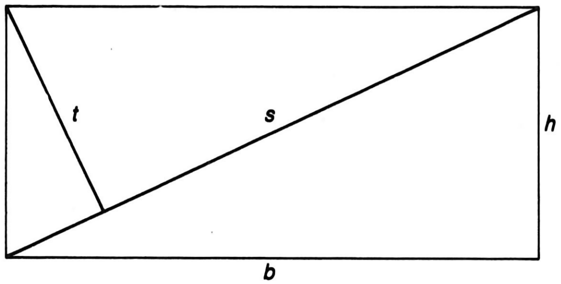

FIGURE 1.1
Diagram illustrating partial derivatives.

the rectangle can be expressed by any of several formulas, such as

$$A = bh \tag{1.1}$$

$$A = b(s^2 - b^2)^{1/2} \tag{1.2}$$

$$A = b^2 t(b^2 - t^2)^{-1/2} \tag{1.3}$$

$$A = st \tag{1.4}$$

What then is meant by $\partial A/\partial b$? We get different results by differentiating Eqs. (1.1), (1.2), or (1.3). Standard mathematical notation would get around this by defining different functions, such as

$$f(x, y) \equiv xy$$

$$g(x, y) \equiv y(x^2 - y^2)^{1/2}$$

and then writing Eqs. (1.1) and (1.2) as

$$A = f(b, h)$$

$$A = g(s, b)$$

Then the derivative $\partial f(b, h)/\partial b$ and $\partial g(s, b)/\partial b$ are unambiguous. However, in thermodynamics we prefer to use the same symbol to represent a particular physical quantity regardless of what variables it is expressed in. Thus, once A is chosen to represent area, we write the functions in Eqs. (1.1) through (1.4) as $A(b, h)$, $A(s, t)$, $A(s, b)$, and $A(b, t)$ despite the different functional forms involved. The symbol $\partial A/\partial b$ indicates that b is one of the variables in which A is expressed; the other is indicated by enclosing the entire symbol in parentheses and placing the other variable—the one that is held constant in the differentiation—as a subscript on the right side. Thus $(\partial A/\partial b)_s$ to be read "the partial derivative of A with respect to b at constant s"—means that A is to be expressed in terms of b and s, and then the partial derivative of this expression with respect to b is to be taken. Since Eq. (1.2) states explicitly the function that is needed, we can differentiate it to get

$$\left(\frac{\partial A}{\partial b}\right)_s = \frac{s^2 - 2b^2}{(s^2 - b^2)^{1/2}}$$

(From Reid, Chemical Thermodynamics, McGraw-Hill)

Similarly, from Eq. (1.1),

$$\left(\frac{\partial A}{\partial b}\right)_h = h$$

The second of these represents the variation of the area when the base is changed but the height is kept constant; the first when the base and height are both changed so as to keep the diagonal constant.

In thermodynamics the actual form of the functional dependence is seldom known, and explicit relations such as these cannot be written, but the concept is nevertheless important. Suppose, for example, that the energy (U) of a thermodynamic system depend on any two of the variables pressure (p), volume (V), and temperature (T). Then derivatives such as $(\partial U/\partial T)_p$ and $(\partial U/\partial T)_V$ are of interest.

1.3. CHANGE OF VARIABLES IN DIFFERENTIATION

The discussion in the previous section suggests that we may wish to find a relation connecting such derivatives as $(\partial A/\partial b)_h$ and $(\partial A/\partial b)_s$. More generally, we may need to find $(\partial f/\partial x)_z$ when f is expressed as a function of x and y, and y is a function of x and z. The straightforward way is to substitute $y(x, z)$ into $f(x, y)$ to obtain a function of x and z, and then differentiate this. However, in thermodynamics the forms of the functions are not generally known, and an alternative procedure is needed.

Differentiation of $f(x, y)$ gives

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{1.5}$$

Now since y is a function of x and z, it can be differentiated similarly:

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \tag{1.6}$$

Substituting Eq. (1.6) into Eq. (1.5) gives

$$df = \left[\left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z\right] dx + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz$$

However, when f is expressed as a function of x and z and differentiated, the result is

$$df = \left(\frac{\partial f}{\partial x}\right)_z dx + \left(\frac{\partial f}{\partial z}\right)_x dz$$

If we now equate the coefficients of dz in these two equations, we find

$$\left(\frac{\partial f}{\partial z}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x$$

(From Reid, Chemical Thermodynamics, McGraw-Hill)

while the coefficients of dx yield the relation

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \tag{1.7}$$

The first of these is a familiar formula from elementary calculus, though the notation used for it here is different. The second is not so familiar but is extensively used in thermodynamics.

An alternative derivation of Eq. (1.7) is valuable because it simplifies the remembering and setting up of equations of this type. Equation (1.5) is valid for all variations of x and y, including those that keep z constant. Restricting consideration to these variations, we can divide by dx and interpret the ratios df/dx and dy/dx as partial derivatives at constant z. The result is Eq. (1.7).

We will also frequently need another relation that is similarly derivable from Eq. (1.6). If dz is expressed in terms of dx and dy and substituted into this equation, the coefficients of dx yield the relation

$$\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = 0$$

Alternatively, this may be obtained by noting that Eq. (1.6) can be applied at constant y, so that $dy = 0$, dividing by dx, and interpreting the ratios as partial derivatives at constant y. Probably the easiest form for remembering equations of this sort is

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{1.8}$$

since any derivative involving the three variables can be written down, and then the other two obtained from it by cyclic permutation of the variables. Another useful and easily remembered form is

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial x}{\partial z}\right)_y}{\left(\frac{\partial y}{\partial z}\right)_x} \tag{1.9}$$

In general, any expression of this sort can be set up by treating the symbols such as ∂x as if they were numerators and denominators of fractions and canceling, always remembering to introduce a minus sign. It is important to keep in mind, however, that this is only a convenient shortcut, not a valid mathematical procedure. The need to introduce a minus sign, which would be erroneous if these were real fractions, will help remind you of this.

As an illustration, consider the relation

$$\left(\frac{\partial b}{\partial t}\right)_s = \left(\frac{\partial b}{\partial t}\right)_h + \left(\frac{\partial b}{\partial h}\right)_t \left(\frac{\partial h}{\partial t}\right)_s \tag{1.10}$$

(From Reid, Chemical Thermodynamics, McGraw-Hill)

formed by applying Eq. (1.7) to the variables defined in Fig. 1.1. To find the derivatives, we can start with $bh = st$, derived from Eqs. (1.1) and (1.4). Squaring it and eliminating h by the Pythagorean theorem, we find

$$b^2(s^2 - b^2) = s^2t^2 = b^2s^2 - b^4$$

Implicit differentiation with respect to t, treating s as a constant, then gives

$$2s^2t = 2s^2b\left(\frac{\partial b}{\partial t}\right)_s - 4b^3\left(\frac{\partial b}{\partial t}\right)_s$$

from which we find

$$\left(\frac{\partial b}{\partial t}\right)_s = \frac{s^2t}{bs^2 - 2b^3} = -\frac{hs}{b^2 - h^2},$$

where $bh = st$ and the Pythagorean theorem have been used to get the last form. The other derivatives can be found similarily; they are

$$\left(\frac{\partial b}{\partial h}\right)_t = -\frac{h(b^2 - t^2)}{b(h^2 - t^2)}$$

$$\left(\frac{\partial b}{\partial t}\right)_h = \frac{hs}{h^2 - t^2}$$

and

$$\left(\frac{\partial h}{\partial t}\right)_s = \frac{bs}{b^2 - h^2}$$

where the relation $bh = st$ has been used to simplify the expressions. If these are substituted into the right side of Eq. (1.10), a moderate amount of algebraic manipulation will show that the result is the same as that given for $(\partial b/\partial t)_s$.

1.4 EXACT DIFFERENTIALS AND LINE INTEGRALS

Expressions of the type $P(x, y)\,dx + Q(x, y)\,dy$ are of frequent occurrence; such an expression may or may not be the differential or some function $f(x, y)$. If it is, it is called an *exact differential*; in this case

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = P\,dx + Q\,dy$$

Since dx and dy are independent, the coefficients must be the same in the two expressions; that is,

$$P = \left(\frac{\partial f}{\partial x}\right)_y \qquad \text{and} \qquad Q = \left(\frac{\partial f}{\partial y}\right)_x \tag{1.11}$$

(From Reid, Chemical Thermodynamics, McGraw-Hill)