Version of June 14, 2010

Discussion of Some Less Essential Topics in Thermodynamics

A Companion File to Thermodynamics of Natural Systems, Second Edition by Greg Anderson

Introduction

In this article are discussions of a few subjects that did not make it into the text for various reasons. These subjects are

- 1. All components in all phases.
- 2. Components, constraints and the Phase Rule
- 3. Potentials in stoichiometric compounds.
- 4. Inexact differentials.
- 5. Time as a thermodynamic variable.
- 6. The bursting balloon.
- 7. The Meaning of $d\mathbf{G} = -\mathbf{S} dT + \mathbf{V} dP \mathscr{A} d\xi$
- 8. Fugacities Do Not Control Anything
- 9. Denbigh on Entropy as Mixing
- 10. Hardy on Differentials
- 11. A Very Common Misunderstanding
- 12. The One Minute Test

The first three of these topics are discussed more fully in a petrological context by Thompson (1959). There are references to material in the text here and there, but for the most part none of this material requires having the text.

1 All Components In All Phases

1.1 No Pure Phases

A commonly cited conclusion of thermodynamics is that in a system at equilibrium, the chemical potential of each component is the same in every phase. This means that every component must actually be present in every phase, because a component having zero concentration will have a chemical potential of $-\infty$, according to dilute solution theory, and one might conclude from this that according to thermodynamics, there are no pure phases in a multicomponent system. This causes a problem for some people.

For example, Ricci (1951) discusses a hypothetical experiment in which crystalline NaCl is equilibrated with water containing an organic solute. The organic solute may have properties

which make it highly unlikely that any of it will enter the NaCl structure, yet at equilibrium its chemical potential is supposed to be the same in both phases. Ricci then discusses a rather intricate way of calculating compositions to get around this supposed problem. More geologically, you could imagine a crystal of quartz in a salt solution in a beaker, or at the bottom of the sea. The solution will achieve an equilibrium concentration of SiO_2 , but NaCl does not diffuse into the silica structure to achieve an equilibrium concentration, whatever that is. You could extend this idea, and suppose that the quartz crystal was grown synthetically in an aqueous solution having zero NaCl by the finest analytical techniques available, and therefore the quartz contains zero NaCl. After sitting for a few years in a concentrated NaCl solution, it comes to equilibrium, but on analysis is found to still contain zero NaCl. We have a pure phase, but thermodynamics says we should not.

There are two aspects to this topic. One is that thermodynamics does *not* actually say that chemical potentials must be the same in all phases at equilibrium, and the other is that equilibrium and phase composition are among those terms that we use in two senses, one for real systems, and one for thermodynamic model systems.

1.2 Thermodynamic Equilibrium

Gibbs examined this problem in some detail, in terms of "actual" and "possible" components. However, before looking at this we must derive the conditions of equilibrium a little more fully than is done in the text. This is taken directly from Gibbs (1876, pp. 63–65).

Equation (4.65) in the text is, for *c* components,

$$d\mathbf{G} = -\mathbf{S}dT + \mathbf{V}dP + \sum_{i}^{c} \mu_{i}dn_{i}$$

$$[4.65]$$

and we did not write, but it is equally true that

$$d\mathbf{U} = T\,d\mathbf{S} - P\,d\mathbf{V} + \sum_{i}^{c} \mu_{i}dn_{i} \tag{1}$$

which is Gibbs (1876) equation (12).

Now suppose we have a system containing a number of phases that may exchange matter in response to changing conditions, but that the system as a whole is of fixed composition. From Chapter 4, we know that if a closed system is constrained to a constant entropy and constant volume, its energy content will seek a minimum value, and the system will be at equilibrium when $d\mathbf{U}_{S,\mathbf{V}} = 0$. Now we want to consider a system that is closed overall, but within which matter is free to move between phases, i.e., in which the phases are open. Still, because the system is closed overall, the same criterion $d\mathbf{U}_{S,\mathbf{V}} = 0$ applies. If we denote the various phases in the system by accents, we can consider that during any increment of change of energy $d\mathbf{U}$ the various phases contribute $d\mathbf{U}', d\mathbf{U}''$, etc., so that

$$d\mathbf{U} = d\mathbf{U}' + d\mathbf{U}'' + d\mathbf{U}''' + \cdots \text{ etc.}$$
⁽²⁾

and similarly for the other terms in equation (1), so that if $d\mathbf{U}_{\mathbf{S},\mathbf{V}} = 0$, then combining (2) and (1),

$$T' d\mathbf{S}' - P' d\mathbf{V}' + \mu_1' dn_1' + \mu_2' dn_2' + \dots + \mu_c' dn_c' + T'' d\mathbf{S}'' - P'' d\mathbf{V}'' + \mu_1'' dn_1'' + \mu_2'' dn_2'' + \dots + \mu_c'' dn_c'' + \text{etc.}$$

$$= 0$$

$$(3)$$

For the system, S, V, and the quantity of each component are constant, so that

$$d\mathbf{S}' + d\mathbf{S}'' + d\mathbf{S}''' + \dots = 0$$

$$d\mathbf{V}' + d\mathbf{V}'' + d\mathbf{V}''' + \dots = 0$$

$$dn'_{1} + dn''_{1} + dn'''_{1} + \dots = 0$$

$$dn'_{2} + dn''_{2} + dn'''_{2} + \dots = 0$$

$$\vdots$$

$$dn'_{c} + dn'_{c} + dn''_{c} + \dots = 0$$

$$(4)$$

For this to be true it is necessary and sufficient that

$$T' = T'' = T''' = \cdots \text{ etc.} P' = P'' = P''' = \cdots \text{ etc.} \mu'_1 = \mu''_1 = \mu'''_1 = \cdots \text{ etc.} \mu'_2 = \mu''_2 = \mu'''_2 = \cdots \text{ etc.} \vdots \qquad \vdots \\\mu'_c = \mu''_c = \mu''_c = \cdots \text{ etc.}$$
(5)

Equations (5) express the conditions for thermal, mechanical, and chemical equilibrium of the system, i.e., that temperature, pressure, and the chemical potential of every component must be constant throughout. It is at this point that most analysis stops, and the conclusion is that according to thermodynamics, the chemical potential of all components must be the same in all phases, and therefore must actually be present in all phases. But Gibbs' analysis did not stop there.

1.3 μ as a Driving Force for Mass Transfer

Just as inequalities (gradients) in T or P are driving forces for the transfer of heat and work, a chemical potential gradient is a driving force for the transfer of matter. Equation [4.65] shows that in the case of two coexisting phases at a constant T and P, each of which is a homogeneous solution of two components,

$$d\mathbf{G}'_{T,P} = \mu'_1 dn'_1 + \mu'_2 dn'_2, \text{ and} d\mathbf{G}''_{T,P} = \mu''_1 dn''_1 + \mu''_2 dn''_2$$

If the system is closed, any matter that leaves one phase must enter the other, so that

$$dn'_1 = -dn''_1$$
 and $dn'_2 = -dn''_2$

Therefore, because $d\mathbf{G} = d\mathbf{G}' + d\mathbf{G}''$,

$$d\mathbf{G}_{T,P} = (\mu_1' - \mu_1'')dn_1' + (\mu_2' - \mu_2'')dn_2'$$

 $\text{If }\mu_{2}^{\prime}=\mu_{2}^{\prime\prime},$

$$d\mathbf{G}_{T,P} = (\mu_1' - \mu_1'')dn_1'$$

For the system as a whole, which is closed, the general relation

$$d\mathbf{G}_{T,P} \leq 0$$

still holds, so

$$(\mu_1' - \mu_1'')dn_1' \le 0 \tag{6}$$

So the condition of equilibrium $(d\mathbf{G}_{T,P} = 0)$ is that $\mu'_1 = \mu''_1$. But in addition we see that for $d\mathbf{G}$ to be negative (< 0), which is the criterion for spontaneous change, either

$$(\mu'_1 < \mu''_1)$$
 and dn'_1 is positive,

or

$$(\mu'_1 > \mu''_1)$$
 and dn'_1 is negative.

In either case, spontaneous change calls for the transfer of mass (in this case component 1) from the phase in which it has a higher potential to the phase in which it has a lower potential. Thus the chemical potential is aptly named, as it tends to cause matter to transfer such as to equalize the potential in all parts of the system..

1.4 Actual and Possible Components

On page 64 of the Dover edition, Gibbs (1876) defines actual and possible components:

- An actual component is one whose amount or concentration in a phase may be either increased or decreased. It therefore has a finite concentration in that phase.
- A possible component is one whose concentration in a phase may be increased but not decreased. Its concentration is therefore zero.

Gibbs makes it clear (p. 65) that in both cases, there are no kinetic or structural factors which inhibit the movement of the components into or out of phases. Thus equations (5) assume that all components are capable of being independently added or subtracted from every phase, i.e., that all dn_i terms can be positive or negative. This means that all components have been assumed to be in all phases, and that they are free to enter or leave each phase. They are all actual components. If however substance 1 is not a component, either actual or possible, in phase ', then dn'_1 is zero, the $\mu'_1 dn'_1$ term is missing from equations (3) and the dn'_1 term from (4), and there is no change in the general conditions of equilibrium, equations (5), except that the μ'_1 term is missing. How a substance can be a component in the system but not a component, either actual or possible, in phase ', is not made explicit by Gibbs, but cases where mass transfer to and from certain phases is negligible ($dn_i = 0$ in the model) are very common in real systems, as discussed below (§1.4.2).

1.4.1 Pure Phases

Now let us suppose that there is such a thing as a pure phase in a heterogeneous system at equilibrium. Let's say there are two phases, ' and ", in a binary system, and component 1 is a possible component in phase '. Its concentration is therefore zero, but it is not inhibited from increasing, and the system is at equilibrium. Phase ' therefore consists of pure component 2, and phase " contains both components 1 and 2.

Equation (6) looks at the system from the point of view that its **G** is either at a minimum or that it could be decreased by some reaction or process which in this case would be the transfer of some component 1 into phase ' $(dn'_1 \text{ positive})$. What about the situation where **G** is at a minimum, and there is no possibility of it decreasing? For a ball resting at the bottom of a U-shaped valley, there is no way to go but up. In this situation,

 $d\mathbf{G}_{T,P} \geq 0$

and (6) becomes

$$(\mu_1' - \mu_1'')dn_1' \ge 0 \tag{7}$$

Our binary system is at equilibrium, phase ' contains no component 1, but that component is not prevented or constrained from entering phase '. Because the system is at equilibrium, **G** cannot decrease, and any conceivable change would be an increase. In this case, (7) tells us that if dn'_1 cannot be negative,

$$\mu_1' \ge \mu_1'' \tag{8}$$

In other words the potential of component 1 cannot be less in the phase in which it does not occur than in the phase in which it does occur (Gibbs 1876, eqns. (22)). This conflicts with the fact that according to solution theory homogeneous substances always have μ_i decreasing with decreasing n_i , and in fact in the limit as $x_i \rightarrow 0$, $\mu_i \rightarrow -\infty$, as shown by

$$\mu_i - \mu_i^\circ = RT \ln x_i \tag{9}$$

So apparently thermodynamic theory calls for a component at zero concentration in one phase to have a potential which is not less than in an adjacent phase in which it has a finite concentration, while dilute solution theory, equation (9), says this potential must be infinitely negative.

Gibbs was aware of the implications of dilute solution theory, and drew attention to it in a footnote on page 138 (see below, $\S1.5$), but in 1876 was apparently not willing to accept equation (9) as a generality, so continued to talk about possible components. Today we do not doubt the generality of (9), so it follows that the thermodynamic model developed by Gibbs prohibits the existence of possible components at equilibrium in a heterogeneous system, i.e., it postulates an equilibrium state that has all components in all phases, *except in cases where a component is prevented from entering or leaving phases*, as discussed below.

This derivation seems to be a rather complicated way of expressing a simple idea, and that is that if components can move freely in and out of phases, and phase ' contains zero concentration of component *i* but the adjacent phase " contains a finite amount of *i* having $\mu_i^{"}$, then there is a potential gradient trying to push *i* into phase ', and phase ' must have a potential of *i* equal to or greater than this to resist the push. So $\mu_i' \ge \mu_i^{"}$, even though phase ' contains no *i*. Accustomed as we are to solution theory (equation (9)) this seems a bit silly, or perhaps not very useful, but it is perfectly logical.

1.4.2 Inhibited Equilibrium

Gibbs did not explicitly consider the more realistic case of phases which *are* inhibited¹ from absorbing components. For example, diffusion in a phase might be just too slow to allow this. If component 1 is somehow prevented from entering or leaving phase ', dn'_1 in equation (4) is fixed at zero and the appropriate terms simply drop out of the other equations as discussed above. In Gibbs' terminology, component 1, although a component in other parts of the system, is then not a component, either possible or actual, of phase ', and μ'_1 just does not occur in the equations of equilibrium.

For example, in a real system consisting of quartz and water, we know that silica enters the water phase, but water does not enter the quartz. In our thermodynamic model of the quartz-water system there are two components, SiO₂ and H₂O. Our theory says that if both components could move freely between the phases, then at equilibrium the chemical potential of both components would be the same in both phases. At equilibrium, $\mu_{SiO_2}^{quartz} = \mu_{SiO_2}^{water}$, and we use this condition as discussed in Chapter 9. But there is no evidence that $\mu_{H_2O}^{quartz} = \mu_{H_2O}^{water}$, because of

¹We use the term "inhibited" rather than "constrained" to avoid confusion with the concept of constraints defined in Chapter 4.

the slow diffusion rate, so in the model, $dn_{H_2O}^{quartz} = 0$, and $\mu_{H_2O}^{quartz}$ does not appear in any equations. There may be a few molecules of H₂O in the real quartz structure, but there is no H₂O in the model quartz. H₂O is thus neither a possible nor an actual component of the quartz phase in thermodynamics.

In real systems, mass transfers between phases are commonly prevented due to kinetic factors, as in this case, and this is easily accommodated by thermodynamic theory, which, as just shown, does *not* require that chemical potentials be the same in all phases at equilibrium, or that all phases contain all components. Although no real phases may be pure in an absolute sense, pure phase compositions are commonly used in thermodynamic model calculations. For phases which are solutions, an appropriate solution model must be provided. For example, for aqueous solutions we use equation (9) and its modifications.

1.5 Further on Chemical Potentials of Dilute Components

As mentioned above, Gibbs knew that the chemical potentials of dilute components in many cases took the form of equation (9), and in fact he derived a form of this equation on pages 135–138. The way he did this is interesting. Starting with what Gibbs called equation (97), and what we call the Gibbs-Duhem equation (equation (4.68) in the text), at constant T and P we get for a binary system

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{10}$$

Differentiating by n_2 then gives

$$n_1 \left(\frac{d\mu_1}{dn_2}\right)_{T,P,n_1} + n_2 \left(\frac{d\mu_2}{dn_2}\right)_{T,P,n_1} = 0 \tag{11}$$

Now for pure component 1, $n_2 = 0$, and it follows that (Gibbs equation (211))

$$\left(\frac{d\mu_1}{dn_2}\right)_{T,P,n_1} = 0 \tag{12}$$

But Gibbs points out that there is another possibility, which is that (Gibbs equation (212))

$$\left(\frac{d\mu_2}{dn_2}\right)_{T,P,n_1} = \infty \tag{13}$$

Gibbs then has a typically rigorous discussion pointing out the importance of the possible values of n_2 .

Suppose first that our components 1 and 2 represent "end-member" components, for example the system Cu-Au, or N₂-O₂. In this case both n_1 and n_2 must have positive values throughout, and n_2 cannot have negative values. In this case, where n_2 cannot be negative, equation (12) is not true, a subject discussed in Chapter 17 under the general heading of freezing point depression (§17.3.5). In other words, adding a second component to a one-component system will lower the chemical potential of the first component. Therefore in this case equation (13) must be true. This is a corollary of dilute solution theory, equation (9), because if $\mu_2 \rightarrow -\infty$ as $n_2 \rightarrow 0$ (or $x_2 \rightarrow 0$), then the slope of μ_2 vs. n_2 at $n_2 = 0$ must be infinite, which is equation (13).

However, if component 1 represents a binary compound, such as AB in the system A-B (so that our system is A-B, but our components are AB and B), to describe compositions between A and AB, n_2 (or in this case n_B) must be negative, so that n_2 can be positive or negative. In this case increasing or decreasing n_2 from pure composition AB will cause μ_{AB} (which is μ_1) to decrease on both sides, hence it must be zero at composition AB, which is equation (12), and so equation (13) is not true. Equation (13) becomes true at pure composition A and so must be

finite at composition AB.² Gibbs then uses the case where n_2 cannot be negative to derive a form of equation (9), i.e., the dilute solution equation, a development I leave for the reader (see also Froese, 1981, pp. 5-6). This equation was derived in two different ways in Chapter 7.

The footnote on page 138 in Gibbs (1876) mentioned above says

The reader will not fail to remark that, if we could assume the universality of this law (*referring to equation* (13)), the statement of the conditions necessary for equilibrium between different masses in contact would be much simplified. For

which means that equation (8) and its lengthy derivation and discussion need not be considered. Thompson (1959) summarizes all this as follows:

We are then led to the conclusion that a component with a composition expressible in any way in terms of actual components of other phases in the assemblage cannot be a possible component of any phase in the assemblage, at complete internal equilibrium, even though its presence as an actual component may be too small to detect analytically under certain instances.

As it stands, this is a statement of "all components in all phases", and is the logical conclusion of accepting equations (5), free mass transfer between phases, and dilute solution theory. However one need not postulate free mass transfer for all components. There remains the option of asserting that some components are neither possible nor actual, i.e., that they are inhibited from transferring to or from a particular phase, as in our quartz-water example (\S 1.4.2).

2 Components, Constraints, and the Phase Rule

2.1 Components And The Phase Rule

. . .

So if thermodynamics says all components are in all phases, how does that affect the Phase Rule? The answer to this perennial question was expressed best by Terry Gordon:

I have heard the (mischievous) argument that every natural system has as many components as elements in the periodic chart — we only need analyze for them. The corollary is that all natural systems have somewhere in the neighborhood of 100 degrees of phase rule freedom, discounting isotopes. My reply is that this is nonsense — natural systems don't have components — only our models do, and if we're sensible, we choose model components that have predictive value for the problem at hand.

T.M. Gordon (personal communication, 1989)

There are actually two answers, both mentioned in the quote. One is that components are chosen for their usefulness; they are not the result of a chemical analysis. The other is that even if you wanted to count each trace element as a component, each is also a degree of freedom, so they cancel one another in the Phase Rule.

2.2 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

²This case is related to the problem mentioned in the footnote on page 531 of the text.

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 ξ is extensive.

For example in the system CaCO₃, the chemical potentials in calcite and aragonite are only equal on the two-phase equilibrium boundary. If we change some calcite to aragonite 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 *T* and *P*) throughout, so that the system does obey the Phase Rule, but with no added degrees of freedom. For example a system having aragonite, without calcite, in a phase assemblage in the calcite stability field, could be at equilibrium with equality of chemical potentials in all phases. Similarly, a granite in which all the crystals of SiO₂ happened to be trydimite 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 defined in Chapter 4, 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.

3 Potentials In Stoichiometric Compounds

Phases are often grouped for convenience into those having a fixed ratio between the constituent elements (e.g., quartz has a fixed ratio of Si:O of 1:2), and those having a variable ratio (e.g., pyrrhotite, $Fe_{1-x}S$). If the ratio A:B in the phase AB was truly invariable, then neither A nor B could be added to or subtracted from AB. If this was strictly true, it would be difficult to understand the meaning of μ_A^{AB} , the chemical potential of A in AB, defined as it is by

$$\mu_{\rm A}^{\rm AB} = \left(\frac{\partial \mathbf{G}_{\rm AB}}{\partial n_{\rm A}}\right)_{T,P,n_{\rm B}} \tag{3}$$

That is, if n_A is fixed, how can we have a dn_A ? The easiest way to discuss this in thermodynamic terms is to show that it is easy to calculate the activity of A (or B) in any binary compound AB, as well as $\mu_A^{AB} - \mu_A^\circ$, which means that in thermodynamics there is a quantity μ_A^{AB} .

For example, from the data in Appendix B, the reaction

$$Al_2SiO_5 = SiO_2 + Al_2O_3$$

has $\Delta_r G^\circ = 4940 \,\mathrm{J}\,\mathrm{mol}^{-1}$, where Al₂SiO₅ is kyanite, SiO₂ is quartz, and Al₂O₃ is corundum.

From this, the equilibrium constant is

$$K = \frac{a_{\rm SiO_2}a_{\rm Al_2O_3}}{a_{\rm Al_2SiO_5}}$$
$$= 0.136$$

This means that the assemblage quartz plus kyanite buffers the activity of Al_2O_3 at 0.136, and similarly for the activity of SiO_2 in the assemblage corundum plus kyanite. Also,

$$\mu_{\text{Al}_2\text{O}_3}^{\text{kyanite}+\text{quartz}} - \mu_{\text{Al}_2\text{O}_3}^{\text{corundum}} = RT \ln a_{\text{Al}_2\text{O}_3}$$
$$= -4940 \,\text{J}\,\text{mol}^{-1}$$

and

$$\mu_{\text{SiO}_2}^{\text{kyanite}+\text{corundum}} - \mu_{\text{SiO}_2}^{\text{quartz}} = RT \ln a_{\text{SiO}_2}$$
$$= -4940 \,\text{J}\,\text{mol}^{-1}$$

These results have a clear meaning in thermodynamic theory, but may or may not have any meaning (i.e., correspond to some measurable quantity) in real systems, in the same way that the assemblage hematite plus magnetite can predict f_{O_2} under some conditions (high *T*) but not others (low *T*). Furthermore, these calculations say nothing about whether real kyanite is or is not stoichiometric. Other thermodynamic parameters may not be useful under any conditions. For example, thermodynamics says that quartz in air at 25°C has $a_{Si} = 10^{-150}$, but it is difficult to imagine under what conditions this parameter might be useful.

Stoichiometric phases in real life are simply those in which the deviation from perfect stoichiometry is up to now beyond detection. Both variable and fixed stoichiometry are accommodated by thermodynamics, and perfectly stoichiometric phase compositions are commonly used in thermodynamics, as in our quartz-water and kyanite examples above.

4 Inexact (or Imperfect) Differentials

4.1 Introduction

In a letter to me in May of 1977, George Tunell, then Professor Emeritus at the University of California, Santa Barbara, wrote

In many textbooks on physical chemistry and thermodynamics the statement is made that dQ and dW are imperfect differentials, but I have never seen a statement in any textbook of thermodynamics as to what constitutes an imperfect differential. From the usage in these textbooks one has to reason backwards that since dQ and dW are called imperfect differentials, an imperfect differential is whatever dQ and dW are.

The sparse literature on imperfect differentials was sufficiently unclear to me that I came up with my own definition (Anderson and Crerar, 1993), which is repeated in Appendix C. This definition is basically that an imperfect, or inexact, differential is a differential expression which is not the differential of any function. I believe this is has essentially the same meaning as the definition above, because to integrate such a differential expression you must specify a path. I also said that you could assign any symbol you wished to represent such an expression, and although the common choices use δ or \vec{a} as prefixes to Q and W, I chose to use simply q and w



Figure 1: A system changes from state 1 to state 2 along three arbitrary paths.

rather than, say, δq and δw . This may not have been a wise choice, as the other usage is so well ingrained.³

4.2 How Many Independent Variables?

Tunell (1932) explored this subject at much greater length. In that paper he makes the point that inexact differentials are functions of a single variable, which he called σ , and in another letter to me in June of 1977, he said that this parameter "can be taken as the time τ ". In my view, inexact differentials as functions of a single variable is an illuminating idea, but that that variable is or might be time is quite wrong. I prefer to think that Tunell (and Denbigh, see below, §5) are speaking figuratively or intuitively, rather than mathematically or thermodynamically, when they say things about the role of time in thermodynamics.

Consider the work and heat involved in an arbitrary change of state of a system from state 1 (at T_1 , P_1) to state 2 (at T_2 , P_2), shown in Figure 1. Probably no one needs convincing that work and heat depend on the path between two equilibrium states, but a common classroom exercise to demonstrate this is to show that for an ideal gas, ΔV is the same, whether the integration takes place from T_1 , P_1 to T_1 , P_2 to T_2 , P_2 (Path A), or from T_1 , P_1 to T_2 , P_2 (Path B), but that the integration of dW gives different results for the two paths. Alternatively, the symmetrical second derivative test works for dV but not for dW. The path dependence of work was also discussed at length in Chapter 3.

Starting from dW = P dV, Tunell (1932) writes an equation for the work done between state 1 and state 2 for which there are two variables, *T* and *P*, and converts it to one containing a

³Tunell (1941) also discussed the notation for inexact differentials. Interestingly, he did not favor the use of δ or \vec{a} for inexact differentials, but simply explicit representation of what variables are held constant.

single independent variable σ as follows (his equation [4], but using different notation),

$$W = \int_{T_1,P_1}^{T_2,P_2} P\left(\frac{\partial V}{\partial T}\right)_P dT + P\left(\frac{\partial V}{\partial P}\right)_T dP$$
$$= \int_{\sigma_0}^{\sigma} \left[P\left(\frac{\partial V}{\partial T}\right)_P \frac{dT}{d\sigma} + P\left(\frac{\partial V}{\partial P}\right)_T \frac{dP}{d\sigma} \right] d\sigma$$
[4]

where both T and P are functions of σ , as in

$$T = \phi(\sigma), \text{ and } [5]$$

$$P = \psi(\sigma) \tag{6}$$

This makes sense if you imagine any arbitrary path from state 1 to state 2 such as Path C as being described by a series of (P,T) coordinates. You then have a list of P values extending from P_1 to P_2 and a list with the same number of T values extending from T_1 to T_2 . If you then match each list with a list of linearly spaced values of σ , which can extend between any two values you like, but most usefully between 0 and 1, you can then use numerical analysis to find the functions ψ and ϕ which fit the lists of P and T values. You can then say that σ is a variable which describes path C, and that therefore the work done is a function of a single variable, and by extension that therefore an inexact differential is the differential of a function of a single variable. Starting with dQ = T dS, the same argument can be made for the heat exchanged between state 1 and state 2, and you can develop an equation analogous to [4] for heat. dQ and dW are of course differentials of differentials of the single variable σ .

Another way to look at this would be to note that for a chosen path between state 1 and state 2, *T* and *P* are functionally related, or P = f(T), so *W* is not a function of two independent variables *T* and *P*, because *T* and *P* along any path are not independent of one another.⁴ Tunell then notes that as dQ has been shown to be the differential of a function of a single variable which determines the path, then it satisfies the definition of a differential, and that

dQ is just as truly a differential as dV: dV is the differential of a function of two independent variables while dQ is the differential of a function of a single independent variable.

4.3 **Reversible and Quasistatic Paths**

Note that any path that can be plotted in P-T space, such as those in Figure 1, represents either a reversible process or a quasistatic process (defined in Chapter 18), because each point on the line must represent an equilibrium state, either stable or metastable. An irreversible process which is not quasistatic cannot be plotted on the diagram. If both state 1 and state 2 are stable equilibrium states, paths A, B, and C are reversible. If state 1 is a metastable equilibrium state and state 2 is a stable equilibrium state (or another metastable equilibrium state closer to stable equilibrium than state 1), all three paths are quasistatic.

Therefore what has been shown is that inexact differentials can only be evaluated for a chosen path, and that path must be reversible or quasistatic. But this is no different from exact differentials such as dV and dU. They too must be evaluated along reversible or quasistatic paths, simply because, as we have noted elsewhere, integration requires a continuous function. The difference then between dU and dQ is that to evaluate dQ or dW you must know the path, which is a function of a single variable. The final result, the quantities of heat and work, depends on which path is chosen. Evaluating dU also requires a reversible or quasistatic path, but the integral includes both work and heat, so the result is independent of the path. Although both dW

⁴However, Tunell notes that for any part of the process that is parallel to the *P*-axis (isothermal), *P* is not a function of *T*, so that this approach lacks generality.

and dQ are functions of the same variable σ , they are different functions, and the differences cancel. That dU is a function of two independent variables is shown by other relationships such as dU = T dS - P dV, where dU is a function of the two independent variables dS and dV.

4.4 The Meaning of σ

 σ is a sort of step variable, controlling the change in system parameters as the system changes from state 1 to state 2. Equation [4] refers to reversible paths. For quasistatic paths there are three coordinates for each point, *T*, *P*, and ξ , and equation [4] becomes

$$W = \int_{\sigma_0}^{\sigma} P\left[\left(\frac{\partial V}{\partial T}\right)_{P,\xi} \frac{dT}{d\sigma} + \left(\frac{\partial V}{\partial P}\right)_{T,\xi} \frac{dP}{d\sigma} + \left(\frac{\partial V}{\partial \xi}\right)_{P,T} \frac{d\xi}{d\sigma}\right] d\sigma$$

and in addition to equations [5] and [6] we have

$$\xi = \varphi(\sigma)$$

making ξ another function of σ .

In real life, it takes time for state 1 to change to state 2, so you can intuitively think of σ as time. You can even take the time required for the change to take place (say it is τ), and have σ vary from 0 to τ instead of from 0 to 1. But the *T*, *P*, *Q*, or *W*, you calculate at these values of τ refer to a hypothetical reversible or quasistatic process, not to any measured or real values. You can assign any values you like to σ , but that does not make it a real time variable.

5 Time As A Thermodynamic Variable

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

McGlashan (1979), p. 102.

In my view, McGlashan is wrong, and he has plenty of company. 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 where does this idea come from? Clearly it comes from our understanding of entropy, "the arrow of time". For a much more detailed and lengthy examination of the "arrow of time" concept, see Uffink (2001).

For example, Denbigh (1966, Figure 9, p. 41) shows entropy increasing continuously as a function of time, as in Figure 2. This is clearly misleading, if you hold that only equilibrium states can have meaningful values of temperature, entropy, or other thermodynamic variables, as I do. The diagram shows entropy increasing continuously, with time as a variable, which can only refer to a continuous succession of equilibrium states, which is impossible.

Processes in thermodynamics are like a movie made up of a large number of individual frames. Each frame is fixed—an equilibrium state. When you play the movie forwards, the entropy in each frame increases (if U and V are held constant), so entropy is truly an arrow of time, because we know that time goes forward, not backward. But the individual frames in the movie do not know in which direction you are going to are going play the movie. They don't even know they are in a movie, because equilibrium states contain no information about preceding or subsequent states. Thermodynamics does not 'know' time. We, the users, know time, and it is so firmly entrenched in our consciousness, and so important to us, that we project it into thermodynamic theory.

There is no time variable in equilibrium thermodynamics, and that should be the end of it.



Figure 2: What Denbigh (1966, Figure 9) calls "The trend to equilibrium."



Figure 3: A container of gas enclosed in a larger space.

Well, not quite. In engineering thermodynamics, time is definitely a variable. However it is used to denote the time rate of change of fluid flow, energy changes and so on, and has no connection with the increase in entropy.

6 The Bursting Balloon

Perhaps my emphasis on models and on constraints in the text is sufficient to establish the importance of these concepts, but if not, then perhaps this striking example from Pippard (1960) will help make the case.

A small container of gas is enclosed in a larger container (Figure 3). By some means the wall of the gas container is pierced, and the gas escapes to fill the space. We have no difficulty in believing that given the proper data, we could calculate the entropy or volume change of the gas, once it has expanded. But Pippard (1960, p. 97) claims that⁵

⁵In this section Pippard uses the concept of constraints, and so he should perhaps be included in Appendix H. However, here his main focus seems to be on fluctuations, and constraints do not have a major role in the rest of the book.

"... when the gas is confined to the smaller volume it has one value of the entropy, and when the wall is pierced it has another value, and that it is the act of piercing the wall and not the subsequent expansion that increases the entropy."

Entropy is such a mysterious property that we might grudgingly accept this as part of the mystery; the idea is put in clearer focus by substituting "volume" for "entropy" in the quotation, because it applies to any state variable. No one denies that on piercing the wall, the gas expands, or that a finite time is required to do this, or that measurements could determine the ΔV or ΔS . The point is really one of models and constraints. Pippard is saying that once the constraints on a given system are decided upon, the equations describing the equilibrium state and all its properties are fixed, whether the real system has achieved that equilibrium state or not. By piercing the wall, we have changed the system constraints from one set of values to another, and the changes in all system properties are therefore fixed. In this point of view, there are two different "systems"—there is the real system, in which the gas really expands and requires a finite number of nanoseconds to equilibrate, and there is our model of that system, to which the equations of thermodynamics apply, and in which there are only equilibrium states. In the model, it is irrelevant whether the gas has expanded, or whether the experiment even exists.

7 The Meaning of $d\mathbf{G} = -\mathbf{S} dT + \mathbf{V} dP - \mathscr{A} d\xi$

The meaning of the differential equations in thermodynamics is often made easier to understand by working out a numerical example. This section shows how the equation

$$d\mathbf{G} = -\mathbf{S}dT + \mathbf{V}dP - \mathscr{A}d\boldsymbol{\xi}$$

$$[4.46]$$

is used to calculate the difference in Gibbs energy between aragonite at T_1 , P_1 and calcite at T_2 , P_2 , in both a reversible and an irreversible process. T_1 , P_1 and T_2 , P_2 have been chosen more or less at random as 500°C, 400 bar, and 25°C, 200 bar, so to begin we obtain data from SUPCRT92 for both calcite and aragonite at 200 and 400 bars, from 25 to 500°C at 25°C intervals. These data are shown in Tables 1 and 2.

7.1 Irreversible Processes

There are an infinite number of *GTP* paths between any two stable or metastable equilibrium states. In Figure 4 two of these paths have been chosen between our two equilibrium states. Evidently, the parts of the paths *on* the mineral surfaces are represented by $\int -SdT$ and $\int VdP$, while the vertical drop *between* the surfaces is represented by $\int \mathscr{A}d\xi$, consistent with equation [18.59].

Figure 4 is basically a more realistic version of Figure 4.9 in the text, using different phases as the equilibrium surfaces.⁶ Note that for generality and for dimensional consistency, equation [4.46] must be written using **G** (calories or joules) rather than *G* (cal mol⁻¹ or J mol⁻¹), and accordingly the vertical axis in Figure 4.9 is **G**. We have no data for **G**, but if we specify that our system consists of one mole of CaCO₃, $\mathbf{G} \equiv G$, $\Delta \mathbf{G} \equiv \Delta G$, and similarly for **S** and **V**. We can then plot values of $\Delta_a G^\circ$ from SUPCRT92 on our vertical axis, and the vertical *differences* between points on the diagram will then be values of $\Delta \mathbf{G}$ and ΔG . Equations not containing $\mathscr{A} d\xi$ are valid for both **G** and *G*.

⁶Both this example and the example in Figure 4.9 in the text are reactions between solid phases, in which an equilibrium state is not achieved at the chosen *T* and *P*. In Chapter 18 we consider a reaction taking place in a gaseous solution, in which an equilibrium state between products and reactants *is* achieved. In this case the surfaces representing products and reactants are not fixed in position, but gradually approach one another and finally merge, as $\mathscr{A}(\text{vector } AA' \text{ in Figure } 4.9) \rightarrow 0$.

	200 bar			400 bar		
Т	S°	V°	$\Delta_a G^\circ$	S° −	V°	$\Delta_a G^\circ$
°C	$cal mol^{-1} K^{-1}$	$\rm cm^3 mol^{-1}$	$calmol^{-1}$	$cal mol^{-1} K^{-1}$	$\mathrm{cm}^3 \mathrm{mol}^{-1}$	$cal mol^{-1}$
25	22.15000	36.934	-269704.3	22.15000	36.934	-269527.8
50	23.77368	36.934	-270278.4	23.77368	36.934	-270101.9
75	25.35507	36.934	-270892.7	25.35507	36.934	-270716.1
100	26.88714	36.934	-271545.8	26.8871	36.934	-271369.2
125	28.36724	36.934	-272236.6	28.3672	36.934	-272060.0
150	29.79523	36.934	-272963.7	29.7952	36.934	-272787.2
175	31.17234	36.934	-273725.9	31.1723	36.934	-273549.4
200	32.50056	36.934	-274521.9	32.5005	36.934	-274345.4
225	33.78225	36.934	-275350.6	33.7822	36.934	-275174.0
250	35.01991	36.934	-276210.7	35.0199	36.934	-276034.1
275	36.21603	36.934	-277101.2	36.2160	36.934	-276924.7
300	37.37306	36.934	-278021.1	37.3730	36.934	-277844.6
325	38.49332	36.934	-278969.6	38.4933	36.934	-278793.0
350	39.57902	36.934	-279945.5	39.5790	36.934	-279769.0
375	40.63221	36.934	-280948.2	40.6322	36.934	-280771.7
400	41.65481	36.934	-281976.9	41.6548	36.934	-281800.3
425	42.64860	36.934	-283030.7	42.6486	36.934	-282854.2
450	43.61525	36.934	-284109.1	43.6152	36.934	-283932.5
475	44.55629	36.934	-285211.3	44.5562	36.934	-285034.7
500	45.47313	36.934	-286336.7	45.4731	36.934	-286160.1

Table 1: Data for calcite from SUPCRT92.

	200 bar			400 bar		
Т	S°	V°	$\Delta_a G^\circ$	S°	V°	$\Delta_a G^\circ$
°C	$cal mol^{-1} K^{-1}$	$\rm cm^3 mol^{-1}$	calmol ⁻¹	$cal mol^{-1} K^{-1}$	$\mathrm{cm}^3\mathrm{mol}^{-1}$	$cal mol^{-1}$
25	21.56000	34.150	-269520.6	21.56000	34.150	-269357.3
50	23.15743	34.150	-270079.7	23.15743	34.150	-269916.4
75	24.69203	34.150	-270677.9	24.69203	34.150	-270514.7
100	26.16555	34.150	-271313.8	26.16555	34.150	-271150.5
125	27.58106	34.150	-271985.7	27.58106	34.150	-271822.5
150	28.94213	34.150	-272692.4	28.94213	34.150	-272529.1
175	30.25246	34.150	-273432.4	30.25246	34.150	-273269.1
200	31.51566	34.150	-274204.6	31.51566	34.150	-274041.3
225	32.73514	34.150	-275007.8	32.73514	34.150	-274844.6
250	33.91406	34.150	-275841.0	33.91406	34.150	-275677.8
275	35.05535	34.150	-276703.2	35.05535	34.150	-276540.0
300	36.16169	34.150	-277593.5	36.16169	34.150	-277430.2
325	37.23552	34.150	-278511.0	37.23552	34.150	-278347.8
350	38.27905	34.150	-279455.0	38.27905	34.150	-279291.8
375	39.29433	34.150	-280424.7	39.29433	34.150	-280261.5
400	40.28319	34.150	-281419.5	40.28319	34.150	-281256.3
425	41.24732	34.150	-282438.7	41.24732	34.150	-282275.4
450	42.18827	34.150	-283481.7	42.18827	34.150	-283318.4
475	43.10744	34.150	-284547.9	43.10744	34.150	-284384.7
500	44.00612	34.150	-285636.9	44.00612	34.150	-285473.6

Table 2: Data for aragonite from SUPCRT92.



Figure 4: Calcite (yellow) and aragonite (blue) surfaces in *GTP* space. The calcite surface has been moved down by 5000 cal mol⁻¹. (a) and (b) show two different overall irreversible paths between aragonite at 500°C, 400 bar, and calcite at 25°C, 200 bar.



Figure 5: Entropies of calcite and aragonite. The quadratic fit equations are shown as well as the fitted lines.

7.1.1 Figure 4a

Path AB On this path there is no change in V or ξ , so we need only integrate the -SdT term from 773.15 K down to 298.15 K. The equation describing the variation of S with T for aragonite is (from Figure 5)

$$S = -3.0197 \times 10^{-5} T^2 + 0.079064 T + 0.80973$$

so

$$\Delta G = -\int_{773.15}^{298.15} S dT$$

= $-\left[\frac{-3.0197 \times 10^{-5} T^3}{3} + \frac{0.079064 T^2}{2} + 0.80973 T\right]_{773.15}^{298.15}$
= $-3488.8 + 19604.8$
= $16116.0 \text{ cal mol}^{-1}$

<u>Path BC</u> On this path we need only integrate the V dP term, which is simple as V is assumed constant at 34.150 cm³ mol⁻¹ (Table 2), or 34.150 × 0.0239 = 0.8162 cal bar⁻¹ mol⁻¹.

$$\Delta G = \int_{400}^{200} 0.8162 \, dP$$

= 0.8162(200 - 400)
= -163.2 cal mol⁻¹

<u>Path CD</u> ΔG for this path is obtained directly from Tables 1 and 2. Doing this, we don't have to bother determining \mathscr{A} , or actually integrating $\mathscr{A}d\xi$. These things are done in Chapter 18. Figure 18.3 shows the fractional amounts of calcite and aragonite as a function of ξ , and Figure 18.9 shows **G** as a function of T and ξ for a different system.

$$\Delta G = \Delta_a G^\circ \text{ (calcite at 25°C, 200 bar)} - \Delta_a G^\circ \text{ (aragonite at 25°C, 200 bar)}$$

= -269704.3 - (-269520.6)
= -183.7 cal mol⁻¹
= - $\int \mathscr{A} d\xi$ consistent with equation (18.59) in the text.

Total ΔG The total change in G is then

$$\Delta G = -\int S dT + \int V dP - \int \mathscr{A} d\xi$$

= AB + BC - CD
= 16116.0 + (-163.2) - 183.7
= 15769 cal mol⁻¹ \Delta G for the irreversible path ABCD

7.1.2 Figure 4b

<u>**Path AE**</u> ΔG for this path is again obtained directly from Tables 1 and 2.

$$\Delta G = \Delta_a G^\circ \text{ (calcite at 500°C, 400 bar)} - \Delta_a G^\circ \text{ (aragonite at 500°C, 400 bar)}$$

= -286160.1 - (-285473.6)
= -686.5 cal mol⁻¹
= - $\int \mathscr{A} d\xi$

<u>Path EF</u> This path is like Path BC, but uses V for calcite instead of aragonite.

$$\Delta G = \int_{400}^{200} (36.934 \times 0.0239) dP$$

= 0.8827(200 - 400)
= -176.5 cal mol⁻¹

<u>Path FD</u> The equation describing the variation of S with T for calcite is (from Figure 5)

 $S = -3.220 \times 10^{-5} T^2 + 0.083209 T + 0.28932$

so

$$\Delta G = -\int_{773.15}^{298.15} S dT$$

= $-\left[\frac{-3.220 \times 10^{-5} T^3}{3} + \frac{0.083209 T^2}{2} + 0.28932 T\right]_{773.15}^{298.15}$
= $-3500.15 + 20132.76$
= $16632.6 \text{ cal mol}^{-1}$

Total ΔG The total change in G is then

We should not fail to notice too, that $\Delta G_{T,P} = -686.5 \text{ cal mol}^{-1}$. That is, for an an irreversible process from a metastable to a stable equilibrium state, $\Delta G < 0$ (equation [4.58]). It is the $\int \mathscr{A} d\xi$ term which gives rise to the inequality, not the fact that $q < \int T dS$ ([4.3]) as is sometimes stated.

7.1.3 Summary of the Irreversible Paths

The two different irreversible paths give the same ΔG , within 1 cal mol⁻¹, which can reasonably be ascribed to rounding error. Of course, if we really wanted to know this difference, we would not do such lengthy calculations, we would simply look up the two values of $\Delta_a G^\circ$ from the tables.

 $\Delta_r G = \Delta_a G^{\circ} \text{ (calcite at 25°C, 200 bar)} - \Delta_a G^{\circ} \text{ (aragonite at 500°C, 400 bar)}$ = -269704.3 - (-285473.6) = 15769 cal mol⁻¹

which is of course the same value.

7.2 Reversible Processes

The process in which aragonite at 500°C, 400 bar changes to calcite at 25°C, 200 bar is normally considered to be irreversible, and in real life it is. But as is the case for many chemical reactions, a hypothetical reversible path can be found and calculations carried out along this path. We expect that, because *G* is a state variable, ΔG between our two chosen equilibrium states will be the same no matter how we do the calculation.

For the simple aragonite \rightarrow calcite reaction, a reversible change is one that proceeds from aragonite at T_1, P_1 up in pressure along the aragonite surface to the equilibrium boundary with calcite, then back down on the calcite surface to T_2, P_2 . One such path is shown in Figure 6a.⁷

⁷Near the bottom of p. 120 in the text, I say that calculating this reversible path would not work very well. This is incorrect. The fact that the molar volumes are assumed constant in fact makes it quite simple.

Figure 6b is simply a reminder that no real transformation of aragonite to calcite follows any of these paths. You might imagine a little red equilibrium light on the aragonite surface at 500°C, 400 bars going off, and some time later, a little red equilibrium light going on, on the calcite surface at 25°C, 200 bar. The irreversible path cannot be plotted in *GTP* space. The paths implied by integrating equations [4.40], [4.46] and the like are used to *calculate* the change in Gibbs energy, not to describe how the change takes place.

The Equilibrium Pressure First, we need to calculate the pressure at which the calcite and aragonite surfaces intersect at 25° C, the temperature at point F. This is different than the pressure calculated in the text (page 164) because we are using SUPCRT92 data. The calculation follows that on p. 164.

$$\Delta_r V^\circ = 34.150 - 36.934$$

= -2.784 cm³ mol⁻¹
= -0.06654 cal bar⁻¹ mol⁻¹

 $\Delta_r G^{\circ} = \Delta_a G^{\circ} \text{ (calcite at 25°C, 1 bar)} - \Delta_a G^{\circ} \text{ (aragonite at 25°C, 1 bar)}$ = -269880 - (-269683) = -197 cal mol⁻¹

 $P_{\text{eqbm}} = \frac{-197}{-0.06654} + 1$ = 2962 bar calcite-aragonite equilibrium at 25°C

<u>Path AB</u> This path is the same as before, so $\Delta G = 16116.0 \text{ cal mol}^{-1}$.

Path BG From aragonite at 25°C, 400 bar to aragonite at 25°C, 2962 bar, we have

 $\Delta G = (34.150 \times 0.0239) \times (2962 - 400)$ = 2090.8 cal mol⁻¹

At Point G

$$\Delta G = G_{\text{calcite}} - G_{\text{aragonite}}$$
$$= 0$$

Path GD From calcite at 25°C, 2962 bar to calcite at 25°C, 200 bar, we have

$$\Delta G = (36.934 \times 0.0239) \times (200 - 2962)$$

= -2437.8 cal mol⁻¹



Figure 6: Calcite (yellow) and aragonite (blue) surfaces in *GTP* space. The calcite surface has been moved down by 5000 calmol⁻¹. (a). ABGD is a reversible path between aragonite at 500°C, 400 bar, and calcite at 25°C, 200 bar. Point G is off the diagram, and is the point at which the two surfaces intersect at 25°C. (b). No real aragonite—calcite transformation follows any of these paths.

Total ΔG The total change in G for the reversible path (one that never leaves the equilibrium surfaces) is then

$$\Delta G = -\int S dT + \int V dP$$

= AB + BG + GD
= 16116.0 + 2090.8 - 2437.8
= 15769 cal mol⁻¹ \Delta G for the reversible path ABGD

7.3 Summary

These calculations make the meaning of equations

$$dG = -S\,dT + V\,dP \tag{4.40}$$

and

$$d\mathbf{G} = -\mathbf{S}dT + \mathbf{V}dP - \mathscr{A}d\xi \qquad [4.46]$$

very clear. If a process begins and ends on the same equilibrium *GTP* surface, integration of equation [4.40] allows calculation of ΔG for that process. It doesn't matter if the process stays on the surface (reversible; e.g., $A \rightarrow B \rightarrow C$ in Figure 4a, or if the process cannot be plotted in *GTP* space (irreversible), or if the system is metastable, as long as the number of constraints does not change. However if the process involves release of a constraint (e.g., allowing aragonite to change to calcite), then equation [4.46] must be used.

Nevertheless, ΔG for the initial state \rightarrow final state is the same, no matter what happens in between. This is also true for all other state variables.

8 Fugacities Do Not Control Anything

Over the years I have noticed a tendency for authors to speak or write about their interpretations of rock or ore deposit origins as if the fugacity of oxygen or of sulfur was a controlling factor. This always appeared to me to show a fundamental misunderstanding of the role fugacity plays in condensed (non-gaseous) systems. I addressed this topic in the first edition, carried over now to page 364 in this edition, with the statement (referring to fugacity):

For a closed system at a given T and P, it is completely determined by the bulk composition, as are all intensive parameters, and changes in redox state are accomplished by changing bulk composition.

This means, in other words, that it is the composition of the system that controls the fugacity, and not the other way around. A system or rock mass will become more oxidized because its composition changes, not because its oxygen fugacity increases.

I think now that more emphasis on this point is needed. A stronger statement would be

Saying that the fugacity of oxygen has some control on the observed mineral assemblage is like saying the weather got warmer because the mercury in the thermometer went up. In condensed systems, fugacity is just an indicator of the ratio of reduced to oxidized species. In experimental work fugacity is often controlled in order to control composition, and this is very likely the origin of the confusion. In natural processes, fugacity is not a control but a result of whatever bulk compositions are achieved by geological processes.

9 Denbigh on Entropy as Mixing

The following section from Denbigh (1966, pp. 48–49) is a discussion of entropy which fits rather well with the discussion in Chapter 4 of the text (italics in the original).

1.17. Natural processes as mixing processes

The reason for the irreversibility of natural phenomena and the significance of entropy can be made much clearer as soon as we have recourse to the atomic theory of matter. A discussion on these lines is actually foreign to pure thermodynamics, but it is so helpful to the understanding that a preliminary account will be given in this section, ...

As soon as it is accepted that matter consists of small particles which are in motion it becomes evident that every large-scale natural process is essentially a process of *mixing*, if this term is given a rather wide meaning. In many instances the spontaneous mixing tendency is simply the intermingling of the constituent particles, as in the interdiffusion of gases, liquids and solids. It arises because at the interface between two phases there are always a certain number of atoms or molecules whose direction of movement tends to carry them across the boundary. Similarly, the irreversible expansion of a gas may be regarded as a process in which the molecules become more completely mixed over the available space.

In other instances it is not so much a question of a mixing of the particles in space as of a mixing or sharing of their total energy. For example, if blocks of tin and copper are placed in contact there is, on the one hand, a slow diffusional mixing of the atoms themselves and, on the other hand, a very much more rapid exchange of energy, taking place through the mechanism of the atomic vibrations at the interface. The irreversible process of temperature equalization may thus be regarded as a mixing of the available energy. Similarly, in the irreversible process of friction, the kinetic energy of a body as a whole is converted into the random energy of its component molecules.

Rather less obvious is the example of a chemical reaction. Here it is a question of the mixing or 'spreading' of the total energy of the system over the whole range of quantized energy levels of the reactants and products. The occurrence of the reaction causes a larger number of these quantum states to become accessible, namely, those corresponding to the products. The final equilibrium composition of an adiabatically isolated reaction system is the composition at which the available energy is distributed over the various quantum states in the most completely random manner.

10 Hardy on Differentials

The following discussion of derivatives and differentials is the clearest and most comprehensible that I have come across. I realize that some readers of the text may find my use of "macroscopic differentials" unusual, if not disturbing. It may therefore be comforting to find that a famous mathematician (Hardy, 1958) says essentially the same thing.

Chapter VI, pages 218–219

116. The notation of the differential calculus. We have already explained that what we call a *derivative* is often called a *differential coefficient*. Not only a different name but a different notation is often used; the derivative of the function $y = \phi(x)$ is often denoted by one or other of the expressions

$$D_x y, \quad \frac{dy}{dx}$$

Of these the last is the most usual and convenient: the reader must however be careful to remember that dy/dx does not mean 'a certain number dy divided by another number dx': it means 'the result of a certain operation D_x or d/dx applied to $y = \phi(x)$ ', the operation being that of forming the quotient $\{\phi(x+h) - \phi(x)\}/h$ and making $h \to 0$.

Of course a notation at first sight so peculiar would not have been adopted without some reason, and the reason was as follows. The denominator *h* of the fraction $\{\phi(x+h) - \phi(x)\}/h$ is the difference of the values x + h, *x* of the independent variable *x*; similarly the numerator is the difference of the corresponding values $\phi(x+h)$, $\phi(x)$ of the dependent variable *y*. These differences may be called *increments* of *x* and *y* respectively, and denoted by δx and δy . Then the fraction is $\delta x/\delta y$, and it is for many purposes convenient to denote the limit of the fraction, which is the same thing as $\phi'(x)$, by dy/dx. But this notation must for the present be regarded as purely symbolical. The *dy* and *dx* which occur in it cannot be separated, and standing by themselves they would mean nothing: in particular *dy* and *dx* do not mean $\lim \delta y$ and $\lim \delta x$, these limits being both zero. The reader will have to become familiar with this notation, but so long as it puzzles him he can avoid it by writing the differential coefficient in the form $D_x y$, or using the notation $\phi(x)$, $\phi'(x)$, as we have done in the preceding sections of this chapter.

In Ch. VII, however, we shall show how it is possible to define the symbols dx and dy in such a way that they have an independent meaning and that the derivative dy/dx is actually their quotient.

Chapter VII, pages 307–308

160. Differentials

In the applications of the calculus, especially in geometry, it is usually most convenient to work with equations expressed not, like equation (1) of § 159,⁸ in terms of the increments δx , δy , δz of the functions *x*, *y*, *z*, but in terms of what are called their *differentials dx*, *dy*, *dz*.

Let us return for a moment to a function y = f(x) of a single variable *x*. If *f* is differentiable then

$$\delta y = \{f'(x) + \varepsilon\}\delta x \tag{14}$$

where ε tends to zero with δx . The equation

$$\delta y = f'(x)\delta x \tag{15}$$

is 'approximately' true.

We have up to the present attributed no meaning to the isolated symbol dy. We now agree to *define* dy by the equation

$$dy = f'(x)\delta x \tag{16}$$

⁸The equation referred to is " $\delta z = (f'_x + \varepsilon)\delta x + (f'_y + \eta)\delta y$, where ε and η are small when δx and δy are small.".

If we choose for *y* the particular function *x*, we obtain

$$dx = \delta x \tag{17}$$

so that

$$dy = f'(x)dx \tag{18}$$

and if we divide both sides of (5) by dx we obtain

$$\frac{dy}{dx} = f'(x) \tag{19}$$

where dy/dx denotes not, as heretofore, the differential coefficient of y, but the quotient of the differentials dy, dx. The symbol dy/dx thus acquires a double meaning; but there is no inconvenience in this, since (6) is true whichever meaning we choose.

We pass now to the corresponding definitions connected with a function z of two independent variables x and y. We define the differential dz by the equation

$$dz = f'_x \delta x + f'_y \delta y \tag{20}$$

Putting z = x and z = y in turn, we obtain

$$dx = \delta x, \quad dy = \delta y \tag{21}$$

so that

$$dz = f'_x dx + f'_y dy \tag{22}$$

which is the exact equation corresponding to the approximate equation (1) of §159.

One property of the equation (9) deserves special remark. We saw in §157 that if z = f(x, y), x and y being not independent but functions of a single variable t, so that z is also a function of t alone, then

$$\frac{dz}{dt} = \frac{\delta f}{\delta x}\frac{dx}{dt} + \frac{\delta f}{\delta y}\frac{dy}{dt}$$

Multiplying this equation by dt and observing that

$$dx = \frac{dx}{dt}dt, \quad dy = \frac{dy}{dt}dt, \quad dz = \frac{dz}{dt}dt,$$

we obtain

$$dz = f'_x dx + f'_y dy,$$

which is the same in form as (9). Thus the formula which expresses dz in terms of dx and dy is the same whether the variables x and y are independent or not. This remark is of great importance in applications.

It should also be observed that if z is a function of the two independent variables x and y, and

$$dz = \lambda dx + \mu dy$$

then $\lambda = f'_x$ and $\mu = f'_y$. This follows at once from §159.

It is obvious that the theorems and definitions of the last three sections are capable of immediate extension to functions of any number of variables. The differential notation has great technical advantages, particularly in geometry.

11 A Very Common Misunderstanding

$$dU \le T \, dS - P \, dV, \quad \text{or} \qquad [4.19]$$

$$dG \le -S \, dT + V \, dP, \quad \text{or}$$

$$dH \le T \, dS + V \, dP$$

or any of the many variations of these equations. It is well understood, and invariably stated, that the equality (=) refers to reversible processes and the inequality (<) to irreversible processes. The misunderstanding is the belief that the inequality is a result of the fact that q < T dS for irreversible processes. This is not true.

The fact that the equality applies to *both* reversible and irreversible processes is explained as clearly as I can in §4.8, so I will not repeat that discussion here, except to say that because these equations involve only state variables it cannot possibly make any difference how the change referred to is carried out, reversibly or irreversibly, *as long as the beginning and ending states of the change or process are both stable equilibrium states*, in other words, as long as they both lie on the same *USV* (or *GTP* or *HSP*) surface. What is not well understood is that there are two kinds of irreversibily.

The first kind is the irreversibility which results, for example, when the pressure on a gas is suddenly reduced to a lower pressure. This kind of irreversibility is discussed at length in Chapter 3. It results in less than the maximum amount of work being done, and less than the maximum amount of heat transferred (w < P dV and q < T dS). The gas is in a stable equilibrium state before and after the expansion; both states lie on the same state surface. The irreversibility which results from a spontaneous chemical reaction or from a metastable state changing irreversibly to a stable state is quite different. In these cases the initial state lies *off* the stable *USV* (or whatever) surface, and energy is released as the process takes place. This energy is *in addition* to the *T dS* and *P dV* energy (or whatever two terms are on the right side of the inequality). It must be represented by a third term on the right side, which is normally the affinity-progress variable ($\mathscr{A} d\xi$) term. If it is not included, the inequality results.

It is my belief that this problem results from the fact that most of us learn our thermodynamics from chemists and chemistry texts. In chemistry, metastable states are such things as supercooled liquids. They are thought of as transitory and not very important. It may be mentioned somewhere that the inequality results if the system contains chemical reactions, but this is not emphasized, and the full form of the energy balance, for example

$$d\mathbf{G} = -\mathbf{S}dT + \mathbf{V}dP - \mathscr{A}d\boldsymbol{\xi}$$

$$[4.46]$$

is not usually presented. I say that a spontaneous chemical reaction is represented in thermodynamics (as opposed to in the lab or in nature) by a metastable to stable transition, just as much as the aragonite to calcite transition. The energy difference between the initial and end states is the source of the inequality.

12 The One Minute Test

A handy "one minute test" of any thermodynamic text is as follows:

⁹The most recent example of this misunderstanding that I have seen is in Stolper, E., and Asimow, P. (2007) Insights into mantle melting from graphical analysis of one-component systems. American Journal of Science, v. 907, pp. 1051–1139, equation (7) and its derivation.

- 1. Look at the derivation of dU = T dS P dV. It is invariably explained there that this equation is valid for both reversible and irreversible processes.
- 2. Then look at the derivation of $dU_{S,V} \le 0$, or $dG_{T,P} \le 0$, where it is claimed that the < symbol applies to irreversible processes. Without any other discussion, these two statements are inconsistent, and the book fails the test.

The problem is of course the failure to distinguish clearly between an irreversible process between two stable equilibrium states, such as a sudden gas expansion ($\S3.4.1$), and an irreversible process from a metastable equilibrium state to a stable equilibrium state ($\S4.8$).

Acknowledgments

I thank Edgar Froese and Terry Gordon for their perceptive comments on these exotic subjects.

References

- Anderson, G.M., and Crerar, D.A., 1993, Thermodynamics in Geochemistry—The Equilibrium Model. Oxford University Press, New York, 588 pp
- De Donder, Th. (with F.H. van den Dungen and G. van Lerberghe), 1920, Leçons de Thermodynamique et de Chimie-Physique. Gauthiers-Villars, Paris.
- Denbigh, K., 1966, The Principles of Chemical Equilibrium, Second Edition: Cambridge, Cambridge University Press, 494 pp.
- Froese, E., 1981, Applications of thermodynamics in the study of mineral deposits. Geological Survey of Canada, Paper 80-28, 38 pp.
- Gibbs, J.W., 1876, On the equilibrium of heterogeneous substances. Reprinted in: "The Scientific Papers of J.Willard Gibbs" Vol.1 Thermodynamics, pp. 55–349, Dover Publications Inc., New York, 1961.
- Hardy, G.H., 1958, A Course of Pure Mathematics, 10th Edition. Cambridge University Press, 1958
- Lewis, G.N., and Randall, M., 1961, Thermodynamics. Second Edition. Revised by K.S. Pitzer and L. Brewer. New York, McGraw-Hill Co. Inc., 723 pp.
- McGlashan, M.L., 1979, Chemical Thermodynamics. Academic Press, London, 345 pp.
- Pippard, A.B., 1966, Elements of Classical Thermodynamics. Cambridge University Press, 165 pp.
- Prigogine, I., and Defay, R., 1954, Chemical Thermodynamics. London, Longmans Green, 543 pp.
- Ricci, J.E., 1951, The Phase Rule And Heterogeneous Equilibrium. D. Van Nostrand Inc., pp. 19–21.
- Thompson, J.B. Jr., 1959, Local equilibrium in metasomatic processes, in: P.H. Ableson, ed., Researches in Geochemistry v. 1: New York, Wiley and Sons, pp. 427–457.
- Tunell, G., 1932, On the history and analytical expression of the first and second laws of thermodynamics, and the rôle of the differentials, dW and dQ. Jour. Phys. Chem., v. 36, pp. 1744–1771.
- Tunell, G., 1941, Notation for the derivatives of the two types of line integral in thermodynamics. Jour. Chem. Phys., v. 9, pp. 191–192.

Uffink, J., 2001, Bluff your way in the second law of thermodynamics. Studies in History and Philosophy of Modern Physics, v. 32, No. 3, p. 305–394.