

# AN INTRODUCTION TO EQUILIBRIUM THERMODYNAMICS

## *A Rational Approach to Its Teaching*

### PART 1: Notation and Mathematics<sup>1</sup>

DONALD F. WILLIAMS, DAVID GLASSER  
*University of the Witwatersrand  
Johannesburg, South Africa*

Traditionally, undergraduate students of thermodynamics have difficulty understanding the subject and its material. While we do not deny that there are conceptual difficulties to overcome, it seems to us that there are two factors in the usual approach that make a student's introduction to thermodynamics more difficult than is necessary.

First, there is the underlying mathematics of the state functions and the notation associated with it. This often seems to suggest that the "state functions" and their mathematics are different from the functions which the student has already met in his previous mathematical education. Second, the way in which the state functions (internal energy, entropy, and temperature) are introduced is not easily related to the students' previous background in physics.

In order to address these two problems, we developed an approach which has now been taught to third-year chemical engineering undergraduates for the last six to seven years. It has been our experience that the students have been able to relate the material to their previous work in mathematics and physics with relative ease, and that they have been able to assimilate the subject without undue difficulty. As a result, the general level of understanding—of both the students and the teachers—has been significantly improved.

Since the approach tackles the two factors mentioned above, which have applicability in quite dif-

<sup>1</sup> Part 2 of this paper, "Internal Energy, Entropy, and Temperature," will appear in the next issue of *CEE*.



*Donald Williams has taught at the University of the Witwatersrand since 1967. He has a special interest in teaching chemical engineering to students at the junior end of the curriculum and has recently devised a new course to be taught to first-year students. His interest in improving the teaching of thermodynamics was first aroused while being taught by David Glasser in one of his earliest efforts.*

*David Glasser is a professor of chemical engineering at the University of the Witwatersrand. He holds degrees from the University of Cape Town and Imperial College (London). His main areas of interest are reaction engineering and mathematical modeling. He has been interested in teaching thermodynamics ever since he first became involved after being "made an offer" as the most-junior member of the academic staff.*



ferent areas, it is convenient to divide our presentation into two parts. Part 1 will consider notation and the mathematical development, and Part 2 (which will appear in the next issue of *CEE*) will be concerned with the introduction of the state functions. The notation which we introduce was developed by Harris,<sup>[1,2]</sup> and the axiomatic approach adopted in Part 2 is based on Callen,<sup>[3]</sup> who suggested this method as long ago as 1960. We find it surprising that Callen's approach has not found more favor with educators. It is the purpose of this paper to show how these ideas can be combined to form a logical and consistent introduction to thermodynamics.

#### **Notation and Mathematical Development**

Thermodynamics traditionally employs a derivative notation which is rarely used elsewhere and which is not obviously consistent with the mathematics which students learn and use in other courses. Thus, the conceptual difficulties are compounded by the need to learn a sort of "thermodynamic mathe-

matics" which has special kinds of partial derivatives and non-exact differentials. The mere manipulation of the notation becomes such an arcane process that this ability is in itself regarded as "thermo," and purely mathematical results are confused with the results of thermodynamics.

These non-standard forms arise for historical reasons and from the problems which arise in using the same symbol to denote a value as well as a function. We will outline below an alternative method of presenting the material which is entirely consistent with the mathematics of functions to which students are accustomed.

We start by emphasizing that the development at this stage is purely algebraic, and no physical significance is intended to be attached to any of the variables we use. Everything could, in fact, be developed in terms of  $x$ ,  $y$ , and  $z$ . However, we prefer to adopt a set of symbols in which the equations we develop will turn out (when at a later stage we do give significance to some of the symbols) to be directly useful.

### Notation

Consider a variable  $H$  which may be expressed as a mathematical function (that is a rule for obtaining a value for a dependent variable from given values of a set of independent variables) of two other variables  $T$  and  $P$ . For example, we might write that

$$H = T^2 + 2T \log(P) \quad (1)$$

Now suppose that another variable  $V$  may also be expressed as a function of  $T$  and  $P$ ; suppose, for example, that  $V = T/P$ . Since we can solve this relationship to give  $P = T/V$ , we can substitute in Eq. (1) to express  $H$  as a function of  $T$  and  $V$

$$H = T^2 + 2T \log(T / V) \quad (2)$$

We thus have two possible functions for  $H$ . The first gives us the rule for calculating a value of  $H$  from given values of  $T$  and  $P$ . The second is the rule for calculating a value of  $H$  from values of  $T$  and  $V$ . We might be tempted to indicate these two possible functions for  $H$  by some such notation as  $H(T,P)$  and  $H(T,V)$ . However, this is contrary to all the rules for functions we have learned in mathematics, where if  $H(T,P)$  is given by Eq. (1), then it follows that

$$H(T, V) = T^2 + 2T \log(V) \quad (3)$$

which is not the same as Eq. (1) and will *not* give the required value for  $H$  as Eq. (2) will when the state of the system is given by corresponding values of the variables  $P$ ,  $V$ , and  $T$ . To keep to the mathematical

---

***We find it surprising that Callen's approach has not found more favor with educators. It is the purpose of this paper to show how these ideas can be combined to form a logical and consistent introduction to thermodynamics.***

---

formulation to which we are accustomed, we need to write something like

$$H = f(T, P)$$

for Eq. (1), and

$$H = g(T, V)$$

for Eq. (2), the corresponding relationship in terms of  $T$  and  $V$ , where we use  $f$  and  $g$  to indicate that *different* functions are involved. It is clear that we need to avoid confusion between the *value* of  $H$  at certain conditions and its functional form in terms of the chosen independent variables.

The difficulty in thermodynamics arises from two factors. First, the actual functional relationships are rarely known explicitly, and we are usually forced to work only with their derivatives and other properties. Second, given the large number of dependent variables of interest ( $H$ ) and the even larger possible number of combinations of independent variables ( $P, T, V, \dots$ ), there are not really enough function symbols ( $f, g, \dots$ ) to go around. Even if there were enough, it would be very tricky to remember which function symbol represented which variable as a function of which independent variables.

We solve this problem by adopting a notation where  $f$  and  $g$  are replaced, respectively, by  $H^{TP}$  and  $H^{TV}$ . We may then write **equations** such as  $H = H^{TP}(T, P)$  and  $H = H^{TV}(T, V)$ , where the superscripts remind us both that we are dealing with independent functional forms and of the independent variables with which we are concerned, while the terms in brackets tell us the values of these variables at which to evaluate the function. For the example above, we will now have the functions

$$H^{TP} = T^2 + 2T \log(P) \quad (4a)$$

and

$$H^{TV} = T^2 + 2T \log(T / V) \quad (4b)$$

Note also that values such as  $H^{TP}(273,1)$  and  $H^{TV}(273,22.4)$  are clear and unambiguous.

### Derivatives

Of course, we usually find in thermodynamics that we are concerned not so much with the functions, that is  $f$  or  $g$  or  $H^{TP}$  (which indeed often turn out to be unknown), but with their derivatives. For

the function  $f$  of Eq. (1) there are two possible derivatives:

$$\frac{\partial f}{\partial T} \quad \text{and} \quad \frac{\partial f}{\partial P}$$

These derivatives are defined in the usual fashion. For example

$$\frac{\partial f}{\partial T} = \lim_{\Delta T \rightarrow 0} \left( \frac{f(T + \Delta T, P) - f(T, P)}{\Delta T} \right) \quad (5)$$

Using our superscript function notation, we may write the two derivatives of  $f$  as

$$\frac{\partial H^{TP}}{\partial T} \quad \text{and} \quad \frac{\partial H^{TP}}{\partial P}$$

This notation is found to be considerably less confusing for the student than the conventional one in which the first of the above derivatives is written as

$$\left( \frac{\partial H}{\partial T} \right)_P$$

where the  $P$  is usually read as "at constant  $P$ ." Beside being somewhat clumsy, this (as we all know) can lead the student into the confusion shown by many classic 'howlers,' such as denying the existence of this derivative at a point in a process in which  $P$  is not constant. In fact, of course, as the superscript notation emphasizes,  $P$  is *not* a constant, but is an independent variable of both  $H^{TP}$  and  $\partial H^{TP}/\partial T$ , of exactly the same status as  $T$ .

We stress the need to *understand* the usual notation, which the students will, of course, find in texts and other sources which they consult, even if (in the initial stages at least) this understanding is reached by translating into our own notation in order to clarify the functional dependencies. It is, in fact, interesting to note that students may frequently be observed using the superscript notation for this purpose when working with the differential equations of other courses, such as transport phenomena.

### Differentials

Consider now the equation  $y = f(x)$ . We define  $dy$  and  $dx$  to be any two variables which satisfy the equation

$$dy = \frac{\partial f}{\partial x} dx \quad (6)$$

and we call  $dy$  and  $dx$  *differentials*. (We need to write the derivative with the symbol  $\partial$  to avoid confusion with the differentials using the symbol  $d$ .) Note that  $dy$  and  $dx$  are *any* quantities which satisfy this equation; in particular, there are no implications about the "smallness" of these quantities. It is clear that  $dx$  and  $dy$  define a line which is tangent to the  $f(x)$  curve at the point  $(x, y)$ .

Similarly, for our function  $H^{TP}$  we define the dif-

ferentials  $dT$ ,  $dH$ , and  $dP$  as quantities which satisfy

$$dH = \frac{\partial H^{TP}}{\partial T} dT + \frac{\partial H^{TP}}{\partial P} dP \quad (7)$$

If we divide Eq. (7) by  $dT$ , we obtain

$$\frac{dH}{dT} = \frac{\partial H^{TP}}{\partial T} + \frac{\partial H^{TP}}{\partial P} \frac{dP}{dT} \quad (8)$$

where we emphasize that the first and last terms are merely the ratios of two differentials, *not* derivatives.

Notice that from Eq. (7), if  $dP$  is zero (which is perfectly acceptable since we have not divided through by  $dP$  at any stage), we obtain

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

Just as the differentials of Eq. (6) define a tangent line to the curve  $y = f(x)$ , the differentials of Eq. (7) represent movement on a plane which is the tangent plane at the point  $(P, T)$  to the  $H = H^{TP}(P, T)$  surface.

The important point to note is that the left-hand side of Eq. (9) is an algebraic expression, *not* a limit as in Eq. (5). This is a direct consequence of the definition of Eq. (7) and the fact that the differentials are not necessarily small quantities. The important result is that all future manipulations will be algebraic; the limit process only occurs in the definition of the derivative in Eq. (5).

We need to note, however, that when we place a constraint such as  $dP = 0$  on an expression such as the quotient on the left of Eq. (9), the values of  $dH$  and  $dT$  are no longer arbitrary, as we have constrained their variation.

Using these concepts (especially that of Eq. 9), the student may develop all of the familiar relationships using only simple and unambiguous algebra. For example, consider the two differentials  $dH$  and  $dT$ . It is clear that

$$\frac{dT}{dH} = 1 / \left( \frac{dH}{dT} \right) \quad (10)$$

where we emphasize that the two terms are ratios of differentials, *not* derivatives. Now, consider Eq. (10) when  $dP = 0$ . From Eq. (9) we obtain

$$\frac{\partial T^{HP}}{\partial H} = 1 / \left( \frac{\partial H^{TP}}{\partial T} \right) \quad (11)$$

If we consider the following ratios of differentials:

$$\frac{dH}{dT} = \frac{dH}{dV} \frac{dV}{dT} \quad (12)$$

we may, from the situation when  $dP = 0$ , obtain the well-known relation

$$\frac{\partial H^{TP}}{\partial T} = \frac{\partial H^{VP}}{\partial V} \frac{\partial V^{TP}}{\partial T} \quad (13)$$



### Shorthand Notation for Derivatives

The notation which we have adopted for derivatives, although clear, makes for slightly tedious writing and somewhat more tedious typing or typesetting (although certainly no more so than the traditional notation). We may save some effort and space by adopting a shorthand in which

$$\frac{\partial H^{TP}}{\partial T} \text{ is replaced by } H^{T'P}$$

Although useful for simple statements and equations, this notation is somewhat more difficult for the novice to use in performing algebra. It may be preferable to use the expanded form, especially in handwriting, to perform manipulations such as those of Eqs. (10) to (13) above. This notation may easily be extended to higher derivatives, as the functions of thermodynamics are sufficiently "smooth" that the order of differentiation is not important. (Alternatively, if the order of differentiation is important, we may use notation such as  $H^{T'P}$  and  $H^{P'T}$  to indicate the difference.)

### Integrals

We define an integral in the usual way as the limit of a sum. That is, over some path  $V = V(S)$  from  $S_1$  to  $S_2$

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

where  $N \Delta S_i = S_2 - S_1$ . (There is no ambiguity about  $dS$  when used in conjunction with the integral sign.)

### Canonical Variables

Consider a function  $U^{SV}$ . This function leads to differentials given by

$$dU = \frac{\partial U^{SV}}{\partial S} dS + \frac{\partial U^{SV}}{\partial V} dV \quad (14)$$

or, expressed more concisely in the shorthand notation explained above

$$dU = U^{S'V} dS + U^{SV'} dV \quad (15)$$

If we define the functions

$$T^{SV} = U^{S'V} \quad \text{and} \quad P^{SV} = -U^{SV'} \quad (16)$$

then obviously

$$dU = TdS - PdV \quad (17)$$

We may now regard this equation as being a differential relationship between  $U$  and four variables ( $T$ ,  $P$ ,  $V$ , and  $S$ ), only two of which are independent.

As many readers will know, we can show that  
Spring 1991

there is a "special" relationship between  $U$  and the pair of variables,  $S$  and  $V$ , which is not shared by the other variables,  $T$  and  $P$ . The reasoning is outlined as follows.

Consider the (known) relation

$$T = U^{S'V} = T^{SV} \quad (18)$$

Assume that from the function  $T^{SV}$  we may uniquely solve for  $S$ ; that is

$$S = S^{TV} \quad (19)$$

We may substituted  $S = S^{TV}$  into  $U = U^{SV}$  to get

$$U = U^{SV} (S^{TV}, V) = U^{TV} \quad (20)$$

By similar arguments, we may obtain  $U^{SP}$ ,  $U^{PV}$ ,  $U^{TS}$  and all the other various combinations of independent variables.

We now note, however, that the *reverse* processes are *not* possible. If we have  $U^{TV}$  we cannot uniquely obtain  $U^{SV}$ . This is because in the process of differentiating  $U^{SV}$  to obtain  $T$  or  $P$  we lose information. Suppose, for example, that the functional form of  $U^{SV}$  is such that

$$U^{SV} = K + A^S + B^V + C^{SV} \quad (21)$$

Then in the process of differentiating  $U$  with respect to  $S$  in order to obtain  $T^{SV}$  as defined by Eq. (18), we lose all information about  $K$  and the function  $B^V$ . It is therefore not possible to reconstruct  $U^{SV}$  from  $U^{TV}$ , since the integration process which reverses the differentiation involves the addition of arbitrary "constants" (they may be functions of  $V$ ) about which we have no information from  $U^{TV}$ .

This special nature of  $U^{SV}$  is expressed by saying that  $S$  and  $V$  are the *canonical variables* of  $U$ .

The question obviously arises: Is this behavior peculiar to  $U^{SV}$ , or are there other functions which have different canonical variables? It turns out that there are such functions. If we invent a new function  $A = U - TS$ , then  $A$  can be shown (by a similar argument to the one above) to have canonical variables  $T$  and  $V$ . By a similar process, if we let  $H = U + PV$  and  $G = U - TS + PV$ , then  $H$  has as its canonical variables  $S$  and  $P$ , while  $G$  has  $T$  and  $P$ . These new functions  $H^{SP}$ ,  $G^{TP}$ , and  $A^{TV}$  are the only new ones we can define with these properties among the four variables  $T$ ,  $P$ ,  $S$ , and  $V$ , and so they have a special significance. (For students with suitable mathematical backgrounds, one may of course obtain  $H$ ,  $G$ , and  $A$  directly by Legendre transforms; for others, the argument above may suffice.)

### Useful Relations

We may notice from the definition of  $H$  above

that the quantity  $T$ , which we defined by  $T = U^{SV}$ , will also be equal to  $H^{SP}$ . We may thus obtain the familiar relationships for  $T$ ,  $P$ ,  $S$ , and  $V$ , such as

$$T = U^{S'V} = H^{S'P} \quad (22)$$

### Maxwell Relations

These relationships may be obtained as shown in the following example, where we have set the derivatives out in full for clarity. Since

$$T^{SV} = \frac{\partial U^{SV}}{\partial S} \quad (23)$$

then, provided the functions are twice continuously differentiable, it follows that

$$\frac{\partial T^{SV}}{\partial V} = \frac{\partial^2 U^{SV}}{\partial V \partial S} = \frac{\partial^2 U^{SV}}{\partial S \partial V} \quad (24)$$

$$= \frac{\partial}{\partial S} \left( \frac{\partial U^{SV}}{\partial V} \right) \quad (25)$$

$$= - \frac{\partial P^{SV}}{\partial S} \quad (26)$$

This result may be written more succinctly as  $T^{SV} = -P^{SV}$ . By similar methods, we may obtain the usual other results, known as *Maxwell Relations*, or *Cross-Differentiation Identities*.

### Path-Dependent Functions

Consider the difference  $\Delta U$  between the values  $U_1$  and  $U_2$  of the function  $U^{SV}$  at two points  $(S_1, V_1)$  and  $(S_2, V_2)$ . This is given by

$$\Delta U = U_2 - U_1 \quad (27a)$$

where

$$U_1 = U^{SV}(S_1, V_1) \quad (27b)$$

and

$$U_2 = U^{SV}(S_2, V_2) \quad (27c)$$

We may also calculate  $\Delta U$  from  $dU = TdS - PdV$  as

$$\Delta U = \int_1^2 dU = \int_1^2 TdS - \int_1^2 PdV = \int_1^2 U^{SV} dS - \int_1^2 U^{SV'} dV \quad (28)$$

We see that the term  $TdS$  is a function of  $S$  and  $V$ , and will in general therefore have different values at different points on the  $(S, V)$  plane. The  $\int TdS$  term is a line integral whose value will depend upon the *path* from  $(S_1, V_1)$  to  $(S_2, V_2)$  along which we evaluate it. The same applies to the term  $\int PdV$ .

The student might see this more clearly if it is explained in the following fashion. At every point on the  $(S, V)$  plane, there is a value of  $P$ , since we may write  $P = P^{SV}$ . We may therefore draw the path on

the  $(P, V)$  plane corresponding to the path on the  $(S, V)$  plane along which we are integrating from point 1 to point 2. On the  $(P, V)$  plane, the term  $\int PdV$  is simply the area under the curve, which obviously depends upon the  $P$ - $V$  path we are considering.

For future convenience we shall define these two path-dependent integrals as

$$Q = \int TdS \quad (29)$$

and

$$W = - \int PdV \quad (30)$$

so that Eq. (28) becomes

$$\Delta U = Q + W \quad (31)$$

We note that while the value of  $\Delta U$  depends only on the initial and final states  $(S_1, V_1)$  and  $(S_2, V_2)$ , the values of  $Q$  and  $W$  depend on the path between those two states along which we evaluate their defining integrals.

### Functions of More Variables

All the functions which we have considered above have been functions of two variables. The reasoning may be extended in a straightforward fashion to functions of a larger number of variables. Although there is nothing radically new here, experience suggests that in the classroom situation it is better to start, as we have done above, with only two independent variables. Once the concepts are grasped for these functions, students have no trouble understanding the similar results for functions of more variables.

Let us then consider  $n$  further independent variables. We shall give these the symbols  $N_1, N_2, \dots, N_i, \dots, N_n$ . The symbolism  $[N_i]$  represents this whole set of variables. We shall also need the set of  $n-1$  variables  $[N_{j \neq i}]$  that is  $N_1, N_2, \dots, N_{i-1}, N_{i+1}, \dots, N_n$  excluding  $N_i$ .

We may then consider the function

$$U = U^{SV[N_j]} \quad (32)$$

from which we may write the differential

$$dU = U^{S'V[N_j]} dS + U^{SV[N_j]'} dV + \sum_i U^{SVN'_i[N_{j \neq i}]} dN_i \quad (33)$$

We may then define

$$T = U^{S'V[N_j]} \quad (34)$$

$$P = -U^{SV[N_j]'} \quad (35)$$

$$\mu_i = U^{SVN'_i[N_{j \neq i}]} \quad (36)$$

Substituting these definitions into Eq. (33), we obtain

## REQUEST FOR FALL ISSUE PAPERS

Each year *Chemical Engineering Education* publishes a special fall issue devoted to graduate education. It consists of 1) articles on graduate courses and research, written by professors at various universities, and 2) ads placed by chemical engineering departments describing their graduate programs. Anyone interested in contributing to the editorial content of the 1991 fall issue should write to the editor, indicating the subject of the contribution and the tentative date it will be submitted.

Deadline is June 1, 1991.

$$dU = TdS - PdV + \sum_i \mu_i dN_i \quad (37)$$

The above definitions of T and P are no different to those we have used previously. We may define the functions A, H, and G as we have done before. Thus

$$A = U - TS = A^{TV\{N_j\}}$$

and H and G are defined in an analogous fashion.

There are also many new functions we could define with canonical variables involving one or more of our new variables  $[N_j]$ . For instance

$$B = U - \mu_1 N_1 = B^{SV\mu_1\{N_{j \neq 1}\}} \quad (38)$$

but these in general do not turn out to be useful functions, so we shall not explore this avenue further.

We may also obtain, as we did above, a set of Maxwell relations. For example, from the second derivatives of U, we may obtain

$$T^{SV\{N_j\}} = -P^{S^V\{N_j\}} \quad (39)$$

while from A we may obtain

$$S^{TV\{N_j\}} = P^{T^V\{N_j\}} \quad (40)$$

Many other relationships are of course possible. For example

$$\mu_j^{TPN'_j\{N_{k \neq j}\}} = \mu_i^{TPN'_i\{N_{k \neq i}\}} \quad (41)$$

It perhaps needs to be stressed again at this point that all the above development is purely mathematical. All the relations we have developed follow from the properties of functions and their derivatives and from our (arbitrary) definition of the symbols P and T in terms of the derivatives of  $U^{SV}$ . We have not yet done any "thermodynamics"!

The development that may be referred to as "thermo" (including the identification of our symbols T and P with their usual meaning) will form the subject of Part 2 of this paper.

We may also note that in this approach the mathematics we use is entirely consistent with that which a student has learned in the standard mathematics course. In particular, we have no need for any special kinds of derivatives. We have found in our teaching that students readily assimilate this material

and do not appear to have the same problems of understanding that the authors did when they were undergraduates.

### REFERENCES

1. Harris, W.F., *ChemSA*, 7(12), 259 (1981)
2. Harris, W.F., *ChemSA*, 8(7), 82 (1982)
3. Callen, H.B., *Thermodynamics*, John Wiley & Sons, New York, NY (1960) □

### ChE book review

#### A GUIDE TO CHEMICAL ENGINEERING PROCESS DESIGN AND ECONOMICS

by Gael D. Ulrich

John Wiley & Sons; 472 pages, \$33.95 (1984)

**Reviewed by**  
**Andrew N. Hrymak**  
**McMaster University**

This book is intended as a reference text for a course using case studies such as those from the AIChE design competition. Topics covered in the book fall into three main categories: process design, economics, and technical report writing. Extensive references to well-known chemical engineering texts and handbooks are found throughout the book.

The first section is entitled "Process Design." The chapters within this half of the book cover the design process, process conception, flowsheets, and the specification and design of individual pieces of equipment. In Chapter 2, the reader is introduced to the importance of understanding the process and obtaining typical flowsheets from the literature and Chapter 3 summarizes flowsheet preparation and common symbols.

Chapter 4 is a lengthy chapter devoted to the specification and design of individual pieces of process equipment. Separate sections cover different classes of units (such as heat exchangers, pumps, reactors, etc.). Each section gives a brief overview of

*Continued on page 95.*