Water-Rock Interactions, Ore Deposits, and Environmental Geochemistry: A Tribute to David A. Crerar
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Stable and metastable equilibrium: The third constraint

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> ...fundamental equations do not govern objects in reality; they govern only objects in models
>
> —*Cartwright (1983).*

1. INTRODUCTION

Most people who have tried it would agree that teaching thermodynamics is a difficult task. Yet exactly why this is so is hard to explain. Certainly the mathematics involved is not the problem—it includes little more than relatively simple differential and integral calculus. The nature of the experiments involved is not the problem—simple piston-cylinder arrangements, calorimeters and chemical reactions are not usually mystifying to students. The problem seems to lie somewhere in the union of these two aspects—the physical meaning of the thermodynamic variables and processes, and how they are related to the real processes we observe around us every day. The questions that seem to bother us all when learning thermodynamics boil down to wondering how on Earth this collection of hypothetical systems, unattainable states, unknowable parameters and impossible processes can be of any use in the real world. Yet we know it can, and the learning process for most of us probably involves "getting used to it" more than getting to understand it. As Dickerson (1969) said, "It is quite possible to know thermodynamics without understanding it".

I describe here an approach to understanding the subject which has helped me. This approach emphasizes the role of models in science, and hence thermodynamics as a mathematical model of energy relationships, rather than as any description of real states or processes. In this, the role of *constraints* plays a central role, in particular, the *third constraint*, and the emphasis is on the meaning of metastable states.

2. SYSTEM

Virtually every textbook on thermodynamics begins by defining a system as some arbitrary part of the universe that interests us; a crystal, or a beaker containing some solution, or a gas, and so on.[1] Then it goes on to differentiate between closed, open and isolated systems, depending on the type of walls the system has, or how energy is able to be transferred to and from the system. Later, we have discussions of piston-cylinder arrangements, falling weights, and other very simple devices, all presumably real objects.

What's wrong with that? The problem is that thermodynamics, in common with virtually all physical theories, does not deal with any part of the real universe, but with highly simplified models, abstract objects characterized or described by systems of equations, which attempt to represent the behavior of selected parts of the universe. That it is reasonably successful at doing so makes it useful. The definition of system as some part of the universe is fine, if it is made clear that this is the system we are interested in. However, it is not really the system that thermodynamics deals with.

Every scientist is familiar with the concept of models, and normally will get impatient at any suggestion that he/she is deficient in this respect. Most scientists spend their lives devising models of physical or biological behavior, and the most successful ones, such as Newton's Laws of motion, Einstein's relativity, and quantum theory are justly famous. But consider the following:

> Strictly speaking, Newtonian physics must rank as the biggest confidence trick in the history of human learning: it makes all kinds of unrealistic assumptions about the existence of perfect vacuums, ideal gases, and frictionless processes, none of which ever occurs in nature.
>
> —*Dunbar (1995), p.98.*

This is a bit of hyperbole, used to grab the attention of the lay reader, but it illustrates a point well known to scientists, but not, generally, to others. Obviously, "Newtonian physics" does not apply to the real world, except to the extent that the simplified models that it does apply to mimic behavior in the real world. It works wonderfully well in guiding satellites in outer space, but not so well if you drop a feather and a rock together in a windstorm. All scientists know this.

Then why is it so common to pretend that "Gibbsian physics" applies to real geological systems?[2]

Well, you might say, true enough, but why make such a fuss about it? Can it be that important? Let's look a little further.

3. EQUILIBRIUM

Following the assertion that thermodynamics deals with real systems is generally the definition of equilibrium as a state of rest, of no perceptible change, in real systems (see variations of this in the Quotations section). However, some definitions are a little different, in that they mention the equality of temperature, pressure and chemical potentials throughout the system. Both definitions may occur in the same text.

A state of rest, or of returning to an initial state after a disturbance, can be used in observing real systems, and follows nicely from the definition of a system as a real crystal or solution, or whatever. A state of equal chemical potentials, however, can only be *inferred* from other observations, and clearly refers to models of systems, not real systems. In other words, the definition of equilibrium is quite different in real and model systems. As a matter of fact, it might be argued that no real system ever reaches equilibrium by the criteria applied to model systems. That is, there are always impurities, inhomogeneities and gradients of various sorts, however small, in all real systems.

3.1. Stable vs. Metastable

The distinction between stable and metastable equilibrium is generally that the stable equilibrium state is "truly unchanging", or unchanging given indefinite time, whereas the metastable state may be changing, but too slowly to be observed (see Quotations). This distinction clearly refers to real systems, and really misses the essential point.

In working with real systems it is quite common to be not at all sure whether equilibrium has been achieved, or if it has, whether it is stable or metastable. We even have systems which we know are not at equilibrium, but we apply thermodynamics to them anyway, using the local equilibrium concept (Knapp, 1989).[3] On the other hand, our thermodynamic models of these systems are invariably simple, and they are always at (perfect) equilibrium. As many authors have remarked, some thermodynamic quantities are not even defined in unstable states.[4] Furthermore, the distinction between stable and metastable is different, and completely under our control (because we make the model, we control every aspect of it).

The distinction between stable and metastable states in real systems is often difficult, and the usual definitions don't help much. We are quite sure that diamond is a metastable form of carbon at Earth surface conditions, but whether or not it will recrystallize to graphite given "indefinite time" is quite uncertain. On the other hand, aragonite is a metastable form of $CaCO_3$, but although common in recent rocks, it becomes progressively less common in older rocks, so maybe it is changing very slowly. Who knows? Obviously a messy topic, involving kinetics (Fyfe and Bischoff, 1965; Bischoff and Fyfe, 1968). But in both cases we know with certainty that there is a crystal form for that composition with lower energy. How to best express this in thermodynamic terms?

The best way is to discuss thermodynamic models of these systems, in which a metastable equilibrium state is a state of true or unchanging equilibrium, having a higher energy content than another state of the same composition and under the same conditions. It is prevented from spontaneously changing to this lower energy state by a *constraint*. In other words, the real system may be truly unchanging and metastable, or it may be unstable and changing very, very slowly. We don't know. But our model of this system has no such uncertainty. The system is modeled as metastable and unchanging. If the real system is really unstable, our model is in this respect incorrect, but probably useful nonetheless.

The subject of constraints deserves more discussion than is usually devoted to it. I originally realized the importance of constraints from reading Callen (1960) and Reiss (1965), but I now use the term slightly differently. This requires a bit of explanation.

3.2. Constraints

Constraint, like several other terms, has a slightly different meaning in real and model systems. Real systems, such as aragonite, are said to be constrained from reacting to a more stable state (calcite) by an activation energy barrier. The usage is rather imprecise, because we don't actually know if the aragonite is changing on some very long time scale or not. In model systems, the meaning is much more exact.

Thermodynamics deals with systems in various energy states. So we must begin (after defining our system) by defining how energy changes in these systems can occur. This in turn boils down to exchanges of heat and work, which we now know, after a great deal of confusion in the 19th century, are two forms of the same thing—energy. This results in the First Law,

$$\Delta U = q + w \tag{1}$$

where ΔU is the "internal" energy of a system, q is the energy transferred as heat, and w is the energy transferred as work.

There are many forms of work, but if we choose only the most common one, pressure-volume work, and after introducing entropy, equation (1) becomes

$$d\mathrm{U} = T\,d\mathrm{S} - P\,d\mathrm{V} \qquad (2)$$

There are two terms on the right side, because we chose two ways of changing energy (this is the origin of the '2' in the Phase Rule). If we instead chose two forms of work capable of changing our system energy, say pressure-volume work and work done by a magnetic field, equation (2) would have another term on the right side. We choose these terms (out of many possible choices), so this is already a model equation, not one about real systems.

To change the energy of a system at equilibrium, you must change a state variable. Therefore, each way of changing the energy of a system is associated with a state variable. A corollary is that, in model systems, equilibrium states can be characterized by their number of constraints, defined as state variables associated with the ways a closed system can change its energy content. The minimum number of constraints required to define an equilibrium state is two [e.g., S and V in equation (2)]. Equilibrium states having only two constraints have the lowest energy for given conditions and are stable equilibrium states. Equilibrium states having more than two constraints are *metastable* equilibrium states. Calcite, for example, has stable equilibrium states at chosen values of T and P within certain ranges. These are the two constraints. At these T and P values, aragonite has a third constraint, an energy barrier, which prevents it from recrystallizing to calcite. A system consisting of a beaker of water and a gram of solid salt also has three constraints—T, P, and the separation of water and salt. When the third constraint is released by adding the salt to the water, the system reaches stable equilibrium as a salt solution with only two constraints. At the risk of laboring the point, we are talking about model calcite and model aragonite. Real calcite and real aragonite have many other factors to consider, such as grain size, defects, impurities, strain energy, inhomogeneities, and so on. Normally, the simple model works well enough.

It may not be obvious what state variable could be associated with a "third constraint" consisting of an energy barrier or a separation of two parts of a system, but there is one. Whatever the nature of the third (or higher) constraint, the state variable used to describe it is the progress variable. If there are in fact three constraints, then there are three terms on the right side of equations dealing with energy change.

Switching variables from S and V to T and P, equation (2) becomes

$$d\mathrm{G} = -\mathrm{S}\,dT + \mathrm{V}\,dP \qquad (3)$$

for stable equilibrium states, and

$$d\mathrm{G} = \left(\frac{\partial \mathrm{G}}{\partial T}\right)_{P,\xi} dT + \left(\frac{\partial \mathrm{G}}{\partial P}\right)_{T,\xi} dP + \left(\frac{\partial \mathrm{G}}{\partial \xi}\right)_{T,P} d\xi \qquad (4)$$

or

$$d\mathrm{G} = -\mathrm{S}\,dT + \mathrm{V}\,dP - \mathbf{A}\,d\xi \qquad (5)$$

for systems with a third constraint. T and P are the state variables associated with the two constraints defining the stable equilibrium state. S, V, and $\mathbf{A}$ define the slopes of the plane defined by equation (5) in the T, P, and ξ directions, and the progress variable ξ is the state variable controlling departure from the most stable state. It is the "third constraint". The term $\mathbf{A}d\xi$ thus determines how far removed the state is from the stable equilibrium state, in terms of joules. We have complete control over ξ in our model (e.g., in reaction path programs), though often not in real systems. Thus, although the distinction between stable and metastable states is often difficult in real systems, it is perfectly clear cut in model systems.

This kind of definition then leads to a very simple distinction and rationale for reversible *vs.* irreversible processes. In real systems, there are innumerable examples of irreversible processes, providing the motive for introducing entropy. They often involve quite complex situations. In model systems, an irreversible process is what happens when you release a third constraint, and the system is usually very simple.

Of course, in a general sense, everyone knows this. In fact, many topics in thermodynamics can hardly be discussed at all without admitting in some way or other that we are using idealized models. These subjects include, in addition to reversible processes,

- isolated systems
- infinite dilution
- frictionless pistons
- ideal gases
- ideal one-molal standard states
- absolute zero temperature, and
- ideal (Henryan and Raoultian) solutions.

So the problem is perhaps not that we don't use idealized models in teaching and discussing, but that we don't admit that the whole thing is an idealized model, in common with all physical theory.

4. REACTION PATH MODELS

Although there are many ramifications of the "model vs. reality" theme throughout thermodynamics, the one most closely related to the subject of sta-

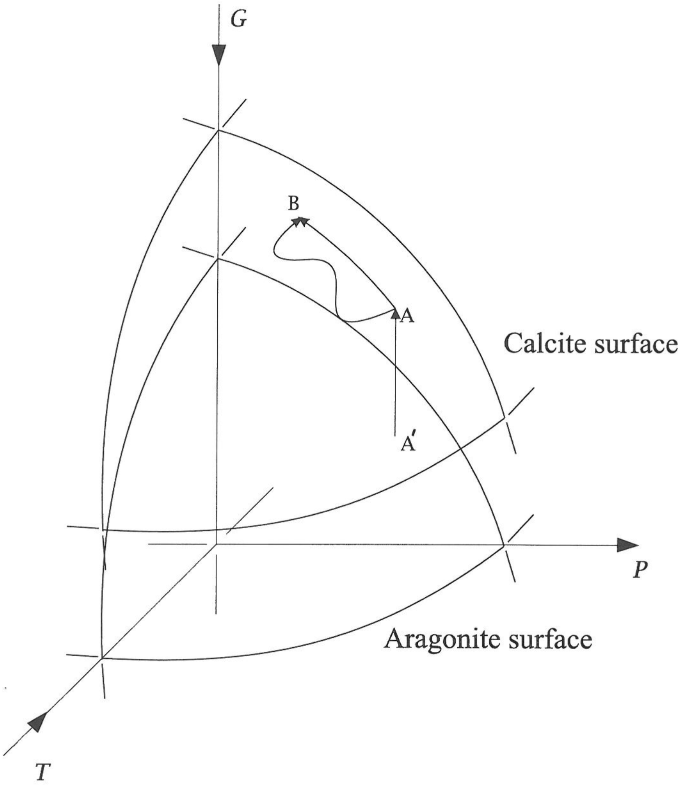

Figure 1. G–T–P surfaces for stable calcite and metastable aragonite. Note that for ease of representation, the G axis increases downwards. The two surfaces intersect somewhere off the diagram. Paths on a surface such as A → B represent reversible processes. Path A′ → A represents an irreversible process.

ble *vs.* metastable equilibrium is a proper understanding of the progress variable and reaction path models. Introduced by De Donder (1920), used extensively by Prigogine and Defay (1965) and made widely useful in the geochemical literature by Helgeson (1968, 1970), the progress variable has by now been discussed by many authors. Nevertheless, perhaps some confusion remains about how an irreversible reaction can be represented or calculated usefully by using strictly equilibrium thermodynamics.

It is here that a clear understanding of metastable equilibria is most useful. Figure 1 shows the G–*T*–*P* surface for a stable and a metastable form of the same compound, $CaCO_3$. At a given value of the two constraints *T* and *P*, aragonite has a more positive G than calcite, and is prevented from recrystallizing to calcite by a third constraint. The nature of the third constraint need not be made explicit, but in this case it is an activation energy barrier. Any line on either surface, such as the two shown (A → B), represents a reversible process, a continuous succession of equilibrium states. Within the calcite stability field, any change of aragonite to calcite (e.g., along A′ → A) is irreversible.

In real life, controlling this irreversible process would be extremely difficult, and more complex examples would certainly be impossible to control. In the model, we simply consider any number of intermediate metastable states, as shown in Figure 2, consisting in this case of various mass ratios of the two minerals.[5]

The classic case used by Helgeson (1979) is K-feldspar dissolving in water. The point of view expressed here is illustrated in Figure 3. The system as a whole is metastable, the third constraint being the separation of the feldspar and water. This separation is altered in small steps, represented by small grains dropping into the water. After each grain is added we have a new metastable state at complete equilibrium.

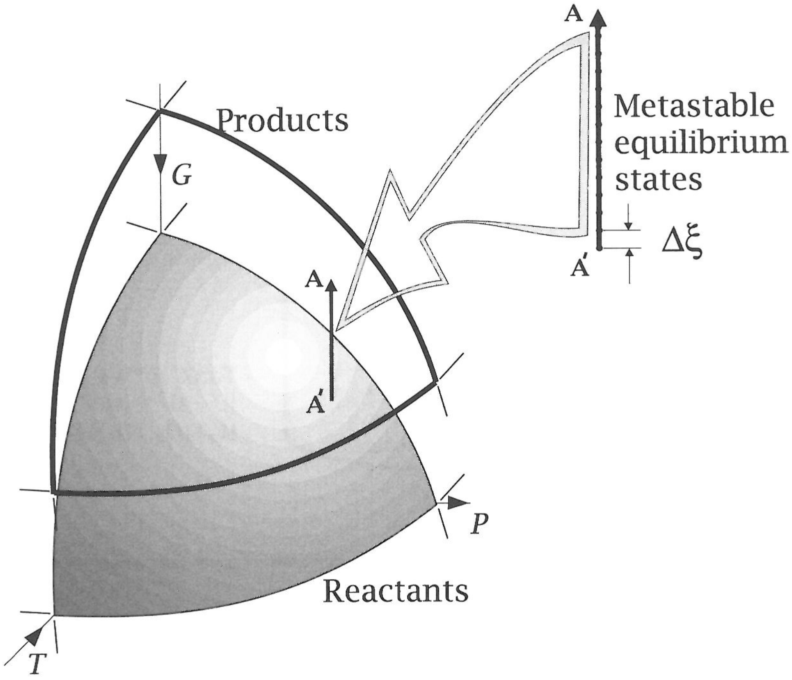

Figure 2. A sequence of metastable equilibrium states for the reaction A′ → A at constant T, P. The progress variable is ξ. Note that for ease of representation, the G axis increases downwards.

The common alternative to this explanation is a discussion of the dissolution of real feldspar in water, during which the feldspar dissolves slowly, and the system achieves what is called "partial equilibrium", because all solutes in the solution are at equilibrium, but the solution is not at equilibrium with the feldspar. This is simply another confusion of real and model systems. There is no such thing as partial equilibrium in model systems except in special cases, such as osmotic or semi-permeable membrane systems. All parts of model systems are in complete (stable or metastable) equilibrium.

5. PROGRESS PATH MODELS

Actually, equation (5) is quite general as to the nature of the third constraint, and the progress variable can be used to represent any kind of third constraint.

For example, if the system consists of an electrochemical cell, it will have an equilibrium voltage, which will gradually decrease to zero as the cell reaction takes place. In the model, this cell voltage can be controlled, and is the third constraint. It matters not how this is done in the model, but in real life it might be done with a potentiometer. This is a case where the metastable → stable transition is easily controlled, in contrast to many other situations.

If the system consists of a crystal having an equilibrium number of defects, we can consider cases with a greater or fewer number of defects, which will be metastable states. The third constraint is whatever we imagine as the control we have over the number of defects, which we can change at will using the progress variable. You might imagine this control being an ability to warm the crystal until the desired number of defects has formed, then quenching it so that they are "frozen in", but any discussion of this sort also misses the point, which, to repeat, is that we are dealing with model defects, not real ones. There is no mention of how one actually controls the number of defects in the model. In fact, one can usually detect "reality *vs.* model" confusion by any mention of time ('slow dissolution'; 'move the piston very slowly'; 'release the constraint for a very brief period'; 'quenching', 'freezing', 'thawing'; and so on). Time is important in real systems, but it has no place in equilibrium thermodynamics, McGlashan to the contrary notwithstanding.[6]

Many seemingly more bizarre cases (in the sense that they do not conform to normal lab practices) are actually quite common in the modeling world. In geochemical modeling, you can use practically any state variable as a third (or higher) constraint, and vary it at will. For example you can specify a *p*H or a particular gas fugacity. Controlling these state vari-

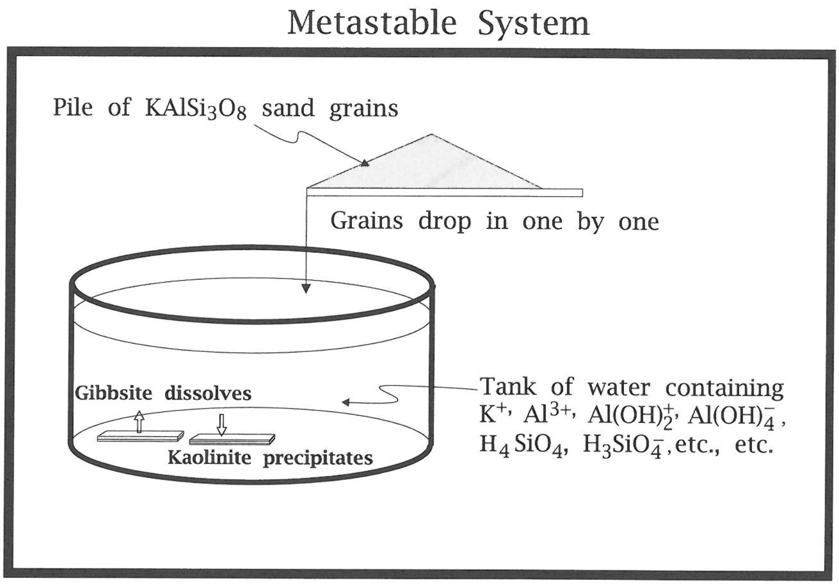

Figure 3. A possible conceptualization of the reaction path model for the dissolution of K-feldspar in water.

ables independently, rather than allowing them to be controlled by, say, *T*, *P*, and bulk composition, means they are additional constraints. This is discussed fully by Bethke (1996).

Of course, there may be more than one extra constraint. For example a system having four constraints (e.g., a battery in which the electrodes have a variable amount of strain energy), there would be two affinity variables and two progress variables, e.g.,

$$dG = -S\,dT + V\,dP - \mathbf{A}_1\,d\xi_1 + \mathbf{A}_2\,d\xi_2 \qquad (6)$$

where $\mathbf{A}_1$ represents the work energy that could be released by the battery running down to equilibrium, $d\xi_1$ represents increments of this process, $\mathbf{A}_2$ represents the amount of strain energy in the electrodes, and $d\xi_2$ represents increments of this strain energy.

6. CONSTRAINTS AND DEGREES OF FREEDOM

Is there any difference between these terms? Yes. First, it must be noted that the derivation of the Phase Rule, in which the concept of Degrees of Freedom normally appears, is based on systems at complete chemical, thermal, and mechanical equilibrium, in which chemical potentials are equal throughout.

Imposing a third constraint (imposing a voltage; changing the degree of order or of stress, recrystallizing to a different polymorphic form, etc.) on a closed system in a stable equilibrium state (one at equilibrium and having only two constraints, such as *T* and *P*) always requires doing work on the system, and releasing that constraint always allows the system to do work, whatever the nature of the constraint (Reiss, 1965). The result of this work being done sometimes results in a system in which the chemical potentials are not equal throughout, in which case the Phase Rule does not apply, and the constraint cannot be considered to be a Degree of Freedom, quite apart from the fact that Degrees of Freedom are defined as intensive variables, while **A** is extensive.

For example in the system $CaCO_3$, the chemical potential of $CaCO_3$ in calcite and aragonite are only equal on the two-phase equilibrium boundary. If we change some calcite to aragonite (or vice-versa) within the calcite stability field, the chemical potentials are clearly not equal in the two minerals, so the Phase Rule does not apply, and the constraint (preventing aragonite from changing spontaneously to calcite) is not a Degree of Freedom.

However, in some cases the resulting system does have equality of chemical potentials (as well as of *T* and *P*) throughout, so that the system does obey the Phase Rule, but with no added degrees of Freedom. For example aragonite, without calcite, in a phase assemblage, could be at equilibrium with equality of chemical potentials in all phases. Similarly, a granite in which all the crystals of SiO_2 happened to be cristobalite instead of quartz, could have μ_{SiO_2} (as well as all other potentials) equal throughout, and the Phase Rule would apply. The assemblage is metastable, a constraint is applied, but there is no added Degree of Freedom in the Phase Rule sense.

Constraints, as they are defined here, are certainly parameters which must be specified to completely define the system, but they do not qualify as Degrees of Freedom in the Phase Rule sense. Thus constraints are independent variables, but not every independent variable is a Degree of Freedom.

7. SUMMARY

It has long seemed to me that the distinction between metastable and stable systems is very central to an understanding of thermodynamics, and that the distinction is made easier by clearly distinguishing between real systems and model systems. In my view, making this distinction is one of the secrets to understanding thermodynamics, because the hypothetical systems, impossible processes, and unknowable parameters are then seen to be parts of a mathematical framework, a model, related to real systems only by virtue of using measured parameters as variables. We make simple models using thermodynamics, and we compare them to much more complex natural systems. In the process, we use many of the same terms in both kinds of systems. As a result, some simple thermodynamic concepts can get unnecessarily confused.

Acknowledgments—This article seems appropriate for a volume dedicated to the memory of David Crerar. David was my first graduate student. He was intensely interested in thermodynamics. We discussed the books by Reiss (1965) and by Callen (1960) many times, the ideas in which eventually led to those expressed here. I thank Tom Giordano and three anonymous reviewers for their comments, which led to improvements in the manuscript.

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APPENDIX

Some Illustrative Quotations

Models

> What is the status of claims that are typically cited as "laws of nature"—Newton's Laws of Motion, the Law of Universal Gravitation, Snell's Law, Ohm's law, the Second law of Thermodynamics, the Law of Natural Selection? Close inspection, I think, reveals that they are neither universal nor necessary—they are not even true.
>
> —*Giere (1999), p. 90.*

> What one learns about the world is not general truths about the relationship between mass, force, and acceleration, but that the motions of a vast variety of real-world systems can be successfully represented by models constructed according to Newton's principles of motion.
>
> —*Giere (1999), p. 95.*

> What one learns about the world is not general truths about the relationship between systems and energy, but that a vast variety of real-world systems can be successfully represented by models constructed according to equilibrium thermodynamics.
>
> —*A paraphrase of Giere (1999), p. 95.*

> The calculus is a mathematical theory, a set of connected concepts, but it emerges in human history as the expression of a fantastic and unprecedented ambition, which is nothing less than to represent or re-create the real world in terms of the real numbers.
>
> ...The world that the calculus reflects cannot be discerned by the senses, and the world that can be discerned by the senses this mirror does not reflect.
>
> —*Berlinski (1995), p. 288.*

> A model is a simplified version of reality that is useful as a tool.
>
> —*Bethke (1996), p. 9.*

> Let us not grace loose thinking with the term `model'.
>
> —*Greenwood (1989), p. 12.*

Constraints

> The basic problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed composite system.
>
> —*Callen (1960), p. 24.*

> Every state of equilibrium is subject to certain constraints which are imposed upon the system.
>
> ...Constraints are always associated with variables. The addition of a constraint implies the addition of an independent variable.
>
> ...Just as constraints and variables are in one-to-one correspondence with one another, they are each in one-to-one correspondence with the kinds of work which a system may perform on its environment or vice versa.
>
> —*Reiss (1965), p. 11–13.*

System

> ...a system, which is any region of the universe, large or small, that is being considered in our analysis.
>
> —*Klotz (1964), p. 35.*

> A thermodynamic system is any part of the universe we choose to study.
>
> —*Fletcher (1993), p. 3.*

> A natural system is any part of the universe we choose to consider, such as the contents of a beaker, a crystal of quartz, the solar system, or a bacterium. Thermodynamic systems, on the other hand, are not real but conceptual and mathematical, and are of three types. The three types are used to distinguish between the ways that changes in composition and energy content can be effected, and therefore they are defined basically by the nature of their boundaries.
>
> —*Anderson (1998)*

Equilibrium

> ...none of its thermodynamic properties are changing at a measurable rate.
>
> —*Reiss (1965), p. 3.*

> If a system is in complete equilibrium, any conceivable infinitesimal change in it must be reversible.
>
> —*Guggenheim (1959), p. 15.*

> A system is said to have attained a state of equilibrium when it shows no further tendency to change its properties with time.
>
> —*Moore (1962), p. 6.*

> ...a state in which no further change is perceptible, no matter how long one waits. The system is then said to be in equilibrium.
>
> —*Pippard (1966), p. 6.*

> For any given closed or isolated system, each substance and group of substances can be in its most stable state, which would be the state of stable equilibrium. If any substance or assemblage of substances had not reached that state but showed no apparent change with time, then it would be in a state of metastable equilibrium.
>
> —*Nordstrom and Munoz (1985), p. 12.*

> We are thus led to consider a system not in chemical equilibrium in which however the chemical reactions leading towards its attainment have been virtually suppressed. The system is then in a special kind of metastable equilibrium sometimes called frozen equilibrium.
>
> —*Guggenheim (1959), p. 42.*

Experimental conditions under which an internal variable ξ does not change will be called freezing-in conditions and an internal variable that does not change due to such conditions will be regarded as being frozen-in.

—*Hillert (1998), p. 11.*

The concept of metastability seems to have been employed mainly to indicate the degree of control the experimenter has over the constraint.... However, from the thermodynamic point of view, differences in degree of control are meaningless.

—*Reiss (1965), p. 17.*

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

—*Herzfeld, (1962), p. 41.*

ENDNOTES

[1] A few examples are quoted at the end of this article. The quotations are illustrative; they do not necessarily reflect the present viewpoint.

[2] Confusion about the use of models in science is also at the heart of much controversy in the philosophy of science, usefully discussed by Giere (1999). See the quotations at the end of this article.

[3] Local equilibrium is a feature that real systems must have, to be modeled successfully by thermodynamics. It is not a part of thermodynamics itself.

[4] By this I mean that no equations in classical thermodynamics refer to unstable states. There are inequality relations, but these are always between metastable equilibrium states, or metastable and stable equilibrium states. Kinetics, on the other hand, always deals with unstable states.

[5] A more detailed mathematical treatment of this simple example is found in Anderson (1995), Chapter 12.

[6] "There are those who say that time has no place in thermodynamics. They are wrong." —McGlashan (1979), p.102.