the other between U and (V,T). But this is accomplished at the expense of creating a notation never seen outside the pages of thermodynamics textbooks. Moreover this notation often is cumbersome. For example, suppose that we consider a multicomponent system containing n different molecular species. The internal energy of this system is a function of p, T, and the number $N_1, N_2, \ldots, N_n$ of each species:

$$U = U(p, T, N_1, N_2, \ldots, N_n) \tag{3.22}$$

When we write the partial derivative of this function with respect to N_j using traditional thermodynamic notation, we create a monster:

$$\left(\frac{\partial U}{\partial N_j}\right)_{p,T,N_1,N_2,\ldots,N_{j-1},N_{j+1},\ldots,N_n} \tag{3.23}$$

Ugly, isn't it? There is already enough ugliness in the world; so why create more? Accordingly, in this book we do not write partial derivatives with subscripts. In our experience, context is sufficient to signal which variables are being held constant in a particular partial derivative. In those rare instances where ambiguity might otherwise result, perhaps a subscript is warranted.

Those Accursed Differentials

In no other branch of physics do differentials play such a central role—and are so confusing and unnecessary—as in thermodynamics. The first law is often written in differential form as $dU = đQ + đW$, the peculiar symbol $đ$ indicating that the differentials for working and heating are a different species from those usually encountered. In our experience, students are never quite sure what a differential is. Moreover, not only are differentials obscure; they impede students from understanding calculus. Strong words. Can we back them up?

What do professional mathematicians have to say about differentials? In the early 1950s a series of articles on differentials appeared in *American Mathematical Monthly*, a journal devoted to the teaching of mathematics. After surveying these articles, the editor, C. B. Allendoerfer, opined that "after reading the numerous papers submitted to Classroom Notes on differentials, and after discussions with other mathematicians, your editor is convinced that there is no commonly accepted definition of differential which fits all uses to which this notation is applied." If mathematicians are uncertain about what a differential is, you can be sure that physicists are even more at sea, and students of physics are hopelessly lost.

Allendoerfer asserts further that "if we wish to make calculus an intellectually honest subject and not a collection of convenient tricks, it is time we made a fresh start." This is what we are attempting to do here, nearly half a century after the suggestion was made. Allendoerfer's short (three pages) discussion of differentials is a model of clarity and forcefulness. He doesn't pull any punches. When he encounters nonsense, he labels it as such.

To cut the tangled knot of differentials, our fresh start begins with the concept of the derivative of the function Eq. (3.6), which is the limit of a quotient

$$\lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x} \tag{3.24}$$

The derivative is a tricky concept, and mastering it is one of the major obstacles that must be hurdled by students of calculus. Both the numerator and denominator in Eq. (3.24) are zero when $\Delta x = 0$, and the quotient 0/0 is meaningless, but the limit of this quotient may have a finite value. When this limit exists, it is called the derivative of f (or y) with respect to x. It would be handy to have some kind of symbol for the limit Eq. (3.24). The most common notation in use today is

$$\frac{df}{dx}, \frac{dy}{dx} \tag{3.25}$$

which is attributed to Leibniz. This notation has certain advantages. It reminds us that the derivative is the limit of a quotient, although the derivative is not the quotient with numerator dy and denominator dx.

The notation Eq. (3.25) also helps us remember certain theorems. For example, suppose that we have a function $y = f(x)$ and another function $x = h(u)$; thus y is also a function of u. To obtain the derivative of y with respect to u, we multiply two derivatives:

$$\frac{dy}{du} = \frac{dy}{dx}\frac{dx}{du} \tag{3.26}$$

This is a theorem, which must be proven, but we can remember it by noting that if we naively cancel dx in the denominator of dy/dx with dx in the numerator of dx/du as if the two dxs were numbers, we get the correct result. This canceling of dx is a fortunate accident, an attribute of the notation that helps us remember theorems, but does not prove them. To drive home this point, we list some of the symbols that have been suggested for derivatives and by whom:

$\dot{y}$	Newton
$\frac{dy}{dx}$, $dy:dx$	Leibniz
$[y \perp x]$	J. Landen
y'	Lagrange
∂y_x	Martin Ohm
Dy	Pierce
y_x	G. S. Carr

Suppose that history had taken a different turn and we had adopted the symbol ∂y_x for the derivative of y with respect to x. Would it then have been impossible to prove Eq. (3.26) because we would have no dx to cancel? Of course not.

At this point you may be saying to yourself, Why all this quibbling? After all, if we cancel numerator and denominator in Eq. (3.26), we get the right answer. Yes, but if you fall into the habit of getting the right answer by wrong reasoning, you eventually are going to get wrong answers. Consider, for example, the fraction

$$\frac{16}{64} = \frac{1}{4}$$

By crossing out the six in the numerator with that in the denominator of this fraction, we reduce it to its correct lowest common denominator. A lucky accident, you might say. To show you that this was not an accident, we'll pick another fraction at random

$$\frac{19}{95}=\frac{1}{5}$$

Again, we get the right answer by cancelling the nines in the numerator and denominator. Since we have proven this result for two fractions, it surely must be true for all fractions. We had better make sure. Pick another fraction at random

$$\frac{26}{65}=\frac{2}{5}$$

Again, the rule works for the third time, and every student knows that "what I have told you three times is true." Thus we have established irrefutably that one can cross out numbers in the numerators and denominators of fractions to reduce them to their lowest common denominator. Not so?

Let us move on to integrals for other examples of how playing carelessly with symbols instead of thinking about what they mean can lead to disaster. The integral of a function f of x over the interval from $x=a$ to b is defined by dividing this interval into n subintervals of width $\Delta x=(b-a)/n$ and taking the limit of the sum

$$\lim_{n\to\infty} \Sigma_1^n f(x_i)\, \Delta x \tag{3.27}$$

where x_i is some value of x in the ith subinterval. As n approaches infinity, Δx approaches zero, yet the number of terms in the series becomes indefinitely large in such a way that the limit Eq. (3.27) may not be zero. This limit, if it exists, is called the definite integral of f over the interval (a,b). The symbol

$$\int_a^b f(x)\, dx \tag{3.28}$$

is often used for the limit Eq. (3.27). But again, many other symbols can be and have been used. Symbols cannot be used to prove anything, although some symbols are more useful than others in aiding our memories. For example, suppose we express x as a function of u: $x=h(u)$. With this transformation of variables the integral Eq. (3.28) becomes

$$\int_a^b f(x)\, dx=\int_\alpha^\beta f(h(u))\, \frac{dx}{du}\, du=\int_\alpha^\beta g(u)\, du \tag{3.29}$$

where $a=h(\alpha)$, $b=h(\beta)$, and $g(u)=f(h(u))\, dx/du$. We can remember, but not prove, this theorem for transforming the variable of integration by noting that we can cancel the du in the symbol dx/du with the du in the symbol for integration over the variable u. But the symbol for integral Eq. (3.28) is neither sacred nor inevitable. If we had chosen a different symbol, containing no du to cancel, the theorem Eq. (3.29) would still hold.

When we turn to integrals over a planar region, the trick of canceling symbols as if they were numbers fails miserably. Consider, for example, the integral of $f(x,y)$ over a planar region:

$$\iint f(x,y)\, dx\, dy \tag{3.30}$$

We can transform the variables x and y (rectangular Cartesian coordinates) to r and θ (polar coordinates):

$$x = r \cos \theta, \qquad y = r \sin \theta \tag{3.31}$$

With this transformation the integral in Eq. (3.30) becomes

$$\iint f(r \cos \theta, r \sin \theta) r \, dr \, d\theta \tag{3.32}$$

Unfortunately, we cannot obtain Eq. (3.32) from Eq. (3.30) by canceling symbols.

We are further along in our efforts to get to the root cause of the great confusion about differentials. Note that the symbol *dx* appears in Eqs. (3.25) and (3.28). Is this the same quantity? No, of course not: *dx* is not a quantity. In Eq. (3.25) *dx* is part of the symbol for the derivative; in Eq. (3.28) *dx* is part of the symbol for the integral. A symbol cannot be ripped apart without destroying it.

To add to the confusion, we may define the differential *dy* as a linear function of the quantity $f' = dy/dx$ (note the change in notation) and the differential *dx* by

$$dy = f' \, dx \tag{3.33}$$

In Eq. (3.33) *dy* and *dx* are numerical values. These symbols are not some kind of nonexistent infinitesimals, quantities too small to be seen with the naked eye. *dy* and *dx* are simply numbers (variables), as is the derivative f'. The *dy* and *dx* in Eq. (3.33) are not the same *dy* and *dx* in Eq. (3.25).

It is also true that the *finite* difference Δy between two values of a function $f(x)$ for two values of x differing by the finite value Δx is *approximately*

$$\Delta y \approx f' \, \Delta x \tag{3.34}$$

This is a handy approximation, which we use all the time. Unfortunately, this approximation is often written in the form of Eq. (3.33).

We unearthed four ways in which the symbol *dx* is used: (1) in the derivative of a function; (2) in the integral of a function; (3) in a differential (a linear function); and (4) in an approximation for finite differences. All these symbolic uses of *dx* are different, and in none of them (except the third) can *dx* be ripped out without doing damage to the symbol. Given the many ways in which the same symbol is used for different mathematical concepts, it is no wonder that students are confused about differentials.

Our experience is that most students think that *dx* represents a number, and hence they are happy to manipulate *dx* in mathematical expressions as if it were a number. But even students draw the line at what can be done with *dx*. For example, it would be unusual for a student to take the square root of *dx*. Why not? If *dx* really is just the symbol for a number, we should be willing to square it, root it, take the sine of it, and so on. But students don't do this. When we turn to partial derivatives, even stronger, unconscious, taboos are at work. It is a rare student who will rip apart a partial derivative and manipulate the resulting pieces. Somehow, students sense, even if they do not know why, that ∂x and *dx* are subject to different rules, and that even *dx* can stand only so much mauling.

Differentials and Infinitesimals

Further confusion about differentials arises from their connection with the outmoded concept of an infinitesimal, a quantity that is not zero but is imagined to be smaller than any positive number (which, of course, is a contradiction, zero is the only non-negative number smaller than all positive numbers). William McGowen Priestley, in his beautifully written *Calculus: An Historical Approach,* asserts that the "notion of the *infinitesimal* is one of the most elusive ideas ever conceived. Attempts to describe it . . . bordered upon the comic." Chapter 10 of Priestly's book puts infinitesimals in their proper historical perspective. His view of infinitesimals is sympathetic but critical. We highly recommend this chapter, which we cannot do justice to here.

Infinitesimals, briefly stated, may be looked upon as training wheels invented by Leibniz to enable him to learn how to ride a bicycle called calculus. But even Leibniz reluctantly had to abandon his training wheels. We don't need them at all. The well-defined concept of a limit has replaced the vague and unsatisfactory infinitesimal—but not in thermodynamics, a kind of museum for archaic mathematics. If engineering is the repository of discarded ideas in physics, physics is the repository of discarded ideas in mathematics.

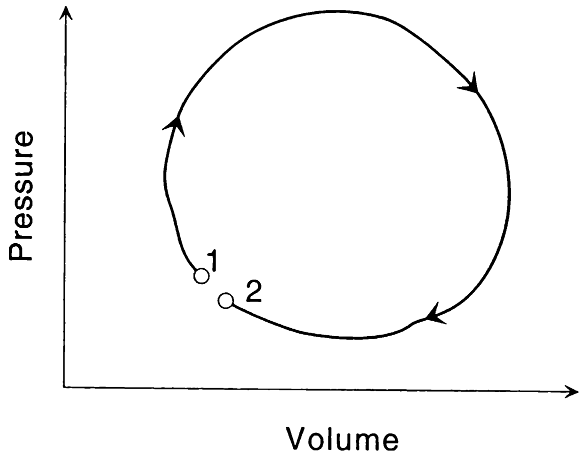
Aside from the vagueness of infinitesimals, they have at least two objectionable features in the teaching of thermodynamics. If an infinitesimal is something so small that no one knows how small, how can one infinitesimal be said to be larger or smaller than another? Yet this is done all the time in thermodynamics textbooks. Further, consider the so-called infinitesimal process described symbolically by $dU = đQ + đW$. Here dU is said to be the infinitesimal change in internal energy of the system, $đW$ is the infinitesimal work done in the process, and $đQ$ is the infinitesimal heat added. Yet it is a piece of cake to imagine processes in which the difference between the initial and final internal energies is arbitrarily (i.e., infinitesimally) small but the working and heating are not. Such a process is shown in Fig. 3.1. This is a process that is almost cyclic (the initial and final states are almost the same). In this process $U_2 - U_1$ is arbitrarily small, hence could be represented by the infinitesimal (or differential) dU, but the working and heating are not infinitesimal.

Are Differentials Necessary in Thermodynamics?

In an expository article on differentials, Mark Kac and J. F. Randolph begin with the assertion that "as easy and desirable as it is to get along without differentials, they seem to be with us to stay." This attitude is one of resignation, of bowing to the inevitable. Karl Menger, however, is more willing to resist. In a superb expository article on the mathematics of thermodynamics, he opines that "physicists in presenting the elements of the theory [of thermodynamics] should refrain from referring to the poorly understood concept of a general differential altogether."

From the resignation of Kac and Randoph to the resistance of Menger we come finally to the thundering defiance of Clifford Truesdell: "thermodynamics never grew up . . . the unfortunate who reads about thermodynamics even today is made to follow KELVIN's preference for differentials . . . and to suffer over again the insecurity CLAUSIUS seems to have felt whenever he used calculus." Truesdell heaps undisguised scorn on the mathematics of thermodynamics, poking fun in particular at

Figure 3.1 A thermodynamic process considered as a succession of equilibrium states can be depicted by a curve on a p–V diagram. The change of internal energy in the process can be made arbitrarily small by making the initial (1) and final (2) states arbitrarily close to each other. Yet the total work done, which is the area enclosed by the (nearly) closed curve, is not vanishingly small.



its notation: "Not only do differentials replace derivatives, but even derivatives look different, e.g.,

$$\frac{\delta^{rev}Q}{dV} = T\left(\frac{\partial S}{\partial V}\right)_p"$$

What a strange hybrid creature!, a mathematical equivalent of the centaur, half man and half horse. And you don't have to search far to find equally strange creatures in thermodynamics, a kind of game refuge for mathematical unicorns, centaurs, satyrs, and sphinxes.

Although Bridgman did not explicitly attribute the mathematical difficulty of thermodynamics to differentials, they are probably what he had in mind. If mathematicians and physicists of great eminence and sagacity have asserted in print that differentials are confusing and unnecessary, why have they not been expunged from thermodynamics books? Alas, the dead hand of tradition still clings to the teaching of thermodynamics. Better to confuse students unto the nth generation than to depart from sacred writ.

Yet you can demonstrate for yourself that differentials are not necessary in thermodynamics. All the mathematics in this book has but one aim: to enable you to understand part of the physical world, namely, the atmosphere of our planet (and other planets). If you acquire this understanding without ever once wrestling with differentials or feeling hamstrung by their absence, then differentials are unnecessary, and hence a waste of time and effort. But differentials are more than an unnecessary barrier over which successive generations of students are forced to leap. Differentials are a swindle. They convey the paranormal view that thermodynamic processes occur but not in time. All physical processes are states evolving in time: A system is different now from what it was a few moments ago, and will again be different in the future. In many applications of atmospheric thermodynamics we are in fact concerned with describing or predicting the time evolution of the thermodynamic state of a system.

We have devoted considerable space to criticizing the mathematics traditionally used in thermodynamics. If you have read this far, you may wonder why we have taken the trouble. Why don't we just eagerly embrace differentials, such lovable little creatures (how can something so small not be cute?), like everyone else? Our experience, like that of Bridgman, is that the major impediment to the teaching of thermodynamics is its confusing, illogical, if not ludicrous notation. The mathematics of thermodynamics is inherently simple but made difficult, if not by conscious design, then at least by failing to remove weeds from the garden of thermodynamics.

3.2 Specific Heats and Enthalpy

Now we are ready to combine the first law with the ideal gas law to obtain results that shed light on atmospheric processes. The first step is the tedious but necessary one of defining various physical quantities that occur again and again in thermodynamic applications.

With the use of the chain rule Eq. (3.4), the first law can be put in the form

$$Q=\frac{\partial U}{\partial T}\frac{dT}{dt}+\left(\frac{\partial U}{\partial V}+p\right)\frac{dV}{dt} \tag{3.35}$$

$\partial U/\partial V$ has the dimensions of pressure and is sometimes called the *internal pressure.* The first partial derivative on the right side of this equation appears with sufficient frequency that it has acquired a name, *heat capacity* (*at constant volume*), and a special symbol:

$$C_V=\frac{\partial U}{\partial T} \tag{3.36}$$

The reason for this name follows from Eq. (3.35) for a constant volume process ($dV/dt=0$):

$$Q=C_V\frac{dT}{dt}, \qquad V=\text{const} \tag{3.37}$$

Here the term *heat capacity,* which is a relic of the caloric theory, is used in the same way that we refer to a high capacity for strong drink. Someone with a large capacity for beer can drink heroic amounts of it without getting drunk. The rate of drinking is analogous to Q, the rate of getting drunk is analogous to dT/dt. The higher the drinking capacity, the lower the rate of getting drunk for a given rate of drinking. Similarly, the higher the heat capacity, the lower the rate of temperature change for a given heating.

Because C_V is an extensive variable, and hence depends on the mass M of the system, we often deal with the heat capacity per unit mass or *specific heat capacity* or simply *specific heat* (at constant volume):

$$c_v=\frac{C_V}{M} \tag{3.38}$$

Another specific heat, much loved by chemists, is the *molar specific heat:*

$$c_{v,m}=\frac{N_a}{N}C_V \tag{3.39}$$