

Thermodynamics of Natural Systems

Theory and Applications in Geochemistry
and Environmental Science

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G.M. ANDERSON



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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 (H_2O) 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?
- 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?

What Is Thermodynamics?

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 H₂O 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 in the following 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 last 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. Strang (1991, p. 102) says

In mechanics, nature chooses minimum energy.

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 reference level. 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

1.3 A Mechanical Analogy

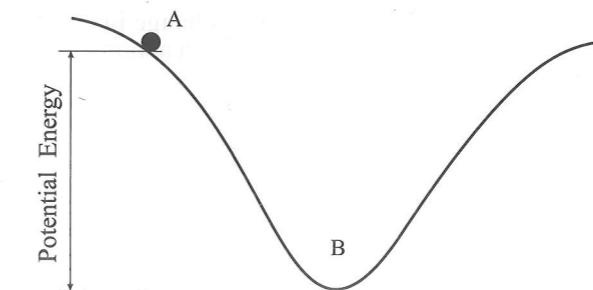


Figure 1.1 A mechanical analogy for a chemical system – a ball on a slope. The ball will spontaneously roll into the valley.

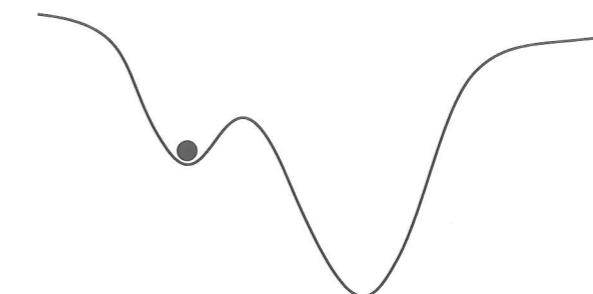


Figure 1.2 The ball has rolled into a valley, but there is a deeper valley.

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.

It was discovered quite early that most chemical reactions are accompanied by a release or liberation of heat. This is most easily seen when you strike a match, but in fact the freezing of water is also a heat-liberating process. It was quite natural, then, by analogy with mechanical systems, to think that various substances contained various quantities of heat, which was thought to be a substance called caloric, and that reactions would occur if substances could rearrange themselves (react) so as to *lower* their heat or caloric content. These days we know that heat is a form of energy transfer, and we prefer to say that reactions lower some kind of *energy*, not just heat. 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 so as to lower (in fact, minimize) their *chemical energy*, although sometimes, like diamond, they may get stuck in a valley (an energy level) higher than another nearby valley. We will see that this is in fact the case. The analogy *is* useful. We know that energy is manifested in different forms, so the problem lies in discovering just what kind of energy is being minimized. What is this *chemical energy*?

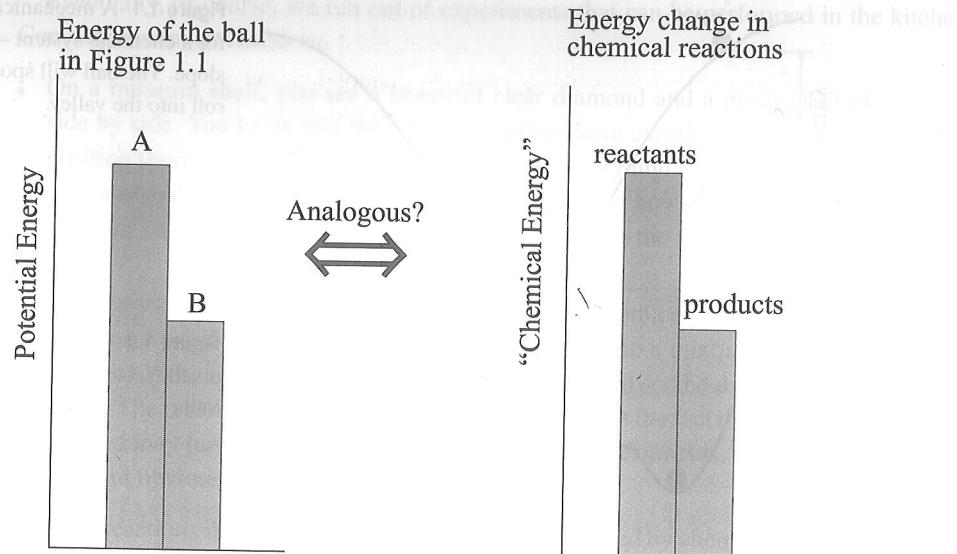


Figure 1.3 Mechanical processes always act so as to lower the potential energy content of the mechanical system. Perhaps, by analogy, chemical systems have some sort of “chemical energy” that is lowered during chemical reactions.

1.3.1 Chemical Energy

We mentioned that an early idea was that it is the heat (caloric) 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 caloric content of the *products* is less than the caloric 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. 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 process 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 factor involved. What other factors might there be? Not too many, we hope!

1.3.2 Plus Something Else?

Another 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. We are using the terms *reaction* and *process* more or less synonymously here. Strictly speaking

there is a difference; a chemical reaction is one kind of process, but there are others. Some spontaneous processes are characterized by *mixing*, rather than by a reorganization of molecular structures like graphite → diamond, or raw egg → fried egg. In fact even just warming or cooling is a process, and some processes, like metamorphism, might include many reactions. We will give a more exact definition in Chapter 2, but clearly our “chemical energy” term will have to take account of all these observations.

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 many complications. 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.

1.4

Thermodynamic Potentials

The ball-in-valley analogy as introduced in Figures 1.1 and 1.2 is intended to show *not only* that chemical systems strive to achieve equilibrium by decreasing some kind of “chemical energy” but also that, when at equilibrium, i.e., at the bottom of some valley, they achieve an *extremum* in the mathematical sense. This is instructive because it turns out that thermodynamics has functions called *thermodynamic potentials* (Section 4.3), which exhibit a minimum or maximum for many systems in a state of equilibrium. To illustrate what this means, we can look more closely at the analogy.

Consider a ball which has achieved a minimum potential energy as in Figure 1.2. It doesn’t have to be the lowest minimum available or a symmetrical valley, so, to be a little more general, we can choose a valley described by the function (Strang, 1991, p. 98)

$$y = x + \frac{1}{x} \quad (1.1)$$

shown in Figure 1.4, for which the derivative is

$$\frac{dy}{dx} = 1 - \frac{1}{x^2} \quad (1.2)$$

The minimum of the function occurs where the derivative, the slope of the curve, is zero, which in this case is where $x = 1$ and $y = 2$. Because the second derivative $d^2y/dx^2 > 0$ it is a minimum. In other words, when the derivative dy/dx equals zero, this tells us that the function has an extremum, and implies that the differential is also zero, or $dy = 0$.

1.4.1

An Exact Differential

Differentials are ubiquitous in thermodynamics. It is absolutely essential to have a clear understanding of what they mean. The differential dy is defined in terms of the derivative of the function; that is,

$$dy = \frac{dy}{dx} dx \quad (1.3)$$

$$= y'(x)dx \quad (1.4)$$

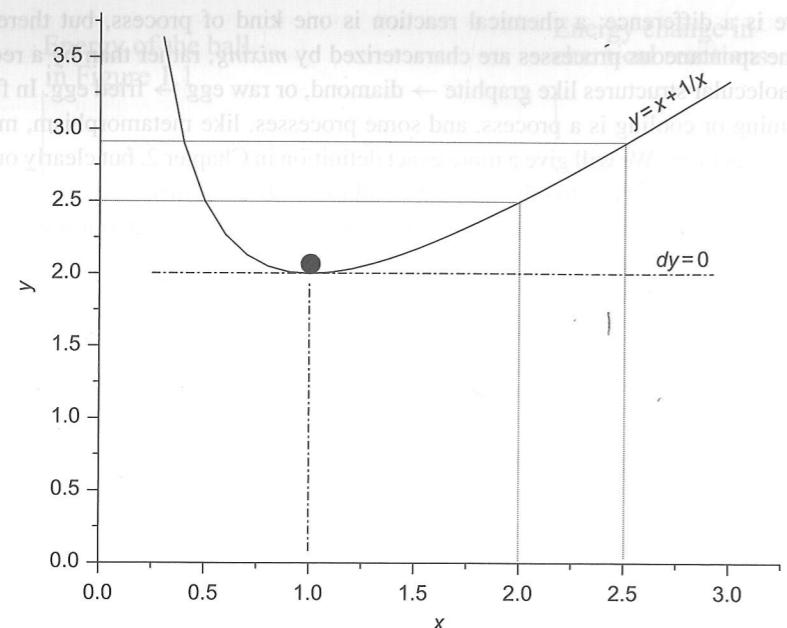


Figure 1.4 A valley described by the function $y = x + 1/x$. The minimum occurs where both the derivative dy/dx and the differential dy are zero.

where, in the case of the function in Equation (1.1), dy/dx is defined in Equation (1.2) and $y'(x)$ is another way of writing the derivative. This way is perhaps preferable because it emphasizes that the derivative is just another function of x . The derivative dy/dx is not, as it appears, a fraction composed of two quantities called dx and dy , but defining the differential separates them; it creates the separate quantities dx and dy . Each can now have any magnitude, and they are not necessarily infinitesimals. Furthermore, if the derivative is zero, as it is at an extremum in the function, then dy is also zero, by Equation (1.3) or (1.4).

If we integrate dy between limits, we get

$$\int_a^b dy = \int_a^b y'(x) dx \quad (1.5)$$

$$= y(b) - y(a) \quad (1.6)$$

$$= \Delta y \quad (1.7)$$

The significance of this in thermodynamics is that, if y is some physical parameter (say volume V) which is a function of some other parameter x (say temperature), then the change in V because of some change in x from a to b can be calculated *no matter what the volume of the real system actually does* as x changes from a to b . The system may be completely out of equilibrium between the equilibrium states V_a and V_b so the system doesn't actually have a defined volume during the change, but we can calculate the change anyway if we have a function describing the change of V from V_a to V_b . In this case dV is called an exact differential; it is derived from a continuous function and can be integrated. The reason for discussing this here is that we will soon come across other differentials (the

differentials of work and heat) which are not derived from any function, and cannot be integrated in this way.

Just to complete this example, let's say $a = 2.0$ and $b = 2.5$. Then

$$\begin{aligned} \Delta y &= y(2.5) - y(2.0) \\ &= (2.5 + 1/2.5) - (2.0 + 1/2.0) \\ &= 2.9 - 2.5 \\ &= 0.4 \end{aligned}$$

As x changes from 2.0 to 2.5, the change in y is 0.4. Perfectly simple when dealing with a mathematical function like $y = y'(x)$. Not quite as simple when the variables are thermodynamic parameters representing real things.

We will find that thermodynamics has functions that behave exactly like this; they are continuous, have exact differentials, and may have a maximum or minimum. We take a closer look at them in Chapter 4. Because these functions, called thermodynamic potentials, are a central feature of thermodynamics, the concept of differentials in calculus becomes important. If you have any doubts about what a differential is, or the difference between a differential and a derivative, see the discussion in the online resources or in one of the many calculus textbooks.

Topics in Mathematics

At several places in the text there is a reference to some mathematical subject in the online resources. Subjects like Legendre transforms, Euler's theorem, homogeneous functions, etc., as well as some of the more arcane aspects of Gibbs' fundamental writings on thermodynamics, are not necessary for an introduction to the subject, but they do offer a different perspective on thermodynamics which in some ways is simpler, though not to everyone's taste. There is also a bit more discussion of some essential topics in the text such as here, on the meaning of differentials.

1.5

Idealization in Thermodynamics

Despite its immense usefulness in real life, thermodynamics, like all physical theories, describes not real systems, but models of real systems. It is easy to confuse these two things. We have already illustrated the difference by referring to a valley as the function $y = x + 1/x$. No real valley is described exactly by this function, though some might come close. The function and the curve it describes constitute a two-dimensional or cross-sectional *model* of a real valley. As Cartwright (1983, p. 129) says,

... fundamental equations do not govern objects in reality; they govern only objects in models.

Feynman *et al.* (1963, p. 12–2) say

...in order to understand physical laws you must understand that they are all some kind of approximation.... The trick is the idealizations.

Thermodynamic theory is a bunch of mathematical expressions such as simple linear differential equations. But Feynman *et al.* also say

... mathematical definitions can never work in the real world.

Engineering design problems are also based on models. Jones and Dugan (1996, pp. 17–18) say

In solving physical problems, we usually focus our attention *not* on the actual system but rather on some idealized system that is similar to, but simpler than, the actual system. ... For example, in calculating the mechanical advantage of a system of ropes and pulleys (*actual system*), we might start by considering a *model* composed of non-stretching weightless ropes and frictionless pulleys.

In this view classical chemical thermodynamics is a model of energy relationships in chemical systems in which many aspects of real systems are represented by equations which work only for idealized systems. Thermodynamics seeks to represent or to simulate reality, but, because it is made up of the differential and integral calculus, it can do this only in an idealized way. We will see that this idealization means that only equilibrium states can be represented by our equations, which is why the subject is often called *equilibrium thermodynamics* or *thermostatics*.

The reason for emphasizing this somewhat philosophical point is that many aspects of thermodynamics (e.g., ideal solutions, reversible processes) are physically unrealistic. It helps to remember that we are using mathematics to simulate real systems.

The Equilibrium Paradox

The fact that our thermodynamic functions represent *only* equilibrium states, plus that natural systems are rarely, if ever, at equilibrium, obviously presents a paradox. How is it that a bunch of equations derived for idealized, non-existent equilibrium conditions can be useful in trying to understand real, not even close to equilibrium, processes like ore deposit formation and groundwater contamination? This is an important question to keep in mind as you progress through the text.

1.6

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 with one another, and determining which is more stable under the circumstances. We will not consider how fast the reaction will proceed, or

how to tell whether 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 that a reaction *should* occur but also *whether* it occurs, and at what rate. A great deal of effort has also been directed toward understanding the structures of crystals and solutions, and 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, 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.

1.7

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 change into diamond, or vice versa? Or why does it *not* change? 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 down 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 the 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 processes that have no energy change. Determining the parameters of our “chemical energy” analogy is at the heart of chemical thermodynamics.

Exercises

E1.1 In Figure 1.4 assume that y is distance in meters. Calculate the change in potential energy of a ball having a mass of 100 g as it rolls from its position at $y = 4.0\text{ m}$