

Thermodynamics of Natural Systems

Theory and Applications in Geochemistry
and Environmental Science

Third Edition
G.M. ANDERSON



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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 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 processes, 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 to real systems, but they also refer to the equivalent things in our models of these systems. 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 a petrologist, a crystallizing magma could 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 CO₂ 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 CO₂ and carbonate and bicarbonate ions). And at (c), we might be

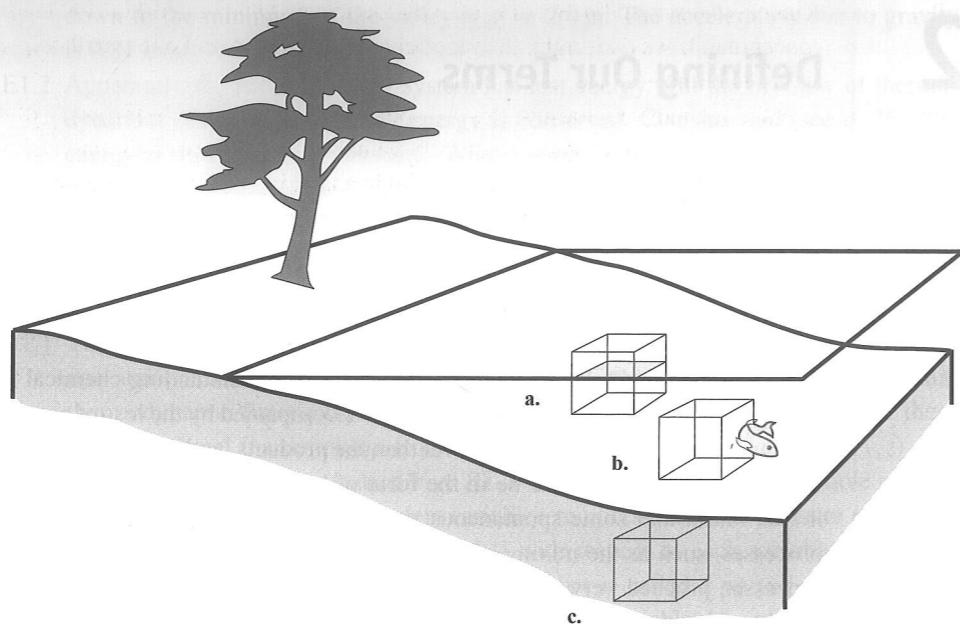


Figure 2.1 A seashore environment. The locations of three natural systems are shown.

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 Section 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.

2.2.2 Thermodynamic Systems

Our goal is to understand energy changes in natural systems. We will do this by considering much simpler models of these systems, having variables that represent what we think are the essential elements of the natural systems. Using such models is a universal practice in

science, as discussed in Section 1.5. Our models will be not material, but mathematical and conceptual. If we do it right, then the behavior of the model system will help us understand and predict the behavior of the real system.

Although most natural systems are open and quite complex, our models of these systems can be much simpler and yet 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 do not occur in nature, because there are no such impermeable and rigid boundaries. Nevertheless, this type of system has 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. There are equations for open systems, those that can change composition, and we will introduce them (in Section 4.13), but we don't use them to any great extent. It is possible and more 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 2.2(b), that is, two open subsystems within an overall closed system. There can be any number of these “open subsystems” or phases, 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.

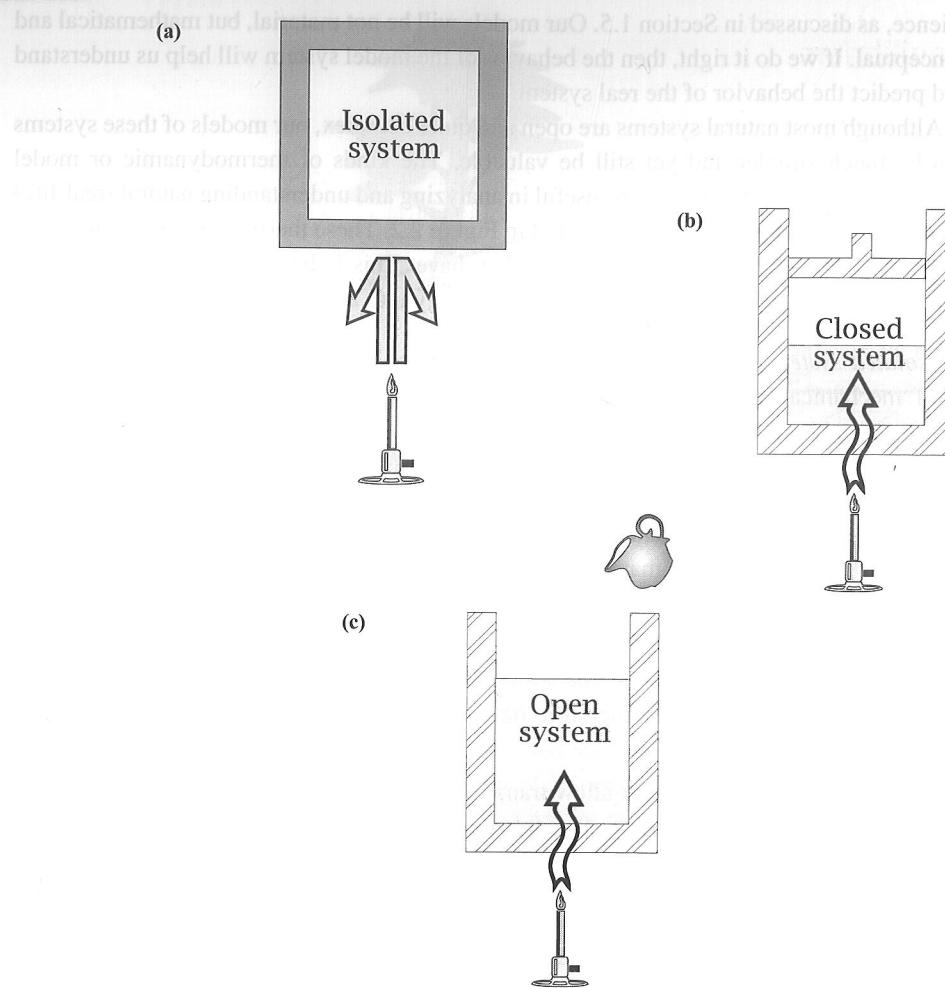


Figure 2.2 (a) Isolated system. Nothing can enter or leave the system (no energy, no matter). Whatever is inside the walls (which could be anything) will have a constant energy content and a constant composition. (b) Closed system. The closure is a piston to indicate that the pressure on the system is 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.

The Isolated System Paradox

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.

Equilibrium

Introduction

The concept of the equilibrium state is, along with entropy, arguably the most important of all thermodynamic concepts. But, in contrast to entropy, which has retained its somewhat mysterious nature ever since Clausius discovered its importance, equilibrium seems to be an intuitively simple idea. It's just a state having a balance of forces, a state which does not change, right? Well, yes, but thermodynamic equilibrium needs more discussion. First, because we have real and thermodynamic systems, we must distinguish between real and thermodynamic equilibrium states. Then we introduce the various varieties – stable, metastable, partial, and local. From the point of view of someone doing experiments, equilibrium is vital, because results must represent equilibrium states, otherwise they are not reproducible and are useless.

In natural systems it is the concept of *local equilibrium* which is vital. Natural systems may be overall far from equilibrium, and we have no control over them. Here the importance is not reproducibility, but the fact that systems which are not at equilibrium do not have fixed values of their thermodynamic properties, so we apparently cannot use our thermodynamic methods with them. The thermodynamic data we use, such as those in Appendix B, are derived from experiments in equilibrium states, so how can they be used in any other states? The answer is that we don't apply our thermodynamic methods to systems in complete disequilibrium, like a turbulent fluid or an exploding volcano. But systems in overall disequilibrium, such as acid mine drainage, crystallizing magmas, metallic ore deposition, or the carbon cycle, operate over long time periods and have small volumes throughout the system which *are* close to equilibrium, and samples from those places provide thermodynamic information. Even active geothermal systems, having large temperature gradients, boiling, alteration reactions, and so on (see Chapter 11 problem sets), have small volumes of local equilibrium, or so we believe. Other systems, like the ocean, have volumes of local equilibrium which are much larger.

We begin with thermodynamic equilibrium as an idealization. We have stressed the idea that there is a difference between real and thermodynamic systems, and the state of equilibrium is defined differently in the two cases.

Equilibrium in Thermodynamic Systems

The definitive definition of the equilibrium state is given by Gibbs (1961a). Based on the fundamental role of entropy discovered by Clausius (1867) which we get to in Chapter 4, he shows in his equations 14–21 (shown in Section C.9.2, Thermodynamic Equilibrium, of the Topics in Mathematics, in the online resources) that a system at equilibrium can have no gradients in temperature T , pressure P , or chemical composition. But all real systems have inhomogeneities and gradients, however small. Herzfeld (1962) says

But no real measurement is reversible, and no real system is completely in equilibrium.

Given the absence of *perfect* equilibrium in real systems, the definition of equilibrium as expressed by Gibbs and others is an idealization. In model systems which include a solution of variable composition, it is a state occurring at a maximum or a minimum of a function called a thermodynamic potential, an important topic introduced in Section 1.4. See Figure 13.3 for an example. In other systems, such as those having only pure solid phases, thermodynamic potentials do not exhibit a maximum or a minimum, but the system can nevertheless be at equilibrium. These situations are explored further in Chapter 9.

Some real systems approach this state more or less closely, but probably never attain it. When real systems or parts of real systems do approach thermodynamic 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.

2.3.3 Equilibrium in Real Systems

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 is a common experimental technique, but is of limited use in the investigation of natural systems.

The hope is, of course, that a system which obeys these criteria will be close to the idealized equilibrium state of absolutely uniform T , P , and composition. Many real systems do satisfy these criteria. For example, a crystal of diamond sitting on a museum shelf obviously has exactly the same properties this year as last year, and, if we warm it slightly and then put it back on the shelf, it will gradually recover exactly the same temperature, dimensions, and so on that it had before we warmed it. The same remarks hold for a crystal of graphite on the same shelf, so that the criteria can apparently be satisfied for various forms of carbon. Many other natural systems just as obviously are not at equilibrium. Any system having macroscopic 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 has cooled down to the temperature of its surroundings.

Despite the simplicity and importance of the equilibrium state, it is very often difficult to know whether any particular real system has achieved that state, or is acceptably close to that state. Experimenters constantly worry whether their experimental systems have achieved equilibrium, and, if so, is it a metastable or stable equilibrium? In the case of a geologist interpreting ancient igneous and metamorphic systems (rocks), the question becomes, did the system achieve equilibrium under some other, perhaps largely unknown, conditions? In such cases thermodynamics is applied, and if the results make sense the system is assumed to be in equilibrium, or to have been in equilibrium. Callen (1985, p. 15) says

In practice, the criterion for equilibrium is circular. Operationally, a system is in an equilibrium if its properties are consistently described by thermodynamic theory!

This might seem like a serious drawback, but the fact that thermodynamics has proved immensely useful and is a cornerstone of scientific training would indicate otherwise.

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?

2.3.4 Stable and Metastable Equilibrium

In this section we use the simple mechanical analogy in Section 1.3 and Figure 2.3 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 Section 4.8.

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 its 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 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 H_2O is water at $+5^\circ\text{C}$, and ice at -5°C (Figure 2.4). The freezing and melting of H_2O is normally fairly rapid, so, although it does happen, 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 (lowered) if they did. These reactions, which get “stuck” in a high energy state, are usually not melting/freezing reactions, but solid-state reactions – for example a reaction in which a mineral having one

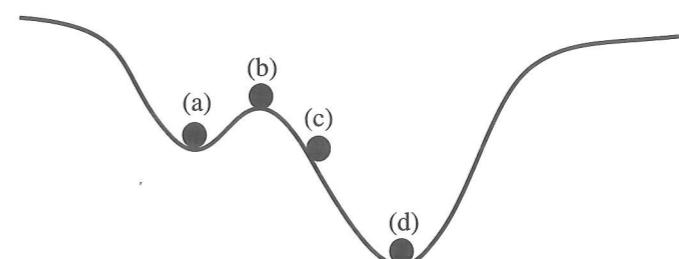


Figure 2.3 Four positions of a ball on a surface, to illustrate the concept of equilibrium.
Position (a) – metastable equilibrium. Position (b) – unstable equilibrium. Position (c) – unstable.
Position (d) – stable equilibrium.

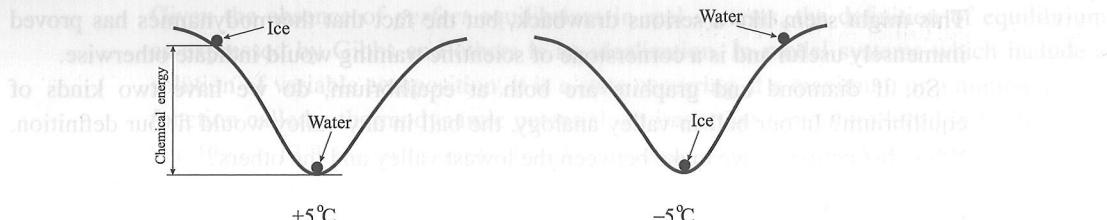


Figure 2.4 The mechanical analogy for H_2O at -5°C and $+5^\circ\text{C}$ and atmospheric pressure.

At -5°C , water is unstable and releases energy until it becomes ice at -5°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?

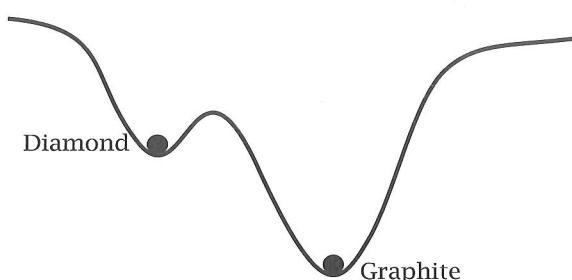


Figure 2.5 The mechanical analogy for carbon at Earth surface conditions. Graphite is the stable form of carbon because it has the lowest energy content of any form of carbon (under Earth surface conditions). Diamond has a higher energy content but is prevented from changing to graphite by an energy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

crystallographic structure should change to a mineral having the same composition but with a different structure but does not.

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

The importance of metastable equilibrium states tends to be overlooked. This is because discussions of thermodynamic theory commonly assume stable equilibrium, or that there is only one kind of equilibrium. Metastable states are thought of as things like supersaturated solutions – temporary deviations or fluctuations away from the most stable state. In fact, real metastable states include almost everything we see around us in daily life (Lambert, 1998), and thermodynamic metastable equilibrium states have an important place in thermodynamic theory which we will explore in coming chapters. In petrology metastable minerals like diamond and aragonite are common, and metastable-to-stable transitions will be an important part of our thermodynamic theory.

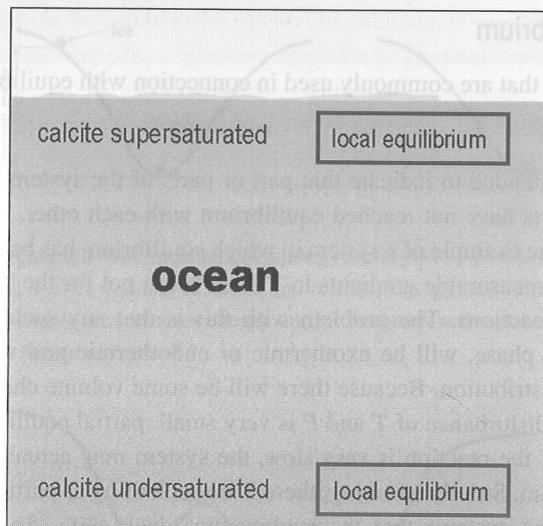


Figure 2.6 Calcite is both slightly supersaturated and slightly undersaturated in the ocean. Local equilibrium must be assumed in order to apply thermodynamics.

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. 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 in natural systems assume local equilibrium, but defining exactly 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 the processes that occur between equilibrium states is reflected in another name for them, *state variables*. State variables are all related by continuous functions, so they all have exact differentials. Several important state variables which we consider in later chapters are not measurable in an absolute sense in any particular equilibrium state, though they do have fixed, finite

values in these states. However, the *changes* in these state variables between equilibrium states are measurable.

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 state variables, but of course the numerical values of these variables are different in the two phases.

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 a system and the quantity per mole or per gram of pure substance considered. We use a different typeface 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 (V) is $18.068 \times 30 = 542.06 \text{ cm}^3$. This relationship for a pure substance such as H_2O is $Z = \mathbb{Z}/n_i$, where \mathbb{Z} is any total property, Z is the corresponding molar property, and n_i is the number of moles of the substance.

These two types of state variables have been given names.

- *Extensive* variables are proportional to the quantity of matter being considered, and will be written in bold-face type. For example, total volume (\mathbf{V}), total internal energy \mathbf{U} .
- *Intensive* variables are independent of the total size of the system and include not only all the *molar* properties just mentioned but also temperature, pressure, concentration, viscosity, and density. These will be written in italic type, for example temperature T , molar volume V , molar internal energy U .

In other words an extensive property such as \mathbf{V} refers to a whole system, no matter what size and no matter how many components or phases. The system might be a partially crystallized magma, so \mathbf{V} is the volume of the whole magma. Some intensive properties such as temperature and pressure also refer to the whole system (assuming equilibrium), but more often they refer to individual phases, such as the density of one of the phases. Thus the most common intensive properties, besides temperature and pressure, are the *molar* or *specific* properties of pure substances, that is, the property per mole or per gram. These are the properties that are listed in tables of data such as Appendix B, and are

Box 2.1 Scientific vs. Engineering Units

In science, *molar* properties, such as molar volumes and 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°C is $1.0029 \text{ cm}^3 \text{ g}^{-1}$. Molar and specific properties are related by the molar mass (or so-called gram formula weight, gfw) of the substance. That for water is $18.0153 \text{ g mol}^{-1}$, so $1.0029 \text{ cm}^3 \text{ g}^{-1} \times 18.0153 \text{ g mol}^{-1} = 18.068 \text{ cm}^3 \text{ mol}^{-1}$.

used to calculate the changes in such properties in individual chemical reactions. A more mathematical and hence more useful way of describing the difference between intensive and extensive variables is the concept of degree of homogeneity, discussed in Section C.7, Euler's Theorem for Homogeneous Functions, of the Topics in Mathematics, in the online resources.

Many equations in thermodynamics look much the same with total and molar properties because ratios are involved. That is, if $(\partial U / \partial S)_V = T$, then it is also true that $(\partial U / \partial S)_V = T$; or, if $(\partial G / \partial P)_T = V$, then $(\partial G / \partial P)_T = V$, so that the distinction may seem to be unimportant. However, in some important cases only the extensive form is true, so we will see in coming chapters that thermodynamic potentials apply only to the whole system (are extensive), and chemical potentials are defined using the extensive form of an energy term, not the intensive form. In other important cases, only the intensive form is true, such as “the most useful equation in thermodynamics” that we will see in Chapter 9. Generally speaking, experimentally measured quantities like amounts of heat and work are extensive and used to derive extensive thermodynamic variables. These are then converted to the intensive (molar) form for use in calculations and in collections of data such as Appendix B. In the pages to follow, where both intensive and extensive forms of equations are equally valid, we will often write only the molar form (intensive; italic type).

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, crystalline 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 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 the answer is that we use *partial molar properties*. So we have partial molar volume, partial molar enthalpy, and so on. One of these, the partial molar Gibbs energy or chemical potential, is particularly important, and we get to it in Chapter 4.

2.5

Phases, Components, and Species

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 formulae required to describe the composition of all the phases in the system. To take a simple example, consider a solution of salt (NaCl) in water (H₂O), in equilibrium with water vapor. This might look like Figure 2.2(b). There are two phases, liquid and vapor, and two components, NaCl and H₂O. A chemical analysis could report the amounts or concentrations of Na, Cl, H, and O in the system, and further analysis would find amounts of the ions H⁺, Cl⁻, Na⁺, and several others, but only two chemical formulae are needed to describe the compositions of both phases.

We must be careful to distinguish between *components* and *species*, because they often have the same name. In the system NaCl–H₂O, H₂O is both a component and a chemical species. The ions just referred to are species, not components, because the composition of the system is described without reference to them. Quite often the term *component* is used to refer to the model of a system rather than the real system. Seawater, for example, has an incredibly complex composition, having numerous components and dozens of chemical species. But a thermodynamic model might consider seawater to have only two components, NaCl and H₂O, and this might be adequate for a particular application. Other applications might require the addition of, say, KCl or CO₂, giving three or more components.

As mentioned, 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 mathematically perfect, but real life comes close enough in many respects, so that the model is useful. The close similarity between reality and our models of reality, and the fact that we use the same terms to describe them, may lead to a certain degree of confusion as to what we are talking about. There is quite a bit more to say about phases, components, and the phase rule, which we get to in Chapter 12. There is also more to say about the way we use thermodynamics to investigate systems that are not even close to equilibrium.

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 stable or metastable equilibrium state to another stable or metastable equilibrium state. Any two equilibrium states of the system may be connected by any number of different processes because only the initial and final states are fixed; anything at all could happen during the act of changing from one to the other. A chemical reaction is one kind of process, but there are others. As noted in Chapter 1, 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.

2.6.1 Reversible and Irreversible Processes

There are several ways of discussing reversible and irreversible processes. Which one is preferable depends a lot on what your interests are. This book is focussed on chemical reactions and particularly those in natural systems, so an approach based on the decreasing energy in metastable to stable reactions and the constraints on such reactions is used. At various points we will point out the links to the other ways of looking at the same subjects.

The various ways of explaining reversible and irreversible are as follows.

1. Reversible processes as mathematical functions.
2. Cycles and the entropy of the universe.
3. Uncompensated heat and the affinity.
4. The traditional way.
5. Constraints and changes from metastable to stable equilibrium states.

Reversible Processes as Mathematical Functions

We mentioned in Section 1.5 that many aspects of thermodynamics are unrealistic, the reason being that we need to use mathematics, specifically calculus. Well, here is one of the most unrealistic yet most central aspects of thermodynamics – the reversible process. In thermodynamics reversible does not mean you can simply reverse a process, like warming a crystal and then cooling it back down to its original state. Any such process, and all natural processes such as the diagenetic and metamorphic processes we mentioned, may start and end in an equilibrium state, but during the process they are out of equilibrium. The essence of thermodynamics is the ability to calculate the changes in the properties of a system, its state variables, during a process and therefore to predict what they will be when the system achieves a new equilibrium state. To do this there must be a function, a mathematical expression, for the value of each property *during the process*, that can be integrated. If the system is out of equilibrium its properties vary from place to place and are continually changing. The properties are not single-valued, so no single-valued continuous function can possibly represent them during a process while it is in disequilibrium. Put it this way: what is the temperature of a system when every time you measure it you get a different answer? As Bridgman (1961, p. 133) says

... thermodynamics is concerned with reversible processes and equilibrium states. ... The reason for the importance of equilibrium states is obvious enough when one reflects that temperature itself is defined in terms of equilibrium states.

You could say systems in states of disequilibrium do not actually have state variables.

The solution is to represent the process as a continuous succession of equilibrium states which *can* be represented by a function. This succession of equilibrium states is what we call a reversible process.¹ It obviously does not represent what actually happens during a real process, but it does allow calculation of property changes, and an extremum in such a function indicates a stable or metastable equilibrium state. We used this approach in Section 1.4.1 when we used a continuous function (Equation (1.1)) to represent a real valley. Klotz (1964, p. 44) summarizes this approach nicely when he says

The great virtue of the concept of reversibility is that it introduces the idea of continuity into our analysis of actual processes and hence permits the use of calculus.



Single-Valued Continuous Functions

Thermodynamics could not exist without the concept of entropy; neither could it exist without single-valued continuous functions. The meaning of the terms single-valued and continuous in mathematics is reasonably self-explanatory, but their significance in thermodynamics is fundamental and is explored further in Section C.4, Single-Valued and Continuous Functions, of the Topics in Mathematics, in the online resources.

Cycles and the Entropy of the Universe

A different way of defining a reversible process, more useful to engineers, is the following (Jones and Dugan, 1996, p. 279):

A process is reversible if, after it has occurred, both the system *and its surroundings* can by any means whatsoever be returned to their original states. Any other process is irreversible.

The importance here is that the “original states” referred to involve not just the system but the system plus its surroundings. Some processes, like mixing cream into coffee or breaking an egg, are obviously irreversible, but even cases where the initial state seems to be recovered, like heating a crystal and then cooling it back down, are also ruled out when the surroundings are included. All kinds of natural effects lead to irreversibility; not just mixing and breaking but friction, heat transfer across a finite temperature gradient, free expansion, inelastic deformation, and a few others. Demonstrating that each such effect leads to irreversibility, i.e., changes in the system plus environment, is a major topic in many thermodynamic texts. A good example is Section 5.4 in Jones and Dugan (1996), and identifying and reducing these effects is important in engineering design problems.

¹ We restrict the term reversible to a succession of *stable* equilibrium states. In Chapter 4 we will see that we can also have a very similar succession of *metastable* equilibrium states, which, however, have an extra constraint variable.

The idea of using a cycle, a return to the original state, to consider processes was first proposed by Sadi Carnot in 1824 (Carnot, 1960), and the Carnot cycle (Section 4.10.3) has had a profound effect on all subsequent presentations of thermodynamics. The fact that reversibility involves not only the system but also its surroundings, given that the “surroundings” might be called the universe, led Clausius in 1865 to make the most famous statement in the history of thermodynamics:

The energy of the universe is constant.
The entropy of the universe tends to a maximum.

Clausius (1867, 1879)

Cosmologists are still debating the entropy of the universe (see Carroll, 2010, for a nice discussion), but fortunately we are concerned only with processes here on Earth. Entropy is introduced in Chapter 4 but, to be consistent with our ball-in-valley idea of decreasing energy of some kind, we do it in a way that concentrates on the system itself rather than the system plus environment.

Uncompensated Heat and the Affinity

Uncompensated heat or uncompensated transformation is a term used by Clausius (and not many others). Prigogine and Defay (1954, pp. 34–35) observe that, although they adopt the term “uncompensated heat” for historical reasons, it is not a particularly happy choice. They show that it is better described as the energy generated or absorbed by an irreversible process *within* a system, as opposed to energy transferred *to or from* a system due to differences between the system and its environment. Prigogine and Defay relate this to the creation of entropy within a system and to a property called the *affinity*, discussed in Section 4.9.1. All the natural irreversible effects just mentioned such as friction can be interpreted as creating entropy, and the creation of entropy within a system is one way to explain the difference between reversible and irreversible processes; reversible processes, being always at equilibrium, create no entropy. That is, a reversible process will change the entropy of the system but will not increase the entropy of the surroundings. We take a different approach to discussing irreversibility, entropy, and affinity, but the distinction between energy generated or absorbed *within* a system and energy transferred *to or from* a system is important and will be discussed in different terms in Section 4.9. The affinity is a thermodynamic concept that will be fully explored in Chapter 13.

The Traditional Way

This point of view originated with Clausius. Badger (1967, p. 128), summarizing a lengthy passage in an article by Clausius, put it this way:

A *reversible process* is one in which the difference between any force of the system and the counterforce of the surroundings, ΔF , is zero. No real process can reach this limit. An *irreversible process* is one in which any $\Delta F > 0$ and for which ΔF may only approach zero in the limit. All real processes are therefore irreversible processes.

This idea is commonly made more concrete by considering a piston–cylinder arrangement in which a gas is compressed or expanded. When a weight is removed from the piston, the resulting expansion has to overcome not only the weight of the piston plus whatever

weights are on it, but also the frictional force between the piston and the cylinder, so less work is produced than predicted by equations which do not include this frictional force, which of course depends on the particular circumstances. The system may start and end in an equilibrium state, but during the expansion the system is in a state of disequilibrium, and the process is irreversible. Then it is shown that, by performing the expansion more and more slowly, the friction which is the cause of the energy loss is gradually reduced, so that *in the limit* of an infinitely slow process the ideal is achieved, and the process is called a reversible process. It follows that all reversible processes are infinitely slow.

This kind of discussion has the somewhat dubious merit of seeming to relate the reversible process to real processes, but it comes with some problems. A process involving an infinite number of steps requiring an infinite amount of time is difficult to visualize. Furthermore, it makes it seem as if time is an important concept in thermodynamics, that time might be a thermodynamic variable. This is a common misconception that we discuss in Section 2.8. It is much simpler to say that the reversible process is simply a result of the fact that we use calculus, which requires continuous functions, which in turn require equilibrium states. Limit-taking is an integral part of calculus and need not be repeated in discussing thermodynamics.

Reversible processes are but one example of a host of concepts of a similarly idealized nature in chemistry and physics – for example, ideal gases and solutions, absolute zero temperature, infinitely dilute solutions, perfect black-body radiation, isolated systems, perfect insulators, friction-free surfaces, and so on. In every case, the adoption of the idealized case simplifies or makes possible the application of mathematics to physical reality.

Constraints and Changes from Metastable to Stable Equilibrium States

We have defined a metastable equilibrium state of a system as a state that has more than the minimum energy for the given conditions, but for some reason is prevented from releasing that energy and reacting or changing to the stable equilibrium 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.

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 there are many other similar examples of metastable minerals. The diamond is constrained from reacting because energy is required to break the strong carbon–carbon bonds in diamond before the atoms can rearrange themselves into the graphite structure. In Figure 1.2 this energy is represented by the fact that the ball must be pushed up a small hill before it can roll down to a lower valley. This energy, the barrier preventing change, is called an *activation energy*. 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 that we will be considering, particular minerals, or minerals plus liquids or gases, react to form different minerals under some given conditions. For example in reaction (2.5), the mineral corundum (Al_2O_3) is stable, considered by itself (i.e., there is no other form of Al_2O_3 that is more stable), but in the

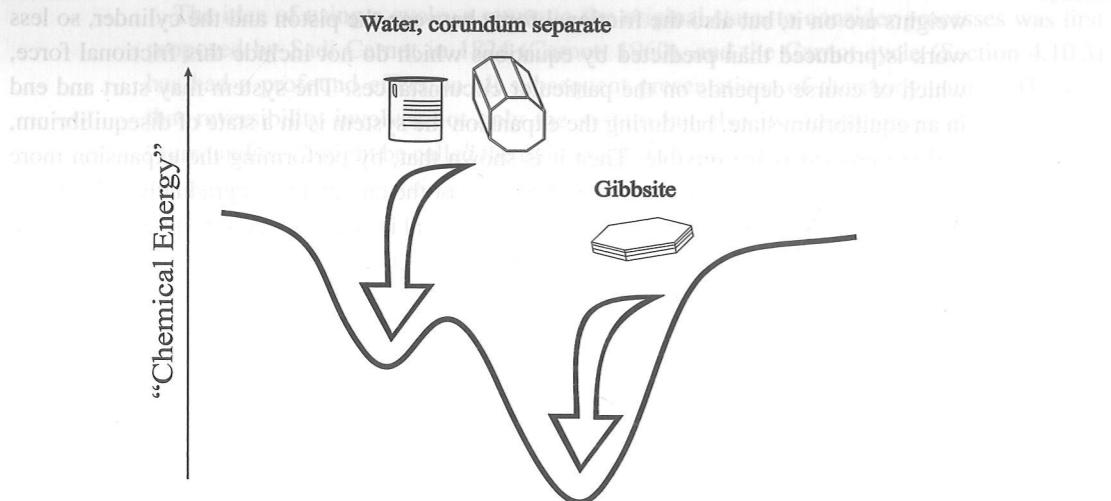


Figure 2.7 Water plus corundum can lower its energy content by reacting to form gibbsite.

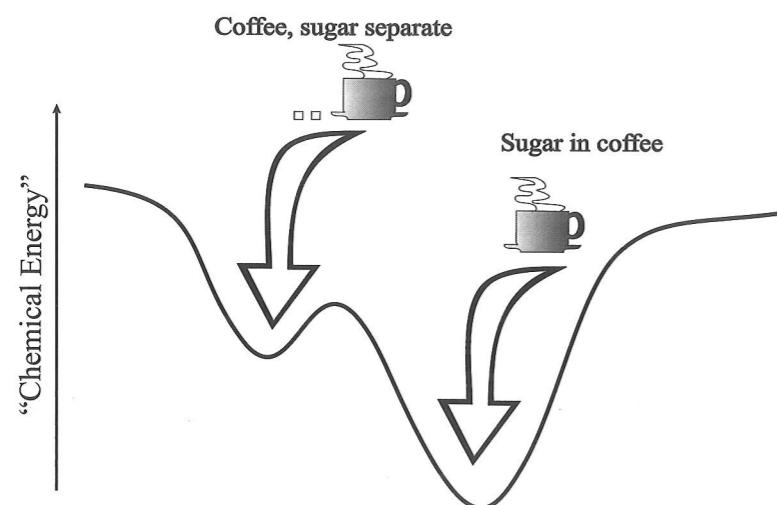


Figure 2.8 Sugar dissolves in coffee because the “chemical energy” of the dissolved state is less than that of the two coexisting separately.

presence of water it reacts to form gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), and the energy relationships are shown in Figure 2.7.

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, much like the cream in coffee example, is the dissolution of sugar in coffee (Figure 2.8). 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 is removed by putting the sugar in the coffee, the reaction occurs, because the “chemical energy” is lowered.

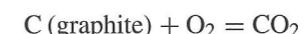
The corundum plus water example and the sugar plus coffee example are different in an instructive way. If you actually put a crystal of corundum in a beaker of water, nothing at all happens, except that the corundum gets wet, whereas when the sugar is put in the coffee, it dissolves immediately. Both assemblages are metastable but the constraints are different. Like diamond, corundum is prevented from reacting by an activation energy barrier, meaning that the atoms in Al_2O_3 are too tightly bound to react, even though the system could lower its energy if they did. The sugar is prevented from dissolving in the coffee by a physical separation.

These are all examples of constraints in real systems. We will introduce the constraint used in thermodynamic systems in Chapter 4. You will not be surprised to learn that this constraint is not a physical situation but a mathematical variable.

Chemical Reaction Examples

Most people, especially Earth scientists, will readily agree that diamond and aragonite under ambient conditions are examples of metastable states which are constrained from reacting to a more stable state. In these cases the constraint is an activation energy. As mentioned, the sugar or cream into coffee examples have a different kind of constraint, the physical separation of reactants from products. In other words we consider sugar plus coffee to be in the same category as the corundum plus water, that is, a metastable equilibrium state.

If we carry this idea to its logical conclusion, we find that it includes *all* spontaneous chemical reactions such as



or reaction (2.5) on p. 31. If $\text{A} + \text{B} \rightarrow \text{C}$ is spontaneous at T, P , then $\text{A} + \text{B}$ is unstable unless constrained from reacting. If so, there is an extra (third) constraint such as separation of the reactants, and $\text{A} + \text{B}$ is then in a metastable state. The separation of A and B may be effected by various means, such as having a partition between them, or by having A and B in separate containers, but when this separation is ended, or *this constraint is released*, $\text{A} + \text{B}$ slides down the energy gradient, forming C . In the reverse case, where C spontaneously reacts to form $\text{A} + \text{B}$ at some different T, P conditions, then A and B are stable together, and no separation is implied.

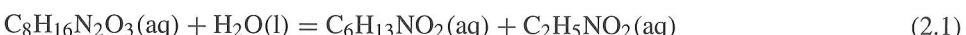
Some metastable systems of course may have *more* than one extra constraint. Consider $\text{A} + \text{B} = \text{C}$ again, this time where A is H_2 gas, B is O_2 gas, and C is H_2O liquid, where the T is 25°C and the P is 1 bar. If the H_2 and O_2 are in separate parts of a container separated by a partition, they are of course constrained from reacting, and the partition represents a first constraint. If the partition is then removed, the gases mix but they do not react to form

water, because there is an activation energy barrier that must be overcome; this represents a second constraint. Finally, if a catalyst is introduced, removing this constraint, the gases react to form the stable phase, water.

So when we speak in coming chapters of metastable \rightarrow stable reactions, we mean to include *any* spontaneous chemical reaction, not just those involving minerals. Whatever the nature of the constraint in reality, there is only one way of representing it in thermodynamics. In thermodynamics a constraint is a mathematical variable, and we see what this is in Chapter 4.

2.6.2 Reactions Involving Organic Compounds

Reactions involving organic compounds, whether in living organisms or not, are no different in principle from any other kind of reaction, such as those between minerals. The only difference is that, for organic compounds, the reaction usually proceeds from one metastable state to another metastable state of lower energy, rather than from a metastable state to a stable state. Consider for example the reaction



which represents the breaking of a peptide bond between two amino acids, one of the more fundamental processes in biochemistry. The (aq) here means that the compounds we are discussing are dissolved in water and, hence, the reaction takes place in water. If we use names rather than chemical formulae, this is



This reaction occurs spontaneously, and the energy relations can be depicted exactly as for simpler compounds. The only difference is that, rather than reacting to compounds in the lowest possible energy state, leucylglycine plus water reacts to form compounds in another metastable state (leucine plus glycine) of lower energy than the initial state, as

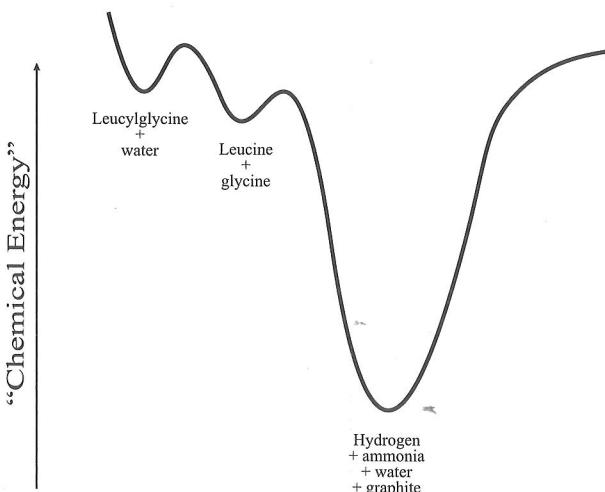


Figure 2.9 Energy relationships between organic compounds. Most organic compounds have much higher energy contents than do combinations of simple inorganic compounds of the same overall composition.

Box 2.2 Volume Change

The volume data in Appendix B are listed under V° . In reaction (2.5) then,

$$\begin{aligned}\Delta_r V^\circ &= V_{\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}}^\circ - V_{\text{Al}_2\text{O}_3}^\circ - 3 V_{\text{H}_2\text{O}}^\circ \\ &= 63.912 - 25.575 - 3 \times 18.068 \\ &= -15.867 \text{ cm}^3 \text{ mol}^{-1}\end{aligned}\quad (2.6)$$

There is therefore a net decrease in volume of $15.867 \text{ cm}^3 \text{ mol}^{-1}$ for the reaction as written. But you could equally well write

$$\begin{aligned}\Delta_r V^\circ &= \frac{1}{3} V_{\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}}^\circ - \frac{1}{3} V_{\text{Al}_2\text{O}_3}^\circ - V_{\text{H}_2\text{O}}^\circ \\ &= -5.289 \text{ cm}^3 \text{ mol}^{-1}\end{aligned}\quad (2.7)$$

Or you could write

$$\begin{aligned}\Delta_r V^\circ &= 2 V_{\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}}^\circ - 2 V_{\text{Al}_2\text{O}_3}^\circ - 6 V_{\text{H}_2\text{O}}^\circ \\ &= -31.734 \text{ cm}^3 \text{ mol}^{-1}\end{aligned}\quad (2.8)$$

Note that each volume must be multiplied by its corresponding stoichiometric coefficient in the reaction. Despite some controversy on this subject (Craig, 1987), stoichiometric coefficients have no units. They are dimensionless. All these results are $\text{cm}^3 \text{ per mole}$, so the question is, per mole of *what*?

The lesson here is that $\Delta_r V^\circ$, or the reaction delta of any other state variable, refers to the reaction *as written*, which can be variable. Generally though, the delta referred to is the volume change per mole of whatever species have a stoichiometric coefficient of 1.0. The volume change is -15.867 cm^3 per mole of Al_2O_3 consumed or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ formed (Equation (2.6)), and -5.289 cm^3 per mole of H_2O consumed (Equation (2.7)). For reactions where *no* species has a stoichiometric coefficient of 1.0, like reaction (2.8), we seem to have a problem. Obviously the volume change here is per *two* moles of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, not one. It would be quite unusual to write a reaction this way, but, if it bothers you, divide by two and rewrite the reaction as reaction (2.6).

2.8

Time as a Thermodynamic Variable

McGlashan (1979, p. 102) says

There are those who say that time has no place in thermodynamics. They are wrong.

According to the presentation of thermodynamics in this text, McGlashan is wrong. Time is mentioned, but (significantly) not used mathematically, by many authors. These authors are all of course aware that there is no variable called “time” in equilibrium

thermodynamic theory, so why is this idea so prevalent? One reason might be that entropy as “the arrow of time” seems to be firmly established.

A simpler example is the hot cup of coffee which cools down to equilibrium with its surroundings. But, it is said, evaporation continues until the water is gone, then the remaining coffee grounds slowly oxidize, and after a few eons the glass or ceramics in the cup may recrystallize to more stable forms, so time must be specified when defining equilibrium. All such cases are examples of the failure to distinguish between real systems and thermodynamic models of these systems.

As discussed in Section 2.3, real systems *never* achieve thermodynamic equilibrium as defined by Gibbs, though they often closely approach this state. Thermodynamic models of these systems, however, represent only thermodynamic equilibrium states, stable or metastable. Given appropriate data, we could calculate the properties of the cooling coffee such as its vapor pressure (or fugacity) at any point in its cooling history, but each calculation would necessarily assume the coffee to be in a metastable equilibrium state. We actually do this kind of calculation in Chapter 13. In thermodynamics integration and differentiation are never performed with respect to time, only with respect to state variables, with equilibrium assumed to be present throughout. There is no time variable in equilibrium thermodynamics, and that should be the end of it.

Well, not quite. In engineering thermodynamics, time is definitely a variable. However, it is used to denote the rate of mass and energy fluxes, and has no connection with equilibrium or the increase in entropy.

2.9

Thermodynamics and Natural Systems

We have emphasized that thermodynamic data and thermodynamic relationships are derived for and in theory can only be applied to idealized equilibrium states, but that real equilibrium states come sufficiently close to the ideal that our thermodynamic methods are useful. These real equilibrium states in natural systems occur in places having local equilibrium, which means that even a system in overall disequilibrium will have places where equilibrium is closely approached, and thermodynamics can be applied to samples from those places providing information about the system.

But there are other ways in which thermodynamics is useful, regardless of local equilibrium. One has to do with the development of thermodynamically consistent theories of geological processes. In Chapter 9 we consider a number of reactions involved in the formation of lead–zinc ore deposits. Field observations have provided an abundance of data on mineral compositions, fluid inclusions, structures, age relations, and so on. The problem is that of how to develop a theory of ore formation, a conceptual series of events that would result in the ore deposit as we see it; and these events must of course be thermodynamically possible. Thermodynamics provides the essential framework within which natural processes must work. We might propose that the ore solution contained A and B, but thermodynamics tells us that in that case we will have C, which doesn’t fit with field observations. We could have A and D, but then we need E, but where does E come from? And so on. Note that in this work field observations are just as important as thermodynamic calculations.

Another way thermodynamics is used to better understand natural systems is geochemical modeling. A common practice in the geochemical literature is to follow, in a computer program, the irreversible reactions in some complex starting composition through any number of irreversible reactions and phase changes to the final stable equilibrium state in a series of small increments of reaction. The classic case, introduced by Helgeson (1968) is the dissolution of K-feldspar in water, where tiny amounts of the mineral, represented by a mathematical variable, are added to the solution until the final equilibrium state is achieved. After each increment all the species involved in all the reactions are adjusted to their equilibrium activities and any phase changes thus made necessary are performed at that point in the reaction. The bulk composition is unchanged. Each of these intermediate compositions represents a metastable equilibrium state within the overall irreversible reaction, and the series of such states represents an idealized reaction path. Such computed reaction paths do not necessarily represent what happens in reality, but they usually provide useful information nonetheless, and are routinely performed by petrologists, oceanographers, and others. A variety of these modeling programs, both free and commercial, is available. Steinmann *et al.* (1994) show how, with some assumptions, one particular reaction path can be calculated using a spreadsheet. In addition to the irreversible reactions and phase changes just described, recent developments have added kinetics, surface effects, advective–dispersive–diffusive transport, cooling, and other factors, but thermodynamics remains essential.

Just because thermodynamics is derived and is strictly speaking true only for idealized and unattainable equilibrium states does not make it useless. It is part of the learning process to find out how this can be.

2.10

Summary

If you look around the physical world today, you realize that there are incredibly many chemical and physical processes going on all around you, and as you look into these in more and more detail, as science has done, you find more and more complexity at all levels, right down to the atomic and subatomic levels. How can we systematize and understand these processes in such a way as to be able to control some of them for our own purposes?

Thermodynamics is one result of our attempts to do this, at the macroscopic level. It is not a description of any real process, but a rather abstract *model* that can be used for all real processes. Processes in the real world are incredibly complex, but our models of them are quite simple, containing a number of carefully defined concepts. *Processes* (reactions, changes) involve changes in energy and/or mass, and these must enter or leave the place where the process is occurring; so thermodynamics begins by defining several types of *systems*, depending on how the energy and/or mass is transferred. Processes must be defined by beginning and ending states, so thermodynamics defines *equilibrium* states, some having more energy (*metastable equilibrium* states) than others (*stable equilibrium* states), and processes or reactions that are able to go from higher energy states to lower energy states (*irreversible processes*), just like a ball rolling down a hill. Of course, a state of lower energy (stable) under one set of conditions may be a state of higher energy (metastable) under other conditions (diamond is metastable at the Earth’s surface, but

stable deep in the mantle). Corundum and water are, by themselves, perfectly stable and unreactive, but together they have a higher energy state than does gibbsite.

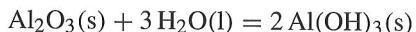
The only thermodynamic difference between organic reactions (including those in living organisms) and inorganic reactions is that both the reactants and the products of organic reactions are invariably metastable compounds; metastable, that is, with respect to simple inorganic compounds and elements. Inorganic reactions *may* involve metastable compounds, but more frequently they involve a metastable *assemblage* changing to a stable one (one having the lowest possible energy state).

Therefore, the determination of the energy states of substances and how they change under changing conditions is fundamental to understanding what processes are possible, and why they happen. The determination of the energy states of individual substances must be done for the most part by experiment and measurement, not by theoretical calculation, and the results are available in tables of data like those at the end of this book. Calculation of the change of these energy terms with changing conditions can be carried out only for hypothetical *reversible processes*, that are not possible in reality but are quite simple in the thermodynamic model.

The most important question now is what kind of energy is released during these reactions? If it is not heat energy, then what is it? We have called it “chemical energy,” but that is just because we haven’t said yet what it really is. This is the topic of the next two chapters.

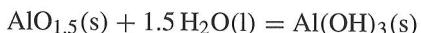
Exercises

E2.1 Calculate the volume change for the reaction



$\text{Al(OH)}_3(\text{s})$ is another way of writing the formula for gibbsite.

E2.2 Calculate the volume change for the reaction



$\text{AlO}_{1.5}(\text{s})$ is another way of writing the formula for corundum.

E2.3 Calculate $\Delta_r V^\circ$ for reaction (2.1),



E2.4 Calculate $\Delta_r V^\circ$ for the reaction



Note that the standard volume of many ions is negative. How can any substance have a negative volume?

E2.5 (a) How many components are there in pure enstatite MgSiO_3 ?

(b) How many components are there in enstatite solid solution $(\text{Mg}, \text{Fe})\text{SiO}_3$?

(c) How many components are there in olivine solid solution $(\text{Mg}, \text{Fe})_2\text{SiO}_4$?

(d) How many components are there in coexisting enstatite and olivine solid solutions?