was found that some spontaneous reactions in fact absorb heat. Also, there are some reactions, such as the mixing of gases, where the energy change is virtually zero yet the processes proceed very strongly and are highly nonreversible. Obviously, something is missing. If the ball-in-valley analogy is right, that is, if reactions do proceed in the direction of decreasing chemical energy of some kind, something more than just heat is involved.

To learn more about chemical reactions, we have to become a bit more precise in our terminology and introduce some new concepts. In this chapter, we will define certain kinds of *systems*, because we need to be careful about what kinds of matter and energy transfers we are talking about; *equilibrium states*, the beginning and ending states for processes; *state variables*, the properties of systems that change during reactions; *processes*, the reactions themselves; and *phases*, the different types of matter within the systems. All these terms refer in fact to our models of natural systems, but they are also used to refer to things in real life. To be quite clear about thermodynamics, it is a good idea to keep the distinction in mind.

### 2.2 Systems

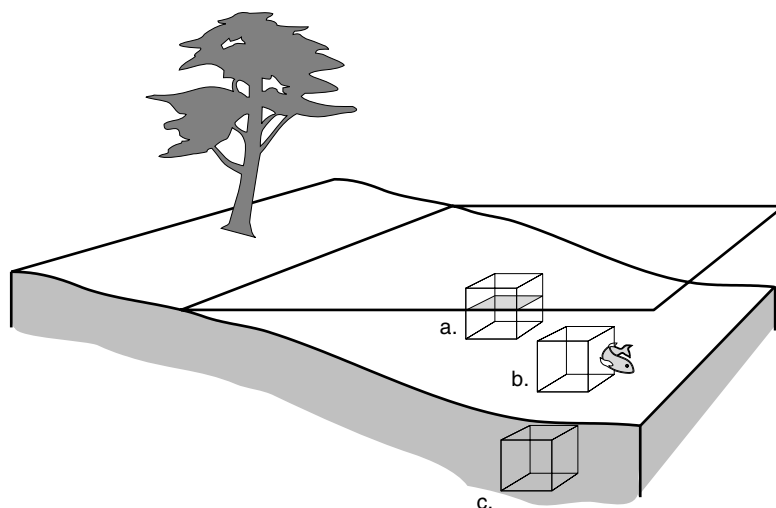
#### 2.2.1 Real life systems

In real life, a *system* is any part of the universe that we wish to consider. If we are conducting an experiment in a beaker, then the contents of the beaker is our system. For an astronomer calculating the properties of the planet Pluto, the solar system might be the system. In considering geochemical, biological, or environmental problems here on Earth, the choice of system is

usually fairly obvious, and depends on the kind of problem in which you are interested.

Figure 2.1 shows a seashore environment with three possible choices of natural system. At (a), we might be interested in the exchange of gases between the sea and the atmosphere (e.g., if the sea warms by one degree, how much  $\text{CO}_2$  will be released to the atmosphere?). At (b), we might be interested in the dissolved material in the sea itself (e.g., the reactions between dissolved  $\text{CO}_2$  and carbonate and bicarbonate ions). And at (c), we might be interested in reactions between the sediment and the water between the sediment particles (e.g., dissolution or precipitation of minerals in the sediment). The chosen systems are shown as boxes, but in most cases we are not concerned with the dimensions or shape of the box; we normally define the system in terms of the masses or moles of components in the system, as well as the nature of its contacts with whatever is outside the system (see §2.2.2).

These are examples of *inorganic* systems. Thermodynamics can also be applied to organic systems, including living organisms. A single bacterium could be our system, or a dish full of bacteria, or a single organelle within a bacterium. The choice depends on your particular interests and is obviously very wide. However, they are all similar in one respect. Because natural systems exist in the real world, whatever system you choose is bounded by (in contact with) other parts of the world and may exchange energy and matter (liquids, solids, gases) with these other parts of the world. Systems of this type are said to be “open.” All living organisms are thus open systems because they take in nutrients, and get rid of waste products. All three systems in Figure 2.1 are obviously open, because water can flow in and out of (a) and (b), and even in (c), compaction of the sediments squeezes water out, and diffusion allows solutes to move in and out.



**Figure 2.1** A seashore environment. The locations of three natural systems are shown.

### Models

A model in the sense used here is an abstract object characterized or described by systems of equations, which attempt to represent the behavior of selected parts of the universe.

Thermodynamics deals with its subject matter (energy levels, energy changes) in an abstract way. The states and processes it describes are idealized; it does not describe or deal with any objects or processes in the real world, except to the extent that the variables in its equations are properties (e.g., volumes, energies) of real substances. Some processes in the real world are very similar to these idealized processes, and some are not. Where they are similar, thermodynamics is directly useful. Where they are not, we invent correction factors (e.g., “activity coefficients”) to account for the differences.

The reason for mentioning this somewhat philosophical point is that many aspects of thermodynamics are abstract, or physically unrealistic. It helps to remember that we are using mathematics to simulate real systems.

Models are certainly used in other senses in the Earth sciences, such as the facies models of the sedimentologists.

### 2.2.2 Thermodynamic systems

Our goal is to understand the energy changes in natural systems. We will do this by mathematically simulating much simpler “models” of these systems, having variables that represent what we think are the essential elements of the natural systems. These models will not be material, but mathematical and conceptual. If we do it right, then the behavior of the model system will be very similar to (or will mimic) that of the real system. We will call this “understanding” the real system at the thermodynamic level.

Although most natural systems are open and are quite complex, our models of these systems can be much simpler and still be valuable. The kinds of thermodynamic or model systems that have been found to be useful in analyzing and understanding natural (real life) systems are as follows, and are illustrated in Figure 2.2. These thermodynamic systems are essentially defined by the types of walls they have. This is because we must be able to control (conceptually) the flow of matter and energy into and out of these systems.

- *Isolated systems* have walls or boundaries that are rigid (thus not permitting transfer of mechanical energy), perfectly insulating (thus preventing the flow of heat), and impermeable to matter. They therefore have a constant energy and mass content, since none can pass in or out. Perfectly insulating walls and the systems they enclose are called *adiabatic*. Isolated systems, of course, do not occur in nature, because there are no such impermeable and rigid boundaries. Nevertheless, this type of system has