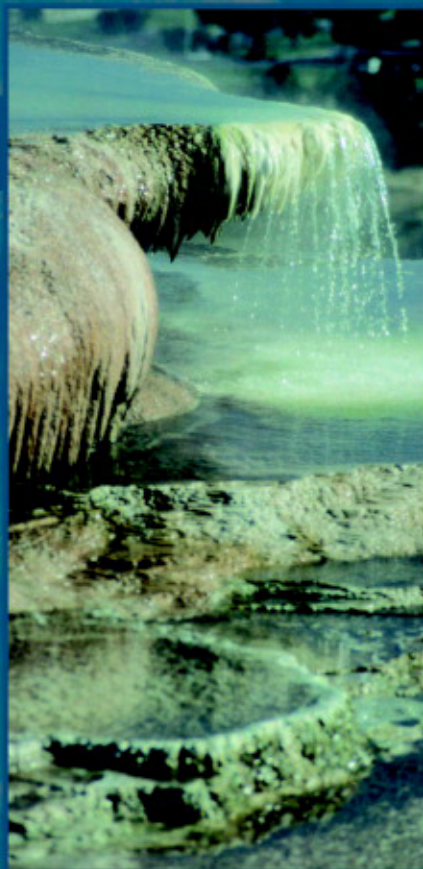


# Thermodynamics of Natural Systems



Greg Anderson

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# **Thermodynamics of Natural Systems**

## **Second Edition**

Thermodynamics deals with energy levels and the transfer of energy between states of matter, and is therefore fundamental to many branches of science. This new edition provides a relatively advanced treatment of the subject, specifically tailored to the interests of the Earth sciences.

The first four chapters explain all the necessary concepts of thermodynamics, using a simple graphical approach. Throughout the rest of the book the author emphasizes the use of thermodynamics to construct mathematical simulations of real systems. This helps to make the many abstract concepts accessible. Many computer programs are mentioned and used throughout the text, especially SUPCRT92, a widely used source of thermodynamic data. Links to useful information sites and computer programs as well as problem sets with detailed answers for instructors are available through <http://www.cambridge.org/0521847729>.

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GREG ANDERSON has been Professor of Geochemistry at the University of Toronto for 35 years and is the author of three textbooks on thermodynamics for Earth scientists: *Environmental Applications of Geochemical Modeling* (2002), *Thermodynamics in Geochemistry* (1993) and *Thermodynamics of Natural Systems* (1995). In 2000 he was awarded the Past President's Medal by the Mineralogical Association of Canada for contributions to geochemistry.

# Thermodynamics of Natural Systems

Second Edition

**G. M. Anderson**

University of Toronto



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# 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:

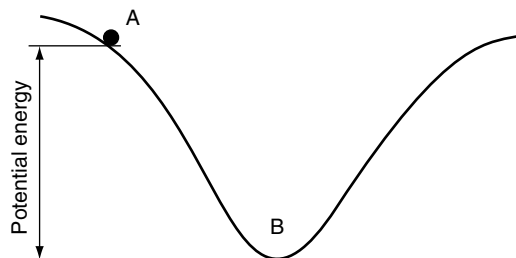
- On a museum shelf, you see a beautiful clear diamond and a piece of black graphite side by side. You know that these two specimens have exactly the same chemical composition (pure carbon, C), and that experiments at very high pressures and temperatures have succeeded in changing graphite into diamond. 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

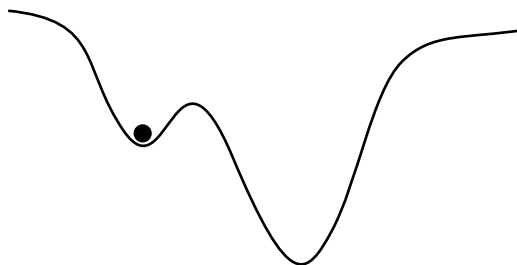


**Figure 1.1** A mechanical analogy for a chemical system – a ball on a slope. The ball will spontaneously roll into the valley.

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.

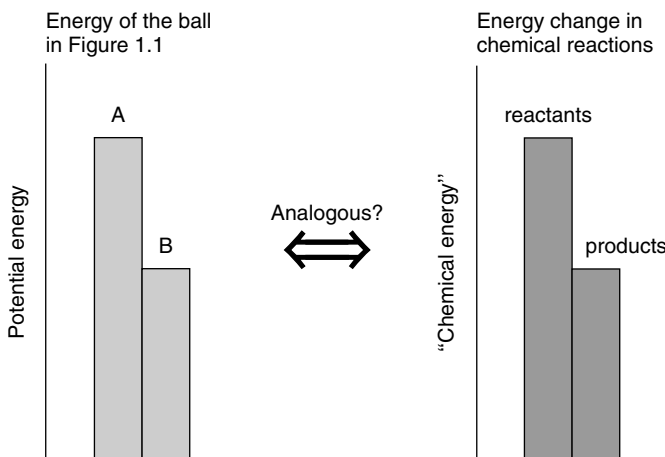
In mechanics, the motion of the body and its trajectory in a three-dimensional valley might be considered, and the dissipated kinetic energy is simply lost from the system. The energy “loss” is dissipated as heat, but mechanics knows nothing about this. The potential energy change is independent of all 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

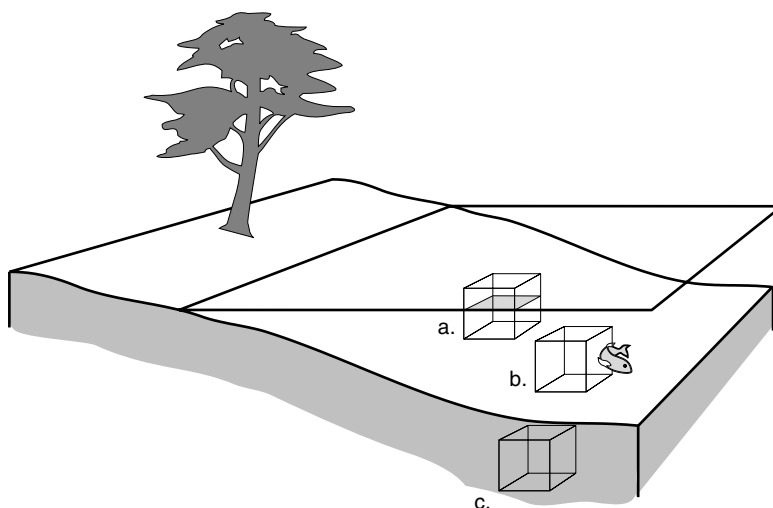
#### 2.2.1 Real life systems

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.

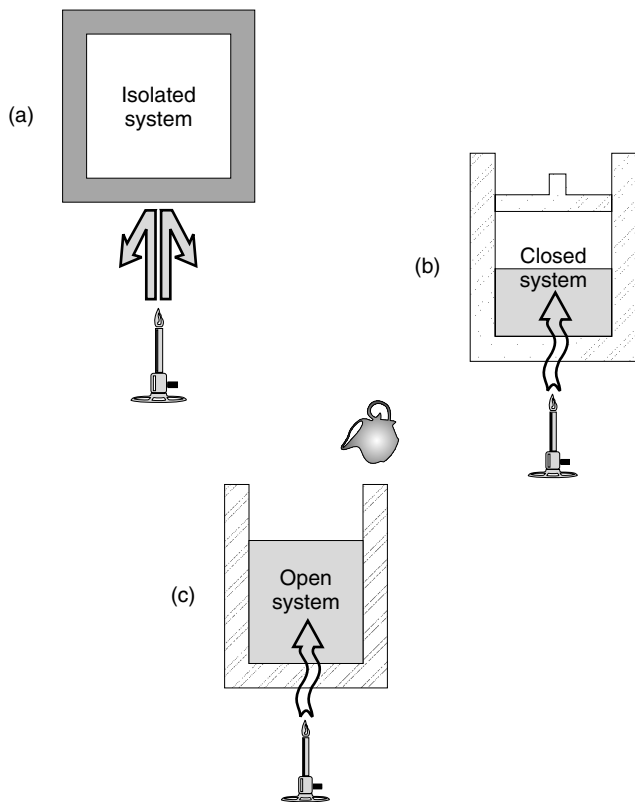
Models are certainly used in other senses in the Earth sciences, such as the facies models of the sedimentologists.

## 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



**Figure 2.2** (a) Isolated system. Nothing can enter or leave the system (no energy, no matter). Whatever is inside the walls (which could be anything) will have a constant energy content and a constant composition. (b) Closed system. The closure is a piston to indicate that the pressure on the system is under our control. Energy can enter and leave the system, but matter cannot. The system here is shown as part liquid, part gas or vapor, but it could be anything. Both the liquid and the gas could also be considered as open systems, inside the closed system. Each may change composition, although the two together will have a constant composition. (c) Open system. Both matter and energy may enter and leave the system. The system may have a changing energy content and/or a changing composition. The pitcher shows one way of adding matter to the system.

great significance because reactions that occur (or could occur) in isolated systems are ones that *cannot* liberate or absorb heat or any other kind of energy. Therefore, if we can figure out what causes *these* reactions to go, we may have an important clue to the overall puzzle.

- *Closed systems* have walls that allow transfer of energy into or out of the system but are impervious to matter. They therefore have a fixed mass and composition but variable energy levels.
- *Open systems* have walls that allow transfer of both energy and matter to and from the system. The system may be open to only one chemical species or to several.

As mentioned above, most natural systems are open. However, it is possible and convenient to model them as closed systems; that is, to consider a fixed composition, and simply ignore any possible changes in total composition. If what happens because of changes in composition is important, it can often be handled by considering two or more closed systems of different compositions. Thus we will be dealing mostly with closed systems in our efforts to understand chemical reactions. Basically this means that we will be concerned mostly with individual chemical reactions, rather than with whole complex systems. In other words, even though a bacterium is an open system, it can be treated (modeled) as a closed system while considering many individual reactions within it. The reactants may need to be ingested and the products eliminated by the organism, but the reaction itself can be modeled independently of these processes. This greatly simplifies the task of understanding the biochemical reactions. The same is true of most geochemical and environmental systems.

The most common kind of open system in chemical thermodynamics is represented in Figure 2.2b, that is, two open subsystems within an overall closed system. There can be any number of these “open subsystems,” and finding out how many there are and what their compositions are, given some physical conditions, is a common problem in the application of thermodynamics. We have a brief look at other kinds of open systems in Chapter 4.

It is one of the paradoxes of thermodynamics that isolated systems, that have no counterpart in the real world, are possibly the most important of all in terms of our understanding of chemical reactions. You will have to wait until Chapter 4 to see why.

### 2.3 Equilibrium

In studying chemical reactions, we obviously need to know when they start and when they have ended. To do this, we define the state of *equilibrium*, when no reactions at all are proceeding. Here we encounter a distinct difference between real and thermodynamic systems, because the state of equilibrium is defined differently in the two cases.

In thermodynamic systems, that is, in our models, equilibrium is defined in terms of *chemical potentials*, which we will get to in a later chapter. This state, as you might imagine, is one of *perfect* equilibrium, perfect rest, with absolutely no gradients or inhomogeneities of any kind. Real systems often approach this state more or less closely, but probably never attain it. When real systems do approach equilibrium, thermodynamics can be applied to them. Obviously, we need to have some way of telling whether real systems are “at equilibrium,” or have closely approached equilibrium.

Equilibrium states in real systems have two attributes:

1. A real system at equilibrium has none of its properties changing with time, no matter how long it is observed.
2. A real system at equilibrium will return to that state after being disturbed, that is, after having one or more of its parameters slightly changed, then changed back to the original values.

This definition is framed so as to be “operational,” that is, you can apply these criteria to real systems to determine whether they are at equilibrium. And in fact, many real systems do satisfy the definition. For example, a crystal of diamond sitting on a museum shelf obviously has exactly the same properties this year as last year (part 1 of the definition), and if we warm it slightly and then put it back on the shelf, it will gradually resume exactly the same temperature, dimensions, and so on that it had before we warmed it (part 2 of the definition). The same remarks hold for a crystal of graphite on the same shelf, so that the definition can apparently be satisfied for various forms of carbon. Many other natural systems just as obviously are not at equilibrium. Any system having temperature, pressure, or compositional gradients will tend to change so as to eliminate these gradients, and is not at equilibrium until that happens. A cup of hot coffee, for example, is not at equilibrium with the air around it until it cools down.

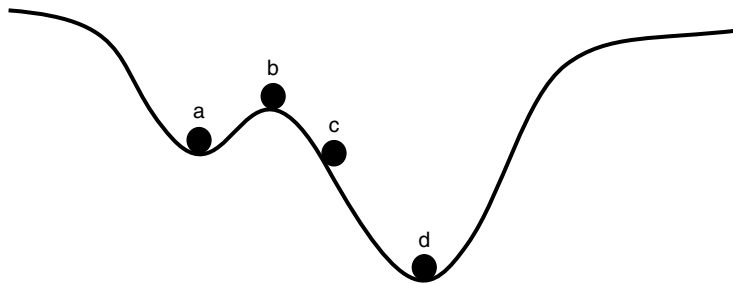
So if diamond and graphite are both at equilibrium, do we have two kinds of equilibrium? In our ball-in-valley analogy, the ball in any valley would fit our definition. What distinction do we make between the lowest valley and the others?

### 2.3.1 Stable and metastable equilibrium

In this section we use the simple mechanical analogy in §1.3 to distinguish between *stable* and *metastable* equilibrium. This explanation is satisfactory for an intuitive understanding, but we return to this subject for a better theoretical understanding in §4.9.1.

Stable and metastable are the terms used to describe the system in its lowest equilibrium energy state and any other equilibrium energy state, respectively. In Figure 2.3, we see a ball on a surface having two valleys, one higher than the other. At (a), the ball is in an equilibrium position, that fulfills both parts of our definition – it will stay there forever, and will return there if disturbed, as long as the disturbance is not too great. However, it has not achieved the lowest possible potential energy state, and therefore (a) is a *metastable equilibrium* position. If the ball is pushed past position (b), it will roll down to the lowest available energy state at (d), a *stable equilibrium* state. During the fall, for example, at position (c), the ball (system) is said to be *unstable*. In position (b), it is possible to imagine the ball balanced and unmoving, so that the first part

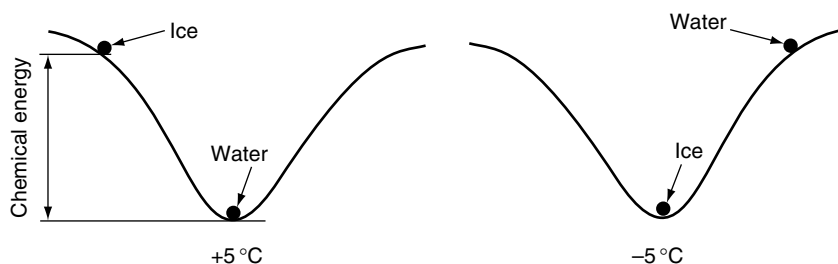
**Figure 2.3** Four positions of a ball on a surface, to illustrate the concept of equilibrium. Position a – metastable equilibrium. Position b – unstable. Position c – unstable. Position d – stable equilibrium.



of the definition would be fulfilled, and this is sometimes referred to as a third type of equilibrium, admittedly a trivial case, called *unstable equilibrium*. However, it does not survive the second part of the definition, so we are left with only two types of equilibrium, stable and metastable.

Of course, we find that the stable form of substances is different under different conditions. For example, the stable form of  $\text{H}_2\text{O}$  is water at  $+5^\circ\text{C}$ , and ice at  $-5^\circ\text{C}$  (Figure 2.4). The freezing and melting of  $\text{H}_2\text{O}$  is normally fairly rapid, so we don't often see metastable ice above its melting temperature, or metastable water below its freezing temperature. But many such phase changes are not so rapid, in fact they may not happen at all, even though energy would be released if they did. These reactions, which get "stuck" in a high energy state are usually not melting/freezing reactions, but solid state reactions – that is, a reaction in which a mineral having one crystallographic structure changes to a mineral having the same composition but with a different structure.

A good example of this is the diamond/graphite reaction. We know now that the stable form of pure carbon at Earth surface conditions is the mineral graphite, but that at high temperatures and pressures, such as found deep in the Earth's mantle, graphite will spontaneously react to form diamond. However,



**Figure 2.4** The mechanical analogy for  $\text{H}_2\text{O}$  at  $-5^\circ\text{C}$  and  $+5^\circ\text{C}$  and atmospheric pressure. At  $-5^\circ\text{C}$ , water is unstable and releases energy until it becomes ice at  $-5^\circ\text{C}$ . At  $+5^\circ\text{C}$ , ice is unstable and releases energy until it becomes water at  $+5^\circ\text{C}$ . The problem is, what kind of energy is being minimized?

when tectonic and igneous processes bring the diamond back to the surface, the diamond does not (fortunately) change back to graphite, so we say that diamond is a metastable form of carbon at Earth surface conditions (Figure 2.5). When we develop this subject further, we should be able to predict or calculate under what conditions it is the stable form of carbon.

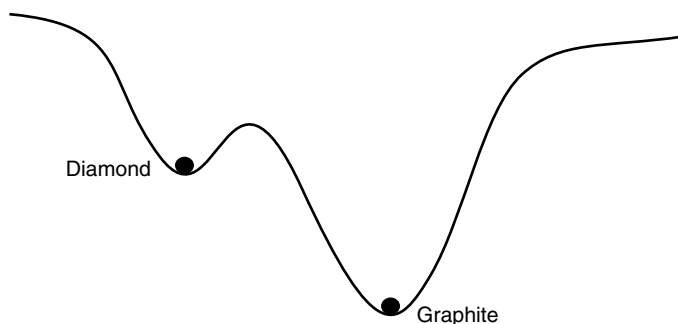
### 2.3.2 Partial and local equilibrium

There are two other commonly used terms in connection with equilibrium states.

#### *Partial equilibrium*

“Partial equilibrium” is intended to indicate that part or parts of the system have reached equilibrium, but those parts have not reached equilibrium with each other. The usual example of partial equilibrium is that of a crystal in an aqueous solution. The crystal is actively dissolving, so the system as a whole is not in equilibrium, but the aqueous solutes re-equilibrate very quickly, so that the solution itself is very close to internal equilibrium. The system is then said to be in partial equilibrium.

That may be true for the real system, but there is no such thing as partial equilibrium in thermodynamics, or the systems that thermodynamics deals with. In thermodynamics equilibrium is defined as equality of potentials in every phase. Partial equilibrium in real systems is modeled in thermodynamics as a metastable equilibrium. This distinction may not be clear at this point, but will be further discussed in connection with metastable equilibrium (Chapter 4) and titration (Chapter 18).



**Figure 2.5** The mechanical analogy for carbon at Earth surface conditions. Graphite is the stable form of carbon because it has the lowest energy content of any form of carbon (under Earth surface conditions). Diamond has a higher energy content but is prevented from changing to graphite by an energy barrier.



### *Local equilibrium*

Real world systems are in constant flux, and never really achieve thermodynamic equilibrium, but we want to apply thermodynamics to them anyway, so we have to choose parts of real systems which are reasonably close to thermodynamic equilibrium.

For example, you cannot apply thermodynamics to the ocean as a whole. Calcite is supersaturated at the surface, but undersaturated at 5 km depth (Chapter 16). Thermodynamics cannot be applied to a system which is both supersaturated and undersaturated. You can apply thermodynamics to volumes close to equilibrium at the surface or at depth, not both together, so we say we apply thermodynamics to areas of “local equilibrium.” It is obviously important to apply thermodynamics appropriately, and generally we do this, but the point is that local equilibrium is not part of thermodynamics, it is a concept we need, a property that real systems must have, in order to apply thermodynamics.

Understanding thermodynamics does not depend in any way on local equilibrium, but applying it to natural systems does. The question then naturally arises as to how one distinguishes between places having local equilibrium from places that do not. This question does not have a good answer. Places having large gradients in temperature, pressure or composition can be ruled out, but how large is “large”? Quite often the practice is to apply thermodynamics and see how it works out. If it seems to work well, then local equilibrium is assumed. Obviously some better approach would be desirable. There have been several attempts at providing a quantitative criterion for local equilibrium. The most accessible for Earth scientists appears to be that of Knapp (1989), which is summarized in Zhu and Anderson (2002, Chapter 3), who also cite a number of other references on the subject.

### Defining local equilibrium

The question of fluid – solid phase equilibrium arises in many subject areas, including environmental problems, studies of diagenesis, long range flow in sedimentary basins, ore genesis, magmatic – hydrothermal systems, regional metamorphism, and laboratory experimental systems. In each of these real systems, local equilibrium in theory requires that any disequilibrium condition relax instantaneously to an equilibrium state. In reality, this relaxation occurs over a finite time and, for a fluid-flow system, a finite distance. Knapp (1989) points out that each of these types of systems has a characteristic scale of interest, which is hundreds of meters or kilometers in studies of sedimentary basins, but perhaps microns in studies of surface processes. If the problem is defined on the kilometer scale, then disequilibrium over distances of centimeters is insignificant. The problem then is to determine, for a given system, the time required for a system in disequilibrium to reach equilibrium, and the distance the fluid has moved in that time period.

Knapp considers the problem in terms of a one-dimensional flow path in a quartz sandstone. The moving water is initially at equilibrium with quartz, then a pulse of pure water is introduced, and the time and distance required for the reattainment of equilibrium are calculated. Quite a few factors are involved, including concentrations (including pH), temperature, fluid velocity, diffusion and dispersion coefficients, and of course kinetics, including the surface area ( $\text{m}^2$  of mineral per  $\text{m}^3$  of fluid). The results, presented in terms of Damköhler and Peclet numbers,<sup>1</sup> show that there is a region where the time and distance to equilibrium is reaction dominated, and there is another region where they are transport or advection dominated. Local equilibrium can occur in both domains. Most natural environments with elevated temperatures fall in the reaction dominated domain, where the effects of dispersion and diffusion can safely be ignored, but local equilibrium would appear to be a questionable approximation in what Knapp (1989) refers to as “human controlled environments” due to characteristically large fluid velocities and low temperatures.

This analysis by Knapp is useful in defining and clarifying the local equilibrium problem in a quantitative way. Unfortunately, despite the rather drastic simplification, most of the parameters required to define the problem in real situations at the present time are poorly known. The quantitative results are then of questionable significance in any practical sense, but they are worth reflecting on. All applications of thermodynamics assume local equilibrium, but defining just what that is has proven difficult.

## 2.4 State variables

Systems at equilibrium have measurable properties. A property of a system is any quantity that has a fixed and invariable value in a system at equilibrium, such as temperature, density, or refractive index. Every system has dozens of properties. If the system changes from one equilibrium state to another, the properties therefore have changes that depend only on the two states chosen, and not on the manner in which the system changed from one to the other. This dependence of properties on equilibrium states and not on processes is reflected in the alternative name for them, *state variables*. Several important state variables (which we consider in later chapters) are not measurable in the absolute sense in a particular equilibrium state, though they do have fixed, finite values in these states. However, their changes between equilibrium states are measurable.

<sup>1</sup> The Damköhler number (Da) expresses the rate of reaction relative to the advection or fluid flow rate. A large Da value means that reaction is fast relative to transport and that aqueous concentrations may change rapidly in time and space. The Peclet number (Pe) expresses the importance of advection relative to dispersion in transporting aqueous compounds. A large Pe value means that advection dominates, which may result in large concentration gradients; a small Pe value suggests that dispersion dominates, which promotes mixing in the fluid phase.

Reference in the above definition to “equilibrium states” rather than “stable equilibrium states” is deliberate, since as long as metastable equilibrium states are truly unchanging they will have fixed values of the state variables. Thus both diamond and graphite have fixed properties. Metastable states are extremely common. For example, virtually all organic compounds are metastable in an oxidizing environment, such as the Earth’s atmosphere. We should be grateful for those “activation energy barriers” that prevent metastable states from spontaneously changing to stable states; otherwise we would not be here to discuss the matter.

### 2.4.1 Total versus molar properties

Many physical properties, such as the volume and various energy terms, come in two forms – the total quantity in the system and the quantity per mole or per gram of substance considered. We use different fonts for these total and molar properties. For example, water has a volume per mole ( $V$ ) of about  $18.0686 \text{ cm}^3 \text{ mol}^{-1}$ , so if we have 30 moles of water in a beaker, its volume ( $\mathbf{V}$ ) is  $542.06 \text{ cm}^3$ . This relationship for a pure substance such as  $\text{H}_2\text{O}$  is  $Z = \mathbf{Z}/n_i$ , where  $\mathbf{Z}$  is any total property,  $Z$  is the corresponding molar property, and  $n_i$  is the number of moles of the substance. In our water example, above,  $542.06/30 = 18.068$ . In more complex systems where more than one substance is present, total and molar properties are related in the same way. A beaker containing, for example, a kilogram of water (55.51 moles  $\text{H}_2\text{O}$ ) and 1 mole of  $\text{NaCl}$  occupies  $1019.9 \text{ cm}^3$ . The molar volume of the system is then  $Z = \mathbf{Z}/\sum_i n_i$ , or  $1019.9/(1 + 55.51) = 18.05 \text{ cm}^3 \text{ mol}^{-1}$ .

These two types of state variables have been given names:

- *Extensive* variables are proportional to the quantity of matter being considered – for example, total volume ( $\mathbf{V}$ ).
- *Intensive* variables are independent of the total size of the system and include concentration, viscosity, and density, as well as all the *molar* properties, such as the molar volume,  $V$ .

#### Scientific versus engineering units

In science, *molar* properties, such as molar volumes, molar energies, are most commonly used. In engineering on the other hand, *specific* properties are more common. Specific properties are mass-related rather than mole-related. Thus the specific volume of water at  $25^\circ\text{C}$  is  $1.0029 \text{ cm}^3 \text{ g}^{-1}$ . Molar and specific properties are of course related by the molar mass (or so-called gram formulas weight, gfw) of the substance. That for water is 18.0153, so  $1.0029 \text{ cm}^3 \text{ g}^{-1} \times 18.0153 \text{ g mol}^{-1} = 18.068 \text{ cm}^3 \text{ mol}^{-1}$ .

Of course, many equations look much the same with total and molar properties because ratios are involved. That is, if  $(\partial U/\partial \mathbf{S})_{\mathbf{V}} = T$ , then it is also true that  $(\partial U/\partial S)_{\mathbf{V}} = T$ ; or if  $(\partial \mathbf{G}/\partial P)_{\mathbf{T}} = \mathbf{V}$ , then  $(\partial G/\partial P)_{\mathbf{T}} = V$ , so that the distinction may seem to be unimportant. However, sometimes it *is* important, as we will see. In general terms, we use the total form of our variables (bold type) in some theoretical discussions, and the molar form (italic type) in most calculations.

### *Partial molar properties*

In addition to total and molar properties, we have *partial* molar properties, which are a little trickier to understand. It's relatively easy to see that the volume (extensive variable) of a system depends on how much stuff you have in the system, but that its temperature or density (intensive variables) do not. This is true no matter how many different phases there are in the system, as long as you are considering the *whole* system, not just parts of it.

A problem arises, though, when you consider the properties of solutions, which can have variable concentrations of solutes. The volume per gram of halite, NaCl, is the same whether you consider 10 or 20 grams of it. But what is the volume per gram of 10 grams of NaCl dissolved in a liter of water? This property depends on the concentration of NaCl – the volume per gram or per mole of 20 dissolved grams is different from that of 10 dissolved grams. And what *is* the volume of something dissolved in something else? How is it defined, or measured? These are important questions, and will be discussed in Chapter 10.

The properties of dissolved substances is discussed in terms of *partial molar properties*, the formal definition of which is

$$\bar{Z}_i = \left( \frac{\partial \mathbf{Z}}{\partial n_i} \right)_{T,P,\hat{n}_i} \quad (2.1)$$

where  $\mathbf{Z}$  is the total or extensive form of any thermodynamic parameter,  $\bar{Z}$  the partial molar form,  $n_i$  is the number of moles of component  $i$ , and  $\hat{n}_i$  is the number of moles of all components other than  $i$  in the same solution. Note particularly that the partial derivative is taken of the total quantity  $\mathbf{Z}$ , not the molar  $Z$ , and that the main constraints are  $T$  and  $P$ . However, the important thing to know about partial molar properties is not this differential equation, but that they are the properties per mole of substances at a particular concentration in a particular solution, as explained in Chapter 10. You think about partial molar properties in exactly the same way you think about molar properties. The only difference is that for a given substance, they are not fixed quantities at a given  $T$  and  $P$ , but vary with the concentration of the substance and the nature of the solution.

The differences between total, molar, and partial molar properties is also discussed in more mathematical terms in Appendix C.

## 2.5 Phases and components

We must also have terms for the various types of matter to be found within our thermodynamic systems. A *phase* is defined as a homogeneous body of matter, having distinct boundaries with adjacent phases, and so is mechanically separable from the other phases. The shape, orientation, and position of the phase with respect to other phases are irrelevant, so that a single phase may occur in many places in a system. Thus the quartz in a granite is a single phase, regardless of how many grains of quartz there are. A salt solution is a single phase, as is a mixture of gases. There are only three very common types of phases – solid, liquid, and gas or vapor. A system having only a single phase is said to be *homogeneous*, and multiphase systems are *heterogeneous*.

The term generally used to describe the chemical composition of a system is *component*. The components of a system are defined by the smallest set of chemical formulas required to describe the composition of all the phases in the system. This simple definition is sometimes surprisingly difficult to use. To take a simple example, consider a solution of salt (NaCl) in water (H<sub>2</sub>O), in equilibrium with water vapor. This might look like Figure 2.2b. There are two phases, liquid and vapor, and two components, NaCl and H<sub>2</sub>O. A chemical analysis could report the amounts or concentrations of Na, Cl, H, and O in the system, but only two chemical formulas are needed to describe the compositions of both phases.

Unfortunately, this does not nearly encompass all we need to say about components. We will have more to say in Chapter 11, but we should at least point out that the definition of components given above (“smallest set of chemical formulas...”) is used for phases in our models, not in real systems. For example, analysis of any calcite crystal will reveal the presence of many elements besides those in the formula CaCO<sub>3</sub>. Nevertheless, component CaCO<sub>3</sub> is very often used to represent calcite, whatever its actual composition.

### 2.5.1 Real versus model systems

Equilibrium, phases, and components are terms that appear to apply to real systems, not just to the model systems that we said thermodynamics applies to, and in general conversation, they do. But real phases, especially solids, are never perfectly homogeneous. And real systems don't really have components, only our models of them do. Seawater, for example, has an incredibly complex composition, containing dozens of elements. But our thermodynamic models might model seawater as having two, three, or more components, depending on the application. As for equilibrium, real systems do often achieve equilibrium as we have defined it, but it is never a perfect equilibrium.

However, the fact that real phases are more or less homogeneous, and that real systems achieve an approximate equilibrium, is what makes thermodynamics useful. The model is perfect, but real life comes close enough in

many respects so that the model is useful. In fact, the close similarity between reality and our models of reality, and the fact that we use the same terms to describe each, may lead to a certain degree of confusion as to what we are talking about. Usually no harm is done, and the distinction gets easier with practice.

## 2.6 Processes

Finally, we get to something that looks more interesting. *Processes* are what we are usually interested in – changes in the real world. In geology, these might be igneous, diagenetic, or metamorphic processes. In biology, they might be cellular processes. In the environmental world, they might be potentially harmful processes near waste disposal sites – the possibilities are endless. However, most of the processes of interest to us have one thing in common – they are extremely complicated. The only hope we have of understanding them is to break complex processes down into their simpler component parts, and to construct simplified models of them. We have already begun to do this by defining several types of simple *systems* that we can use; we will now define a *process* in a way that will help us model real processes.

A thermodynamic *process* is what happens when a system changes from one equilibrium state to another. Thus any two equilibrium states of the system may be connected by an infinite number of different processes because only the initial and final states are fixed; anything at all could happen during the act of changing between them. A chemical reaction is one kind of process, but there are others. For example, simply warming or cooling a system is a process according to our definition.

In spite of there seeming to be an endless number of kinds of processes in the world, we find that in thermodynamic models there are only two – reversible and irreversible.<sup>2</sup>

- The most important *irreversible processes* are those that begin in a metastable equilibrium state and lead to a more stable state, such as aragonite recrystallizing to calcite. Another kind would be a stable equilibrium state changing to a lower energy stable equilibrium state, such as when the weight on a piston is replaced by a smaller weight.
- Processes that begin in a stable equilibrium state and proceed to another stable equilibrium state, without ever leaving the state of equilibrium more than infinitesimally, are *reversible processes*.

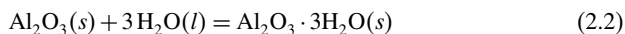
<sup>2</sup> In some treatments of thermodynamics there is a third type – the virtual process. See Reiss (1965) for its use.

### 2.6.1 Irreversible processes

We have defined a metastable state of a system as a state that has more than the minimum energy for the given conditions, but is for some reason prevented from releasing that energy and reacting or changing to the stable state of minimum energy. An irreversible process is one that occurs when whatever constraint is holding the system in its high energy state is removed, and the system slides down the energy gradient to a lower energy state. We consider constraints in more detail in Chapter 4.

The only example we have given thus far of a metastable system is the mineral diamond, that could lower its energy content by changing into graphite but does not, because energy is required to break the carbon–carbon bonds in diamond (which are very strong) before the atoms can rearrange themselves into the graphite structure. There are many other similar examples of metastable minerals. We have also mentioned that most organic compounds, such as all the ones in living organisms, are metastable. When the life processes maintaining their existence cease, they quickly react (decompose) to form more stable compounds.

In most of the chemical reactions we will be considering, a combination of minerals, or minerals plus liquids or gases, reacts to form some different minerals under some given conditions. For example, the mineral corundum ( $\text{Al}_2\text{O}_3$ ) is stable, considered by itself (i.e., there is no other form of  $\text{Al}_2\text{O}_3$  that is more stable), but in the presence of water it reacts to form gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). The reaction is



and the energy relationships are shown in Figure 2.6. We will use  $(s)$ ,  $(l)$ ,  $(g)$ , and  $(aq)$  after our formulas to indicate whether they are in the solid, liquid, gas, or aqueous (dissolved in water) state.

Do not confuse the metastability of diamond at Earth surface conditions with the metastability of corundum or water. Diamond is metastable because the same carbon atoms would have a lower energy in the crystal structure of graphite. But corundum by itself is not metastable, and neither is water, at 25 °C and atmospheric pressure. It is the *combination* of corundum and water that can be regarded as metastable, because their *combined* atoms would have a lower energy level in the form of gibbsite.

Another example is the dissolution of sugar in coffee (Figure 2.7), for which we cannot write a simple balanced reaction. Nevertheless, the assemblage of sugar lumps and a cup of coffee is a metastable assemblage in our usage. They are prevented from reacting (sugar dissolving) by the fact that they are separated, which constitutes a *constraint* on the system. When the constraint