

EQUILIBRIUM THERMODYNAMICS—REVISITED

Dear Editor:

I am pleased that Williams and Glasser^[1,2] have outlined the course in thermodynamics that I introduced at the University of the Witwatersrand in 1982 and lectured there until the end of 1984. There are, however, a few points that I feel need clarification.

One reason for the difficulties students often encounter in thermodynamics is the confusion over variables and functions. One encounters references in the same context to H , $H(T,P)$ and $H(T,V)$, for example, in which the single symbol H means at least three different things: *e.g.*, a variable and two distinct functions.

An important objective of my approach is to attempt to overcome the confusion to which this symbolism gives rise. The symbol for any function is *always* constructed so that it explicitly displays the independent variables (as superscripts) and the dependent variable. Thus the function from T and P to H is written H^{TP} . On the other hand, the *value* of the function at T and P is written $H^{TP}(T,P)$. One can write

$$H = H^{TP}(T,P) \quad (1)$$

but not

$$H = H^{TP} \quad (2)$$

(at least for the present).

Williams and Glasser explain the symbolism and write statements like Eq. (1). However, they then apparently break the rules in a number of ways: a variable is equated to a function and not its value (*e.g.*, $S = S^{TV}$ in their Eq. 19); the same symbol is used for a variable and a function (*e.g.*, $V = V(S)$); they talk of "a new function $A = U - TS$ "; etc. Having warned the reader of the importance of not confusing functions and values of functions, they do just that throughout both papers.

From the outset it is necessary to confine the use of the term function to things that are functions. A function always takes the form H^{TP} :

$$H^{TP}: T, P \rightarrow H \quad (3)$$

Then A may be a variable, but it is certainly not a function. The term *state function* is not used—*parameter* or *property* is better.

If one has particular values for the independent variables, then one can write

$$H = H^{TP}(T_1, P_1) \quad (4)$$

for example. Very often one does not, in which case the presence of T and P twice in Eq. (1) may appear unnecessary. When the students have become familiar with the notation, and confident in its use, I draw attention to this apparent redundancy (if the students have not already done so). I then say that *if the context makes clear that the value of the function is meant*, we can agree, from now on,

Winter, 1992

to an abbreviated notation: we may write H^{TP} for $H^{TP}(T,P)$. The convention is that H^{TP} always means the function unless the context shows that it must mean the *value* of the function. In the latter case, the (T,P) is to be understood even though it is not explicitly displayed. Wherever there is any chance of confusion or doubt, (T,P) is not to be omitted. Now, and only now, does it become legal to write such equations as Eq. (2) above and Eq. (19) of the paper by Williams and Glasser. I found it necessary to resort to the sort of fuss and circumspection resorted to here.

If we are taking care to distinguish functions and their values, we need to do so with *derived functions* or derivatives as well. Thus

$$\frac{\partial U^{SV}}{\partial S} \text{ or } U^{S'V}$$

is a derived function and

$$\frac{\partial U^{SV}}{\partial S}(S,V) \text{ or } U^{S'V}(S,V)$$

its value (the above convention still applying). It now becomes possible to agree with Eq. (18) of Williams and Glasser

$$T = U^{S'V} = T^{SV}$$

The context implies an abbreviation for

$$T = U^{S'V}(S,V) = T^{SV}(S,V) \quad (5)$$

Williams and Glasser write (their Eq. 25)

$$\frac{\partial}{\partial S} \left(\frac{\partial U^{SV}}{\partial V} \right) \quad (6)$$

This violates the rules of notation just as much as

$$\frac{\partial P}{\partial S}$$

does. One needs to write

$$\frac{\partial}{\partial S} \left(\frac{\partial U^{SV}}{\partial V} \right)^{SV} \quad (7)$$

Otherwise one has no means of distinguishing the expression from

$$\frac{\partial}{\partial S} \left(\frac{\partial U^{SV}}{\partial V} \right)^{SP} \quad (8)$$

for example. While the order may normally be reversed with impunity in Eq. (7) (that is, when the superscripts repeat), it cannot in Eq. (8) (that is, when they do not). On the other hand

$$\frac{\partial^2 U^{SV}}{\partial S \partial V}$$

is unambiguous. There are hidden traps in Eq. (6) out of which I have rescued more than one student. Students easily obtain cross-differentiation identities that are simply not true.

My equation

$$\left. \frac{dH}{dT} \right|_{dP=0} = \frac{\partial H^{TP}}{\partial T} \quad (9)$$

(Eq. 9 of Williams and Glasser) I have preferred since

Continued on page 29.

LETTER: Equilibrium Thermodynamics

Continued from page 7.

1984 to write

$$\frac{dH}{dT} = \frac{\partial H^{TP}}{\partial T} \quad \text{if} \quad dP = 0 \quad (10)$$

($dP = 0$ does not have any special attachment to the ratio that precedes it.) It is extremely useful, but I have seen it nowhere else. dH and dT are differentials, smallness not being implied.

Williams and Glasser give the following definition of an integral:

$$\int_{S_1}^{S_2} T^{SV} dS = \lim_{N \rightarrow \infty} \left(\sum_{i=1}^N T^{SV}(S_i, V(S_i)) \Delta S_i \right) \quad (11)$$

(A missing comma has been added on the right.) I believe the definition is faulty. The main point about the proposed notation is that the superscript variables are *independent*. In $\partial U^{SV}/\partial S$, the variable V has nothing to do with the differentiation as such. One can, of course, define a new function U^S by

$$U^S = U^{SV}(S, V^S) \quad (12)$$

for some function (or "path") V^S and then obtain the derivative $\partial U^S/\partial S$. Because

$$T^{SV} = \frac{\partial U^{SV}}{\partial S} \quad (13)$$

one logically writes the corresponding anti-derivative or integral as

$$\int T^{SV} dS = U^{SV} + B^V \quad (14)$$

and

$$\int_{S_1}^{S_2} T^{SV} dS = U^{SV}(S_2, V) - U^{SV}(S_1, V) \quad (15)$$

The latter is a function of the single variable V , say I^V . It is clear that the definition should in fact be

$$\int_{S_1}^{S_2} T^{SV} dS = \lim_{N \rightarrow \infty} \left(\sum_{i=1}^N T^{SV}(S_i, V) \Delta S_i \right) \quad (16)$$

The definition Williams and Glasser give is the definition for the constant

$$\int_{S_1}^{S_2} T^S dS \quad (17)$$

where

$$T^S = T^{SV}(S, V^S) \quad (18)$$

again for a particular function (or "path") V^S . Of course, the integral then depends on the function V^S and is, therefore, function (or "path") dependent. (It is commonly termed a *functional*.) The integral of Eq. (16), on the other hand, is variable dependent, not function dependent. The description "path-dependent function" is clearly ill-advised. Both of the integrals given by Eqs. (16) and (17) are useful.

Incidentally, expressions of the form
Winter, 1992

$$Q = \int T dS \quad (19)$$

are justifiable in this context only as abbreviations for integrals like those above.

In their treatment of my approach to conservation of energy, Williams and Glasser employ what I think is a little unnecessary circularity. They use the concept "well-insulated enclosure" to discover the concept commonly called "heat." But it is not clear what a "well-insulated enclosure" means when one has yet to meet "heat." My approach is to argue that experiments are found to fall into two classes: those for which

$$\Delta U = w \quad (20)$$

holds, and those for which it does not. The former are called anything we like—say, *adiabatic* (but it could as well be *well-insulated* for that matter)—or are said to be surrounded by an adiabatic wall; the latter, non-adiabatic, or surrounded by a *diathermal* wall. At this stage of the argument these terms mean nothing except that Eq. (20) is or is not obeyed. (It is easy to add terms on the left where necessary to account for kinetic and potential energy.) Now one is ready to invent a new quantity which can be given the symbol q ; it is merely the quantity that allows Eq. (20) to be modified so that it always holds. The modified equation (and definition of q) is

$$\Delta U = q + w \quad (21)$$

The confused thinking one encounters elsewhere over "work" and "heat" is quite remarkable. Suggestions that the gerunds "working" and "heating" be used instead^[2] do not seem helpful. I use "mechanical" and "thermal transfer of energy." I also quote Callen's^[3] analogy of the pond and the modes of transfer to it of water by rain and by stream which, when I encountered it, gave me just the sort of aha!-insight into thermodynamics that I had badly needed.

I borrowed (and modified) the postulates from Callen that now appear in the latter half of Williams and Glasser.^[2] Much of what follows there is also based on Callen. But there are other sources and influences; for example, the early ideas of researchers such as Georgian^[4,5] with whom I had corresponded about the units of temperature and the "universal gas constant" R .

Williams and Glasser describe what Callen calls the basic problem of thermodynamics and use his method of solving it when the internal adiabatic constraint is removed: one maximizes entropy over all constrained states. At the end of Part 2 they suggest that the student try three ostensibly similar problems in which other internal constraints are removed. Their first problem requires removal of an internal rigidity constraint and no other. It turns out, however, that the method does not work in this case (as it is not difficult to show). Solution by maximization of entropy always assumes removal of the adiabatic constraint at least. Earlier in Part 2, Williams and Glasser raise the practical difficulty of how to relax the permeability constraint without relaxing the adiabatic constraint as well. The answer is that one does not.

Continued on page 37.

learning has been more difficult to quantify. Anecdotal evidence abounds as to the student's preference for this mode of learning and to instructors who feel that the students learned more and performed as well, if not better, on written exams than did students who previously "learned" the material via traditional lectures.^[5,6]

We are changing some components since they did not work out as we had hoped. In particular, the blend of problem solving with computer programming in the sophomore year did not provide the synergy we anticipated. The students viewed them as two separate parts. So we have integrated computer programming into the mass and energy balances course and maintained a separate 2-credit course on problem solving that applies the skills in the required co-requisite mass and energy balances course. This latter bridge has worked extremely well.

The extra course in reactor design in the senior year, likewise, has not lived up to its expectations. So we combined the non-ideal behavior with the junior course (now 4 credits) and created a richer, elective course in reactor design. Also, the students found that the sophomore fluid mechanics course was very challenging, so we have now switched this to the junior year.

The design project is much more effective in the new format. We have shifted from PROCESS to HYSIM as the computer executive program of choice.

These changes have been minor. All in all, we feel that this new format offers a very viable curriculum model for the year 2000.

ACKNOWLEDGEMENT

I am pleased to acknowledge the efforts and input of my colleagues. To Bob Moore, Leslie Eubanks, Cam Crowe, Terry Hoffman, Joe Wright, Andy Hrymak, Phil Wood, Paul Taylor, Bob Marshall, and Ian Doig for nurturing the problem-solving courses; to Derek Ryder, Steve Kelly, Joe Laricchia, Craig McDougall, Bret Cousins, and Sandra Allen; to Bob Anderson, Les Shemilt, John MacGregor, Irwin Feuerstein, Malcolm Baird, Marios Tsezos, Andy Benedek, Keith Murphy, Archie Hamielec, John Brash, John Vlachopoulos, and Jim Dickson. The Ontario Universities Program for Instructional Development and McMaster University funded the four-year program to understand and develop the problem solving/interpersonal skills components. In particular, I thank Alvin Lee, Vice-President Academic, and Les King and Alan Blizzard, Instructional Development Center, for ongoing support.

Winter, 1992

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LETTER: Equilibrium Thermodynamics

Continued from page 29.

The adiabatic constraint is removed in their second and third problems, which should, therefore, cause the student no difficulties.

(Many of the points discussed here I raised in the literature a decade ago or more.^[6-11])

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