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TRUTH AND BEAUTY IN THERMODYNAMICS

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ABSTRACT

Carmichael (1970) identified crossing isograds in the Whetstone Lake area of Ontario, a finding that had been predicted by Greenwood (1962, 1967). This prediction was based on thermodynamic reasoning applied to a generalized two-volatile mineral reaction, using no data of any kind. Of course, the position of the curves in P–T–$X(CO_2)$ space does require data. A discussion of this example in terms of the thermodynamic concepts of system and equilibrium shows that they are unnecessarily confused by applications to real-world problems. A special case is metastable equilibrium, which is of fundamental importance and is defined in terms of constraints, not reaction rates. Thermodynamics is beautiful, because it is a mathematical theory of great simplicity and great power, and without correction factors, it is true in some ideal world. But it is not only beautiful and true, it is also mysterious, because we don't know why mathematical equations using physical parameters as variables should mimic natural processes so closely.

Keywords: thermodynamics, constraints, metastable, isograds, Whetstone Lake, Ontario, mathematics, equilibrium, system.

SOMMAIRE

En identifiant un croisement d'isogrades dans la région du lac Whetstone, en Ontario, Carmichael (1970) a ainsi découvert un phénomène qu'avait prédit Greenwood (1962, 1967). Cette prédiction est fondée sur un raisonnement thermodynamique appliqué à une réaction généralisée impliquant des minéraux et une phase volatile à deux composantes, et elle repose sur aucune donnée. Comme de raison, la position des courbes représentant les équilibres en termes des coordonnées P–T–$X(CO_2)$ requiert des données. Une discussion de cet exemple en termes des concepts thermodynamiques de système et d'équilibre montre que ceux-ci deviennent confus sans necessité par les applications faites à de vrais exemples. Un équilibre métastable serait un cas spécial, ce qui revêt une importance fondamentale; un tel équilibre se définit en termes de contraintes et non de taux de réaction. L'approche thermodynamique possède une beauté parce qu'il s'agit d'une théorie mathématique de grandes simplicité et puissance; sans facteurs de correction, elle rejoint la réalité dans un monde idéal quelque part. Elle possède non seulement beauté et vérité, mais elle est mystérieuse, parce que nous ne savons pas pourquoi les équations mathématiques utilisant des paramètres physiques comme variables devraient simuler les processus naturels avec tant de succès.

(Traduit par la Rédaction)

Mots-clés: thermodynamique, constraintes, métastable, isogrades, lac Whetstone, Ontario, mathematiques, équilibre, système.

INTRODUCTION

The subjects of truth and beauty are clearly well outside the limits of metamorphic petrology in any philosophical sense. Nevertheless, as petrologists, we do try to get at the truth of what happened in the past in some field area, and we do regard some ideas about this as really beautiful, whatever these terms "really'' mean. The term "beautiful'' is often used by physicists about some theory. No exact definition exists, but it usually includes the notions of explanatory power combined with simplicity. Of course, "simplicity'' is also difficult to define. What is simple to a physicist may be Greek to you and me. Nevertheless, thermodynamics certainly qualifies on both counts.

Thermodynamics is relatively simple, shown by the fact that geologists use it all the time, and it is one of the cornerstones of the physical sciences, which indicates its explanatory power. So perhaps it is beautiful. As for truth, of course no one doubts the "truth'' of thermodynamics. It is one of the most fundamental of all scientific theories: of course it is "true''. But in what sense is it true?

I suggest that in thermodynamics, the concepts of truth and beauty are connected, that to see the real beauty of thermodynamics, one has to see the exact

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sense in which it is true, and that this helps in understanding thermodynamics itself. In the following, my use of the term thermodynamics is limited to equilibrium thermodynamics.

THERMODYNAMICS AND MATHEMATICS

Explanatory power in science invariably involves using mathematics, a fact that is generally taken for granted. Obviously, too, thermodynamics consists of a system of differential equations in which the variables are experimentally measurable quantities. It is helpful to distinguish the fact that thermodynamics is mathematics from the physical reality that it is used to simulate. This is because we are so focused on real-world problems that we often confuse thermodynamic simulations and the real world. We fail to see thermodynamics for what it is, and that makes it harder to understand. Normally, we learn thermodynamics as a part of physical chemistry, and the two become intimately connected, because of course physical chemistry supplies the data that thermodynamics needs in order to be useful.

It is best to mentally separate these fields (Fig. 1). This is equivalent to separating the ideal from the real world, because thermodynamics belongs to the ideal world of mathematics. The fields are of course connected by activity coefficients and equations of state, based on experimental data, which permit integration of the differential expressions.

The real question here is what is mathematics? Why does mathematics provide such a useful framework for physical theory? Why does mathematics work? Is mathematics something humans have invented, or does it have a separate reality? These questions and many others are central to the philosophy of mathematics (Brown 1999, Barrow 1992), but there are no good answers. Rather, there are many answers, but no general agreement. Fortunately, to better understand thermodynamics, we don't need to answer these questions, we need only to recognize the mathematical nature of thermodynamics.

So if thermodynamics is mathematics, then we should not be surprised that its operations in some cases do not look like the real-world problems we are obsessed with. If you find yourself wondering how you are going to change the position of a piston in an isolated cylinder, then you have not fully got the point. The position of the piston is a number, a variable, in a system of equations. You can change it at will. Similarly with many other aspects of thermodynamics; you don't need any well- lubricated, slow-moving pistons to have a reversible process. A reversible process is something that is implied by integrating a continuous function involving only the properties of equilibrium states.

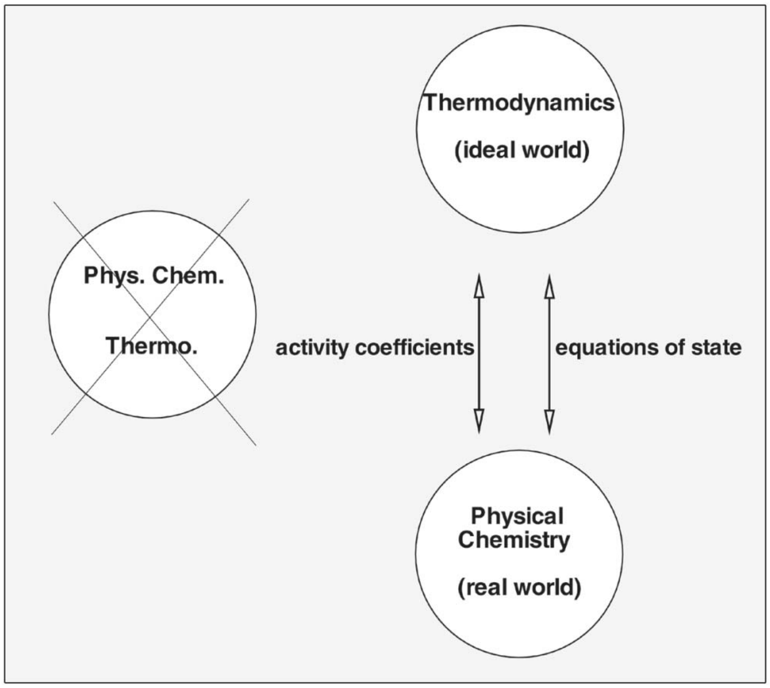

FIG. 1. Thermodynamics belongs to the ideal world of mathematics.

Thermodynamics is a mathematical theory that seeks to represent or to simulate reality, but because it is made up of the differential and integral calculus, it can only do this in an idealized way, in which systems are always at equilibrium, and processes are represented by continuous functions, corresponding to continuous equilibrium.

WHETSTONE LAKE

Let us look at a geological example (Fig. 2). Carmichael (1970) made the Whetstone Lake area famous by identifying crossing isograds. Crossing isograds had been predicted by Greenwood (1962, 1967), who identified the five different *T–X* shapes of mixed-volatile (H_2O–CO_2) equilibria (Fig. 3). How did Greenwood do it? Very simple. That is, it looks simple after it has been done. It follows from the laws of thermodynamics. I'll omit the grisly details, but the fact is it requires no data, no knowledge of the real world, just the laws of thermodynamics and the generalized reaction between minerals and two volatiles,

$$\sum_{\text{minerals}} A = \sum_{\text{minerals}} B + v_1 C_1 + v_2 C_2$$

which I'm sure has become part of almost all courses in metamorphic petrology.

Of course, to get numbers on the temperature axis, experimental data are needed. Thermodynamics is of rather limited usefulness without experimental data, although it does give us a few relationships that do not require data, such as the Phase Rule, which in my view is one of the most beautiful things in all of thermodynamics.

Perhaps you will concede that if you strip all the experimental stuff from thermodynamics, you are left with mathematics. But you may say, of course, obviously it is mathematics – it is calculus, derivatives, integrals, *etc.* Why make a point of it? Is this distinction useful? Well, it may not be useful in interpreting your field area, but it is useful in understanding thermodynamics, one of your main tools.

EXAMPLES OF CONFUSION BETWEEN THERMODYNAMICS AND PHYSICAL CHEMISTRY

Here are some examples of how we confuse thermodynamics (mathematics) with the real world we are obsessed with.

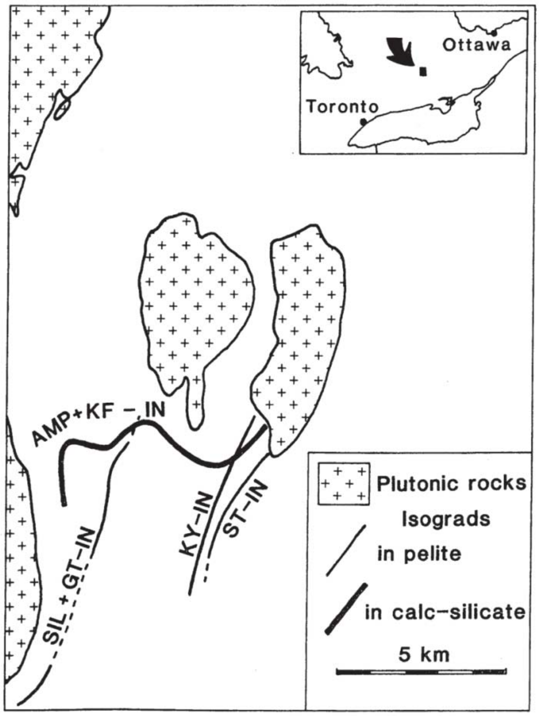

FIG. 2. The Whetstone Lake area as mapped by Carmichael (1970), showing intersecting isograds. Diagram from Yardley (1989).

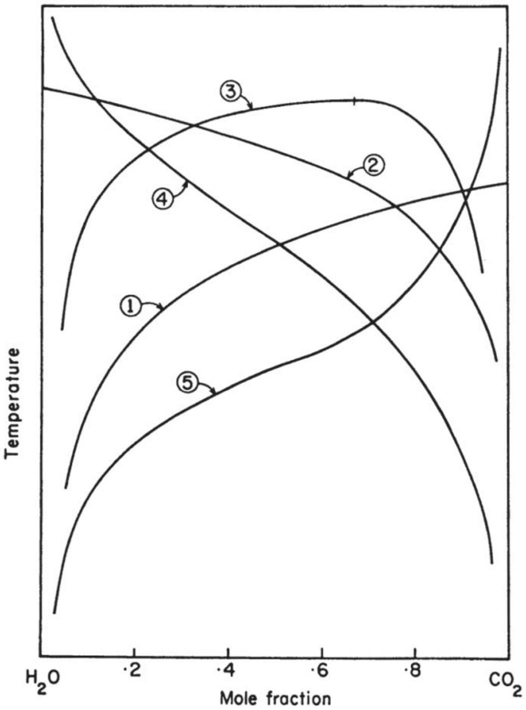

FIG. 3. Schematic *T–X*(CO_2) section showing the *T–X* shapes of the five possible reactions involving two volatiles (Greenwood 1967)..

System

Probably the first thermodynamic concept discussed in every text is *system* – a very simple idea. Obviously you must have a system, something you are interested in. But already that is a serious mistake.

Think of any thermodynamics text you have ever seen. "System" is invariably described as some part of the universe such as a kilogram of lake water, a crystal of diamond, or whatever. Then in the next chapter, the text goes on to describe the systems that thermodynamics *really* deals with, such as isolated systems, which do not exist in the universe. Is this contradictory, or what? Obviously there are real systems and thermodynamic systems, which are not the same. We confuse real and ideal right from the start.

Equilibrium

There is no concept in thermodynamics more fundamental than the concept of equilibrium. Like "system" it seems to be fairly intuitive, and we don't spend much time on it. But actually, there is a lot of confusion involved.

Equilibrium is always defined as unchanging with time, and we use mechanical analogies such as ball-in-valley. Never mind the fact that there is no time variable in thermodynamics, or that this approach does not distinguish stable from metastable equilibria. Real systems such as metamorphic rocks do achieve this kind of equilibrium, but it is not thermodynamic equilibrium. Thermodynamic equilibrium requires the absence of all gradients in T, P, and μ, and how many metamorphic rocks can you find with no armored phases, no trace element or isotopic gradients?

The problem is that "unchanging with time'' really has no meaning in thermodynamics, which uses quite a different criterion for equilibrium: equality of chemistry potentials. We deduce this condition, we do not observe it. Besides, in my view this condition is never achieved. There are always defects, gradients of all sorts, however small. Thermodynamic equilibrium is an ideal condition, not a real-world one.

Well, you may say, give me a break. Those are really minor factors; they don't affect the application of thermodynamics. Exactly. Thermodynamics requires no gradients, but we use it anyway, because even though it imposes "unrealistic'' conditions, our real systems come close enough so that the ideal is useful (they have "local equilibrium"). Nevertheless, in not bothering with the distinction, we confuse real and ideal.

Local equilibrium

Real-world systems are in constant flux, and never really achieve thermodynamic equilibrium, but we want to apply thermodynamics to them anyway, so we have to choose parts of real systems that are reasonably close to thermodynamic equilibrium. For example, one cannot apply thermodynamics to the ocean as a whole. Calcite is supersaturated at the surface, but undersaturated at 5 km depth (Fig. 4).

Thermodynamics cannot handle that. You can apply thermodynamics to volumes close to equilibrium at the surface or at depth, not both together, so we say we apply thermodynamics to areas of "local equilibrium". It is obviously important to apply thermodynamics appropriately, and generally we do this, but the point here is that local equilibrium is not part of thermodynamics, it is a concept we need, a property that real systems must have, in order to apply thermodynamics.

Partial equilibrium

The usual example of partial equilibrium is that of a crystal in an aqueous solution. The crystal is actively dissolving, so the system as a whole is not in equilibrium, but the aqueous solutes re-equilibrate very quickly, so that the solution itself is very close to equilibrium. The system is then said to be in partial equilibrium. That may be true for the real system, but there is no such thing as partial equilibrium in thermodynamics, or the systems that thermodynamics deals with. In thermodynamics, to repeat, we have only equality of potentials in every phase.

Metastable equilibrium

This is where it gets more interesting. The distinction between stable and metastable equilibrium, accord-

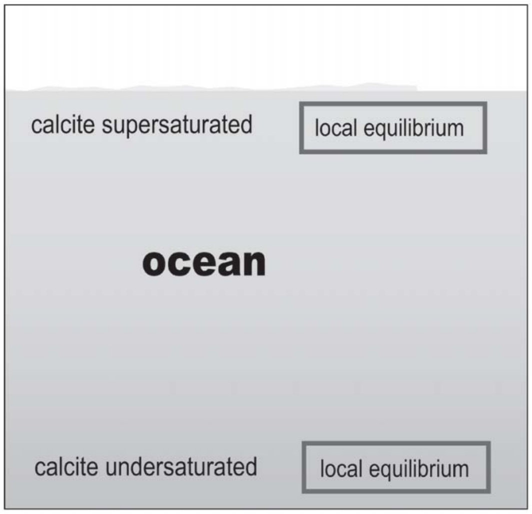

FIG. 4. Calcite is both supersaturated and undersaturated in the ocean. Local equilibrium must be assumed in order to apply thermodynamics.

ing to most sources, is 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. This distinction is generally very difficult to make. We know that at 25°C , 1 bar, calcite is the most stable form of $CaCO_3$. Aragonite is another form, and although it does not change to calcite on museum shelves, it does change in nature under some conditions, given very long periods of time, so is it metastable or unstable? Is volcanic glass an unstable or a metastable phase? These questions can start arguments among geochemists. There are many reactions for which rate constants are known at high temperatures (the reacting assemblage is therefore unstable), but not at 25°C, where the assemblage is considered metastable. At what temperature does metastable change to unstable? The kinetics of very slowly changing systems is a problem for real systems, but it is not a problem in thermodynamics.

This situation is very unsatisfactory, especially as the concept of metastable states is much more important than most realize. In the context of the discussion up to this point, we can easily see that this definition of metastability refers to real systems, not thermodynamic systems. However, unlike partial and local equilibrium, metastable equilibrium *is* a part of thermodynamics, and a very important part. So what is the thermodynamic definition of metastable?

I suggest that in thermodynamics, metastable equilibrium is a state having a third constraint. This requires some explanation.

CONSTRAINTS

A constraint in mathematics is a condition that must be observed. For example, you might want to find the minimum value of a function of many variables, while constraining some variables to nonnegative values. A constraint in thermodynamics is essentially the same thing. We minimize some function of many variables (*e.g.*, U) while constraining two state variables (*e.g.*, S and V) to constant (known) values. We constrain two, because in the First Law we define only two ways of changing the energy of a system, heat and $P–V$ work. If there is a third way of changing energy, a third state variable must be constrained, a third constraint. And, as before, the system must be in some equilibrium state for that variable, or any variable, to be defined. The only state of thermodynamic equilibrium that is not a stable equilibrium state is a metastable equilibrium state. A thermodynamic constraint, then, is *a state variable, associated with some method of changing system energy, which is held constant while minimizing a thermodynamic potential*. Stable equilibrium requires two constraints. Any extra constraints result in equilibrium states with greater energy contents, which we call metastable states.

Metastable defined

The (thermodynamic) definition of metastable is therefore a thermodynamic equilibrium state having at least three constraints. All constraint terms other than the one associated with the exchange of heat (TdS, –SdT) are of course forms of work, as that is the only other way of changing the system's energy. The general form for the internal energy function is

$$dU = \underbrace{T\,dS}_{heat} - \underbrace{\Sigma_i\ X_i\ dx_i}_{all\ forms\ of\ work} \tag{1}$$

where X_i is a generalized force and x_i is a generalized displacement, so that the second term on the right side includes all ways of performing work on the system. In this and the following equations, U, S, and V are *total*, not molar, system energy, entropy, and volume. We single out $P–V$ work as being the most important form of work, so we usually limit X to mean $–P$ and x to mean V, so we write

$$dU = \underbrace{T\,dS}_{heat} - \underbrace{P\,dV}_{PV\ work} \tag{2}$$

However, if the energy is a function not only of heat and $P–V$ work, but in addition some part of the system with mass m can move through a distance dh in the gravitational field g, there are two work terms, and

$$dU = \underbrace{T\,dS}_{heat} - \underbrace{P\,dV + mg\,dh}_{work} \tag{3}$$

If the system is a film with area A and surface tension γ, the energy function is

$$dU = \underbrace{T\,dS}_{heat} - \underbrace{P\,dV + \lambda\,dA}_{work} \tag{4}$$

If a wire is held in tension by a force f and increases elastically in length by dl,

$$dU = \underbrace{T\,dS}_{heat} - \underbrace{P\,dV + f\,dl}_{work} \tag{5}$$

And, of course, for systems having chemical reactions in which "chemical work'' is performed, X_i becomes the chemical potential and x_i the number of moles of reactant, and the equation is the familiar

$$dU = T\,dS - P\,dV + \sum_i \mu_i dn_i \tag{6}$$

Equation (6) is commonly transformed into

$$dU = \underbrace{T\,dS}_{heat} - \underbrace{\underbrace{P\,dV}_{PV\ work} - \underbrace{Ad\xi}_{chemical\ work}}_{work} \qquad (7)$$

where A is the affinity, $-\Sigma\nu_i\mu_i$, and $d\xi$ is the differential of the progress variable, (dn_i/ν_i). It is implicit in both equation (6) and equation (7) that Σ_i is a sum over all compositional terms capable of changing the energy of the system. In (6), this is most easily accomplished by having i refer to independent components, which might change by addition or subtraction from the system, or by a reaction between them. Equation (7), however, normally is used to refer to a single reaction between species, not components. Implicit in this statement is the assumption that all possible reactions in the system, including those between phases, are proceeding toward equilibrium, not just the one referred to in the affinity term.

The point here is that any of these states that depart from the stable equilibrium state by virtue of having a third constraint (having a second form of work applied to the system) must also be equilibrium states with greater energy contents, and in order to have a name for them, we may call them metastable equilibrium states. Conceivably, we should have another name for model states with three constraints to remind us that this state may not conform in all respects to some real metastable state in which we are interested, but it is unlikely that such a new term would be accepted. Metastable will remain, like equilibrium and several other terms, having quite distinct meanings depending on whether we are referring to real or thermodynamic systems.

The inequality relationship

So if we impose a third constraint, *i.e.*, we do non-*PV* work on the system like stretching a wire elastically, we increase the value of U. When the constraint is released, the system will lower its U irreversibly to the stable value. Therefore, an irreversible change in U resulting from the release of the third constraint will always be negative, and so for irreversible processes

$$dU = T\,dS - P\,dV + [\text{a negative quantity}] \text{ or}$$

$$dU < T\,dS - P\,dV \qquad (8)$$

and, combining (8) and (2), a general Fundamental Equation for all types of processes is

$$dU \leq T\,dS - P\,dV \qquad (9)$$

If S and V are constant, $dS = 0$ and $dV = 0$, and it follows from (9) that

$$dU_{S,V} < 0 \quad \text{for irreversible processes,} \qquad (10)$$

$$dU_{S,V} = 0 \text{ at equilibrium, or in general,} \qquad (11)$$

$$dU_{S,V} \leq 0. \qquad (12)$$

Equations (10), (11) and (12) are so familiar that we may not realize that they actually imply the existence of a third constraint. The equations imply the existence of a function U with independent variables S and V *and a third independent variable,* because if S and V are constant, the system cannot change its energy by heat or *PV*-work. U can only change using a second work term involving increments of a third constraint, and that change is always negative for irreversible processes (equation 10). Equation (11) says that U is at a minimum of some continuous function. That function can only be U as a function of the third constraint, because S and V cannot change, so U cannot show a minimum with respect to either variable. It can only show a minimum with respect to changes in some third variable, which can only be a second work term.

For geologists interested primarily in using thermodynamics in connection with chemical reactions, that third constraint is invariably the progress variable ξ. Integrating $Ad\xi$ gives the energy difference between the stable equilibrium state and any other (metastable) equilibrium state, and where $A = 0$, $Ad\xi = 0$, and U has its minimum value. Speciation calculations, in which species concentrations are adjusted until all chemical reactions in the system have reached equilibrium, is the principal means of ensuring that $Ad\xi = 0$.

Composite systems

Callen (1960) summed all this up by saying: "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." Implicit in this statement is that the state of the system *before* the removal of the constraint was also an equilibrium state.

Callen described a system composite as one made up of two or more *simple* systems, defined in turn as "*systems that are macroscopically homogeneous, isotropic, uncharged, and chemically inert, that are sufficiently large that surface effects can be neglected, and that are not acted on by electric, magnetic or gravitational fields*." For example, the system might be a cylinder containing a gas and having an internal piston. If the piston is free to move, the gas pressure on each side is the same, and the cylinder is at stable equilibrium having only two constraints (T and P, or U and V). If the piston is pushed to one side and locked there, the gas pressures are unequal, the system has a third constraint (the position of the piston), and the system is in a metastable equilibrium state (Callen does not, however, use the term metastable in this connection).

Using his definition of a simple system, many types of third constraints can be accommodated, although our gravity and film examples, equations (3) and (4), would be excluded because surface tension and gravity effects are excluded in his definition. Thus if the simple system is isotropic, then the stretched system (equation 5) is a composite system. If the simple system is a crystal of K-feldspar in water, then it is inert, unreactive, and a composite system. Releasing the "unreactive'' constraint in steps of $d\xi$ allows the dissolution to proceed (equation 7). This formulation has the advantage of stressing that the constraint and its release are in fact conceptual, not necessarily real, but it is somewhat unintuitive, except in the case of the internal piston.

An alternative to composite systems

I suggest that for geochemical purposes, it would be simpler to define Callen's composite system as one having any kind of third constraint. Thus we could think of the dissolving K-feldspar case, and indeed all chemical reactions, as cases where the third constraint is simply separation of the reactants, and removing the constraint in steps of $d\xi$ is visualized by removing the separation for small amounts of reactants (Fig. 5). This is preferable to the usual interpretation in terms of partial equilibrium. The term "composite system'' then becomes superfluous; I mention it here because it expresses the fact that releasing a (third) constraint is in fact the central element in most thermodynamic problems.

When using thermodynamics in connection with chemical reactions, every state but the stable equilibrium state must be a metastable equilibrium state, which of course is not true of real chemical reactions. The physical nature of the third constraint need not be explicitly stated, but can often be imagined to be an activation energy barrier, which is reduced in increments, allowing increments of reaction to proceed, or a separation, as discussed above. In reaction-path programs, we implement these increments by simply changing reactants into products in small amounts. In this way, we can change diamond into graphite (or *vice versa*), or follow the progress of an explosive reaction through a series of (unrealistic) equilibrium states. We can change diamond into graphite in our calculations, but because this does not really happen, we see that thermodynamics is describing something other than our world. We also see that the concept of metastable states is implicit in all of chemical thermodynamics, even if never acknowledged.

I am reminded of Monsieur Jourdain in Molière's Le Bourgeois Gentilhomme who, on learning of the difference between prose and poetry, was amazed that he had been speaking prose all his life without knowing it. Users of thermodynamics may be surprised that they have been using three constraints without being aware of it.

TERMINOLOGY PROBLEMS

As mentioned above in connection with the term metastable, it is rather difficult to separate the terminology we use for real and thermodynamic systems. This problem is inherent in almost every term we use, to varying degrees. Two more examples might help to illustrate this.

In some cases, one can envisage that the energy imposed by the third constraint is held in the system by the constraint itself; or example, the wire does not resume its original length because the force stretching it is still

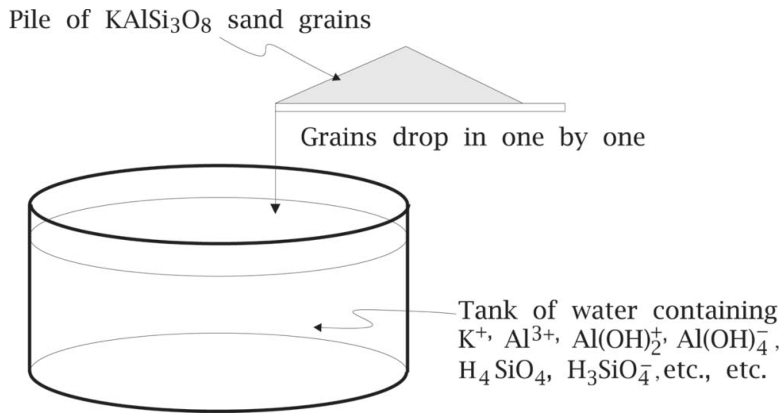

FIG. 5. Dissolving K-feldspar in water is simulated by dropping small bits of mineral in water. The combination of the sand pile of K-feldspar and the tub of water is a metastable system. Modified from Anderson (1996).

there. But generally, other means are used in real life. In the calcite – aragonite transition, and other chemical reactions, the higher-energy state is held in place by a structural rearrangement unknown to thermodynamics. In thermodynamics, it is the progress variable that adds or releases the energy, and as long as it is there (as long as that term is in the equation), the energy stays there. In the stretched wire case, it is as if after stretching, a clamp is applied to keep the wire stretched. If the clamp is released in increments, the stretching force decreases in increments, and that is all that the model needs to know. The clamp is not in the model, and doesn't need to be. The rope and pulley we use to lift the weight in the *mg dh* example (equation 3) is not there either, and in fact neither is the piston and cylinder we use in Carnot cycles. Activation energy is the real-life constraint. The progress variable is the thermodynamic (third) constraint.

Releasing a constraint is actually real-system terminology, and conveys a good sense of the meaning for us. But in thermodynamics, it is just a matter of changing integration limits when integrating the last term in equations (2) to (7). If the upper limit is greater than the lower limit, you impose the constraint, and *vice versa*.

HISTORICAL NOTE

As far as I am aware, only three authors have used the concept of constraints in thermodynamics. Schottky (1929) clearly stated the concept in several sections. He also derived the extent of reaction or progress variable ξ, strangely without a reference to De Donder (1920), who originated the concept. He never stated that he uses ξ as a possible constraint, but I think it is implied.

Callen's (1960) use of constraints and composite systems was discussed above. Reiss (1965) also emphasized the constraint concept in exactly the sense discussed here. However Reiss preferred to consider all states of equilibrium on an equal basis, as long as the number of constraints is specified. He attached no special significance to the third constraint, and considers metastability in the conventional sense (very slow reaction rates).

It seems to me that the concept of metastability, so common in geochemistry, is clarified by defining it in terms of a third constraint, rather than in terms of reaction rates.

SUMMARY

Thermodynamics is a theory of great generality, but if we confine our attention to chemical systems, we find that stable equilibrium states can be defined by fixing two state variables, such as T and P. Borrowing from pure mathematics, we call these the two initial constraints. But because thermodynamics can only deal with equilibrium states, and because we must also consider systems containing chemical reactions that are or might be progressing from some other state toward stable equilibrium, we must introduce a way to handle the chemical energy involved. We introduce a third constraint, a state variable associated with this change in chemical energy, generally called the progress variable. It is so named because it controls the progress of a (simulated) chemical reaction toward (or away from) stable equilibrium. All thermodynamic metastable states (as opposed to real metastable states) have a third constraint. Metastable states and the third constraint are important because all uses of thermodynamics in connection with chemical reactions imply these concepts, even if not generally acknowledged.

It is useful to see thermodynamics as mathematics, which means contrasting the ideal world with the real world. The same can be said of quantum mechanics, relativity, and all quantitative physical theories that simulate reality. It has been said that science does not tell us what nature *is*, it tells us what nature is *like*.

But these theories are not *just* mathematics. They are forms of mathematics carefully and painfully crafted by brilliant minds to simulate real systems. Science and mathematics are not the same thing, but scientific theories fit mathematics to observations of nature, and attempt to simulate it.

CONCLUSION

Thermodynamics is beautiful, because it is a mathematical theory of great simplicity and great power, and without correction factors, it is true in some ideal world. But it is not only beautiful and true, it is also mysterious. Eugene Wigner (1960), who received the Nobel Prize in physics in 1965, put it in this way: "The first point is that the enormous usefulness of mathematics in the natural sciences is something bordering on the mysterious and that there is no rational explanation for it." Mathematics and science at the highest levels are inextricably interwoven. And yet, the meaning and origins of mathematics are among the great philosophical mysteries. However, to understand thermodynamics, we don't need to solve the problem of the meaning of mathematics. We need only recognize that the heart of thermodynamics, no less than the heart of nuclear physics, is mathematics, not reality. The real mystery is not thermodynamics itself, but why mathematical equations using physical parameters as variables should mimic natural processes so closely.

And if you don't think it a bit strange that a bunch of differential equations were useful in helping Dugald Carmichael figure out what happened millions of years ago at Whetstone Lake, then I guess you have not really thought about it.

ACKNOWLEDGEMENTS

It takes some nerve to write about truth and beauty, topics which philosphers have discussed for centuries. I should like to thank Edgar Froese and Norm Evensen for encouraging me to do this, and to write about constraints in this context. I am especially indebted to Edgar Froese for bringing the work of Schottky to my attention, and for translating the relevant sections. I also thank David Pattison, Terry Gordon, Paul Asimow, and Bob Martin for their very useful comments.

In my mind, Dugald Carmichael epitomizes clarity of thinking about complex geological problems. I hope that this article will comprise a small contribution toward that end.

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