1.6 DIFFERENTIAL CALCULUS

Thermodynamics and other branches of physical chemistry use calculus extensively. We therefore review some ideas of differential calculus without bothering to give mathematically rigorous definitions or proofs.

To say that the variable y is a *function* of the variable x means that for any given value of x there is specified a value of y; we write $y = f(x)$. For example, the area of a circle is a function of its radius r, since the area can be calculated from r by the expression πr^2. The variable x is called the *independent variable*, and y is the *dependent variable*. Of course, we can solve for x in terms of y to get $x = g(y)$, so that it is a matter of convenience which variable is considered to be the independent one. Instead of $y = f(x)$, it is often more convenient in physical problems to write $y = y(x)$.

To say that the *limit* of the function $f(x)$ as x approaches the value a is equal to c [which is written as $\lim_{x \to a} f(x) = c$] means that for all values of x sufficiently close to a (but *not* necessarily equal to a) the difference between $f(x)$ and c can be made as small as we please. For example, suppose we want the limit as x goes to zero of the function $(\sin x)/x$. We first note that $(\sin x)/x$ is undefined at $x = 0$ since $0/0$ is undefined. However, this fact is irrelevant to determining the limit. To find the limit, we calculate the following values of $(\sin x)/x$, where x is in radians: 0.99833 for $x = \pm 0.1$, 0.99958 for $x = \pm 0.05$, 0.99998 for $x = \pm 0.01$, etc. It thus seems clear that

$$\lim_{x \to 0} \frac{\sin x}{x} = 1 \qquad (1.24)$$

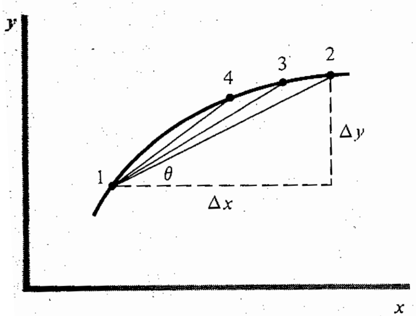

Figure 1.7
As point 2 approaches point 1, the quantity $\Delta y/\Delta x = \tan \theta$ approaches the slope of the tangent to the curve at point 1.

(Of course this isn't meant as a rigorous proof.) Note the resemblance to taking the limit as P goes to zero in Eq. (1.13); in this limit both V and V_{tr} become infinite as P goes to zero, but the limit has a well-defined value even though ∞/∞ is undefined.

Let $y = f(x)$. We shall consider the rate of change of y with x. Let the independent variable change its value from x to $x + h$; this will change y from $f(x)$ to $f(x + h)$. The average rate of change of y with x over this interval equals the change in y divided by the change in x. Using Δ to indicate a change in a variable, we have as the average rate of change

$$\frac{\Delta y}{\Delta x} = \frac{f(x+h) - f(x)}{(x+h) - x} = \frac{f(x+h) - f(x)}{h}$$

The *instantaneous* rate of change of y with x is the limit of this average rate of change taken as the change in x goes to zero. The instantaneous rate of change is called the *derivative* of the function f and is symbolized by f':

$$f'(x) \equiv \lim_{h \to 0} \frac{f(x+h) - f(x)}{h} = \lim_{\Delta x \to 0} \frac{\Delta y}{\Delta x} \qquad (1.25)^*$$

From Fig. 1.7 it is clear that the derivative of a function at a given point is equal to the slope of the line tangent to the curve of y vs. x at that point.

As a simple example, let $y = x^2$. Then

$$f'(x) = \lim_{h \to 0} \frac{(x+h)^2 - x^2}{h} = \lim_{h \to 0} \frac{2xh + h^2}{h} = \lim_{h \to 0} (2x + h) = 2x$$

Hence the derivative of x^2 is $2x$.

A function that makes a sudden jump in value at a certain point is said to be *discontinuous* at that point. An example is shown in Fig. 1.8*a*. Consider the function $y = |x|$, whose graph is shown in Fig. 1.8*b*. This function makes no jumps in value anywhere and so is everywhere continuous. However, the slope of the curve changes suddenly at $x = 0$; therefore, the derivative y' is discontinuous at this point; for negative x the function y equals $-x$ and y' equals -1, whereas for positive x the function y equals x and y' equals $+1$. [Strictly speaking, y' doesn't exist at $x = 0$, since we must get the same limit in (1.25) whether h approaches zero through positive values or through negative values in order for the derivative to exist at a point.]

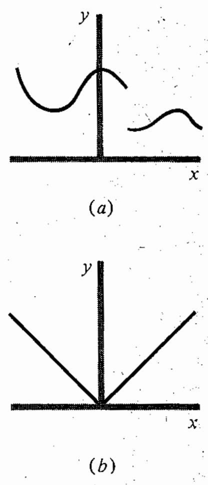

Figure 1.8 (*a*) A discontinuous function. (*b*) The function $y = |x|$.

Since $f'(x)$ is defined as the limit as Δx goes to zero of $\Delta y/\Delta x$, we know that for small changes in x and y, the derivative $f'(x)$ will be approximately equal to $\Delta y/\Delta x$. Thus $\Delta y \approx f'(x)\, \Delta x$ for Δx small. This equation becomes more and more accurate as Δx gets smaller. We can conceive of an infinitesimally small change in x, which we symbolize by dx; denoting the corresponding infinitesimally small change in y by dy, we have $dy = f'(x)\, dx$, or

$$dy = y'(x)\, dx \qquad (1.26)$$

The quantities dy and dx are called *differentials*. Equation (1.26) gives the alternative notation dy/dx for a derivative. Actually, the rigorous mathematical definition of dx and dy does not require these quantities to be infinitesimally small; instead they can be of any magnitude. (See *Thomas*, sec. 2-6; references with the author's name italicized are to books listed in the Bibliography.) However, in our applications of calculus to thermodynamics, we shall find it convenient always to conceive of dy and dx as infinitesimal changes.

Leibniz originally formulated calculus in terms of infinitesimal quantities, but since his formulation is gravely lacking in mathematical rigor, later mathematicians reformulated calculus to eliminate reference to infinitesimals. It was not until 1960 that a mathematically rigorous formulation of calculus that uses infinitesimal quantities was developed; see A. Robinson, *Non-standard Analysis*, North-Holland, 1966; R. A. Bonic et al., *Freshman Calculus*, Heath, 1971, pp. 416–417; *The New York Times*, Feb. 15, 1975, p. 22.

Let a and n be nonzero constants, and let u and v be functions of x: $u = u(x)$ and $v = v(x)$. Using the definition (1.25), one finds the following formulas for differentiation:

$$\frac{da}{dx} = 0, \qquad \frac{d(ax^n)}{dx} = nax^{n-1}, \qquad \frac{d(e^{ax})}{dx} = ae^{ax}$$

$$\frac{d \ln ax}{dx} = \frac{1}{x}, \qquad \frac{d \sin ax}{dx} = a \cos ax, \qquad \frac{d \cos ax}{dx} = -a \sin ax \tag{1.27*}$$

$$\frac{d(u+v)}{dx} = \frac{du}{dx} + \frac{dv}{dx}, \qquad \frac{d(uv)}{dx} = u\frac{dv}{dx} + v\frac{du}{dx}$$

$$\frac{d(u/v)}{dx} = \frac{d(uv^{-1})}{dx} = -uv^{-2}\frac{dv}{dx} + v^{-1}\frac{du}{dx}$$

The chain rule is used frequently to find derivatives. Let z be a function of x, where x is a function of r: $z = z(x)$, where $x = x(r)$. Then z can be expressed as a function of r: $z = z(x) = z[x(r)] = g(r)$, where g is some function. The *chain rule* states that $dz/dr = (dz/dx)(dx/dr)$. For example, suppose we want $(d/dr) \sin 3r^2$. Let $z = \sin x$ and $x = 3r^2$. Then $z = \sin 3r^2$, and the chain rule gives $dz/dr = (\cos x)(6r) = 6r \cos 3r^2$.

Equation (1.26) and the above list of derivatives give the following formulas for differentials:

$$d(ax^n) = nax^{n-1}\, dx, \qquad d(e^{ax}) = ae^{ax}\, dx$$

$$d(au) = a\, du, \qquad d(u+v) = du + dv, \qquad d(uv) = u\, dv + v\, du \tag{1.28}$$

We frequently want to find a maximum or minimum of some function. For a function with a continuous derivative, the slope of the tangent curve is zero at a maximum or minimum point (Fig. 1.9*a*). Hence to locate an extremum we look for those points where $dy/dx = 0$. Figure 1.9*a* shows that for a maximum point the tangent to the curve has positive slope to the left of the maximum and negative slope to its right; in other words, dy/dx is decreasing going through a maximum.

Let the notation $+0-$ indicate a point where dy/dx is positive to the immediate left of the point, zero at the point, and negative to the immediate right of the point. A point with the $+0-$ pattern of slopes is a maximum point. A point with the $-0+$ pattern is a minimum point. What about the pattern $+0+$? This is neither a maximum nor a minimum point but a *horizontal inflection point*. An example is $y = x^3$, which shows this pattern at $x = 0$ (Fig. 1.9*b*). The pattern $-0-$ is also a horizontal inflection point; an example is $y = -x^3$ at $x = 0$. For a horizontal inflection point, it is clear that dy/dx is either a minimum (in the $+0+$ case) or a maximum (in the $-0-$ case) at this point. Hence $(d/dx)(dy/dx) = d^2y/dx^2 = 0$ at a horizontal inflection point. (Any point where d^2y/dx^2 changes sign is called an *inflection point*. Clearly, $d^2y/dx^2 = 0$ at an inflection point; when $dy/dx = 0$ also, it is a horizontal inflection point.) (An example of a horizontal inflection point is the critical point of a fluid; see Chap. 8.)

In thermodynamics we usually deal with functions of two or more variables. Let z be a function of x and y: $z = f(x, y)$. We define the *partial derivative* of z with respect to x as follows:

$$\left(\frac{\partial z}{\partial x}\right)_y \equiv \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x} \tag{1.29}$$

This definition is analogous to the definition (1.25) of the ordinary derivative, in that if y were a constant instead of a variable, the partial derivative $(\partial z/\partial x)_y$ would become just the ordinary derivative dz/dx. The variable being held constant in a partial derivative is often omitted and $(\partial z/\partial x)_y$ written simply as $\partial z/\partial x$. In thermodynamics there are many possible variables, and to avoid confusion it is usually imperative to indicate which variables are being held constant in a partial derivative. The partial derivative of z with respect to y at constant x is defined similarly to (1.29):

$$\left(\frac{\partial z}{\partial y}\right)_x \equiv \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y}$$

There may be more than two independent variables. For example, let $z = g(w, x, y)$. Then the partial derivative of z with respect to x at constant w and y is defined as

$$\left(\frac{\partial z}{\partial x}\right)_{w,y} \equiv \lim_{\Delta x \to 0} \frac{g(w, x + \Delta x, y) - g(w, x, y)}{\Delta x}$$

The evaluation of partial derivatives is quite simple. To find $(\partial z/\partial x)_y$ we take the ordinary derivative of z with respect to x while regarding y as a constant. For example, if $z = x^2y^3 + e^{yx}$, then $(\partial z/\partial x)_y = 2xy^3 + ye^{yx}$; also, $(\partial z/\partial y)_x = 3x^2y^2 + xe^{yx}$.

Let $z = f(x, y)$. Suppose x changes by an infinitesimal amount dx while y remains constant. What is the infinitesimal change dz in the variable z brought about by the infinitesimal change in x? If z were a function of x only, then [Eq. (1.26)] we would have $dz = (dz/dx)\,dx$; because z depends on y also, the infinitesimal change in z at constant y is given by the analogous equation $dz = (\partial z/\partial x)_y\,dx$. Similarly, if y were to undergo an infinitesimal change dy while x were held constant, we would

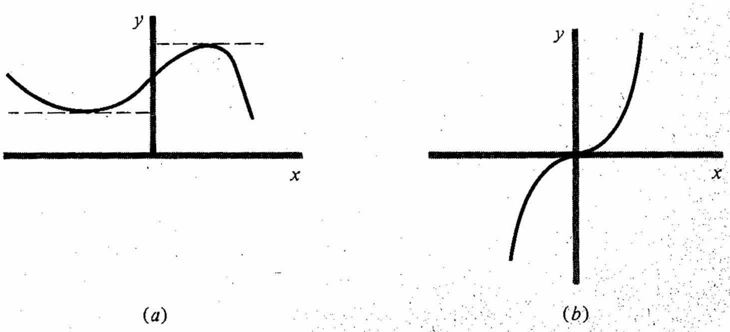

Figure 1.9
(*a*) Horizontal tangent at maximum and minimum points. (*b*) The function $y = x^3$.

have $dz = (\partial z/\partial y)_x\, dy$. If now both x and y undergo infinitesimal changes, the infinitesimal change in z is the sum of the infinitesimal changes due to dx and dy. Thus

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad (1.30)^*$$

In this equation dz is called the *total differential* of $z(x, y)$. Equation (1.30) is one of the most used equations in thermodynamics. An analogous equation holds for the total differential of a function of more than two variables. For example, if $z = z(r, s, t)$, then

$$dz = \left(\frac{\partial z}{\partial r}\right)_{s,t} dr + \left(\frac{\partial z}{\partial s}\right)_{r,t} ds + \left(\frac{\partial z}{\partial t}\right)_{r,s} dt$$

Three useful partial-derivative identities can be derived from (1.30). For an infinitesimal process in which y does not change, the infinitesimal change dy is 0, and (1.30) becomes

$$dz_y = \left(\frac{\partial z}{\partial x}\right)_y dx_y \qquad (1.31)$$

where the y subscripts on dz and dx indicate that these infinitesimal changes occur at constant y. Division by dz_y gives

$$1 = \left(\frac{\partial z}{\partial x}\right)_y \frac{dx_y}{dz_y} = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y$$

since from the definition of the partial derivative, the ratio of infinitesimals dx_y/dz_y equals $(\partial x/\partial z)_y$. Therefore

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{(\partial x/\partial z)_y} \qquad (1.32)^*$$

Note that the same variable, y, is being held constant in both partial derivatives in (1.32); when y is held constant, there are only two variables, x and z, and you will probably recall that $dz/dx = 1/(dx/dz)$. [However, $d^2z/dx^2 \neq 1/(d^2x/dz^2)$.]

For an infinitesimal process in which z remains constant, Eq. (1.30) becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx_z + \left(\frac{\partial z}{\partial y}\right)_x dy_z \qquad (1.33)$$

Dividing by dy_z and recognizing that dx_z/dy_z equals $(\partial x/\partial y)_z$, we get

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \quad \text{and} \quad \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x = -\frac{1}{(\partial y/\partial z)_x}$$

where (1.32) with x and y interchanged was used. Multiplication by $(\partial y/\partial z)_x$ gives

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad (1.34)^*$$

Equation (1.34) looks intimidating but is actually easy to remember because of the simple pattern of variables: $\partial x/\partial y$, $\partial y/\partial z$, $\partial z/\partial x$; the variable held constant in each partial derivative is the one that doesn't appear in that derivative.

Sometimes students wonder why the ∂y's, ∂z's, and ∂x's in (1.34) don't cancel to give $+1$ (instead of -1). One can only cancel ∂y's, etc., when the same variable is held constant in each partial derivative. [Note that (1.32) can be written as $(\partial z/\partial x)_y(\partial x/\partial z)_y = 1$.]

Finally, let dy in (1.30) be zero, so that (1.31) holds. Let u be some other variable. Division of (1.31) by du_y gives

$$\frac{dz_y}{du_y} = \left(\frac{\partial z}{\partial x}\right)_y \frac{dx_y}{du_y}$$

$$\left(\frac{\partial z}{\partial u}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_y \tag{1.35}$$

The ∂x's in (1.35) can be canceled because the same variable (y) is held constant in each partial derivative.

A function of two independent variables $z(x, y)$ has the following four second partial derivatives:

$$\left(\frac{\partial^2 z}{\partial x^2}\right)_y \equiv \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right)_y\right]_y, \qquad \left(\frac{\partial^2 z}{\partial y^2}\right)_x \equiv \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial y}\right)_x\right]_x$$

$$\frac{\partial^2 z}{\partial x\, \partial y} \equiv \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y, \qquad \frac{\partial^2 z}{\partial y\, \partial x} \equiv \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x$$

Provided the first partial derivatives are continuous (as is generally true in physical applications), one can show that the two mixed second partial derivatives are equal (see *Thomas*, sec. 14-12):

$$\frac{\partial^2 z}{\partial x\, \partial y} = \frac{\partial^2 z}{\partial y\, \partial x} \tag{1.36*}$$

Thus the order of partial differentiation is immaterial.

It is often convenient to write fractions with a slant line. The convention is that

$$a/bc + d \equiv \frac{a}{bc} + d$$

2.1 INTEGRAL CALCULUS

Differential calculus was reviewed in Sec. 1.6. We now review integral calculus. (The reader impatient to get on to thermodynamics can skim Secs. 2.1 and 2.2 and come back to them later to pick up the details.)

Frequently, we want to find a function $y(x)$ whose derivative is known to be a certain function $f(x)$:

$$dy/dx = f(x) \tag{2.1}$$

The most general function y that satisfies (2.1) is called the *indefinite integral* of $f(x)$. The following notation is used for the indefinite integral of f:

$$y(x) = \int f(x)\, dx \tag{2.2}$$

Since the derivative of a constant is zero, the indefinite integral of any function contains an arbitrary additive constant. For example, if $f(x) = x$, its indefinite integral $y(x)$ is $\frac{1}{2}x^2 + C$, where C is an arbitrary constant. This result is readily verified by showing that y satisfies (2.1), that is, by showing that $(d/dx)(\frac{1}{2}x^2 + C) = x$. To save space, tables of indefinite integrals usually omit the arbitrary constant C.

From the derivatives given in Sec. 1.6, it follows that

$$\int dx = x + C, \qquad \int ax^n\, dx = \frac{ax^{n+1}}{n+1} + C \qquad \text{where } n \neq -1 \tag{2.3*}$$

$$\int \frac{1}{x}\, dx = \ln x + C, \qquad \int e^{ax}\, dx = \frac{e^{ax}}{a} + C \tag{2.4*}$$

$$\int \sin ax\, dx = -\frac{\cos ax}{a} + C, \qquad \int \cos ax\, dx = \frac{\sin ax}{a} + C \tag{2.5*}$$

where a and n are nonzero constants and C is an arbitrary constant. This list of integrals and the derivatives given in Sec. 1.6 are best memorized. For more complicated integrals than the above, consult a table of integrals.

Particularly recommended is M. Klerer and F. Grossman, *A New Table of Indefinite Integrals*, Dover, 1971 (paperback). Klerer and Grossman used a computer to numerically check each integral in their table; thus their table is probably the most accurate available. (They did computer checks on eight well-known tables of indefinite integrals and found error rates ranging from 0.5 percent to an astonishing 27 percent.)

A second important concept in integral calculus is the definite integral. Let $f(x)$ be a continuous function, and let a and b be any two values of x. The *definite integral* of f between the limits a and b is denoted by the symbol

$$\int_a^b f(x)\,dx \tag{2.6}$$

(The reason for the resemblance to the notation for an indefinite integral will become clear shortly.) The definite integral (2.6) is a number whose value is found from the following definition. We divide the interval from a to b into n subintervals, each of width Δx, where $\Delta x = (b - a)/n$ (see Fig. 2.1). In each subinterval we pick any point we please, denoting the chosen points by $x_1, x_2, \ldots, x_n$. We evaluate $f(x)$ at each of the n chosen points and form the sum

$$\sum_{i=1}^{n} f(x_i)\,\Delta x = f(x_1)\,\Delta x + f(x_2)\,\Delta x + \cdots + f(x_n)\,\Delta x \tag{2.7}$$

[Recall that the definition of the summation notation is

$$\sum_{i=1}^{n} a_i \equiv a_1 + a_2 + \cdots + a_n \tag{2.8}$$

When the limits of a sum are clear, they are often omitted.] We now take the limit of the sum (2.7) as the number of subintervals n goes to infinity, and hence as the width Δx of each subinterval goes to zero. This limit is, by definition, the definite integral (2.6):

$$\int_a^b f(x)\,dx \equiv \lim_{\Delta x \to 0} \sum_{i=1}^{n} f(x_i)\,\Delta x \tag{2.9}$$

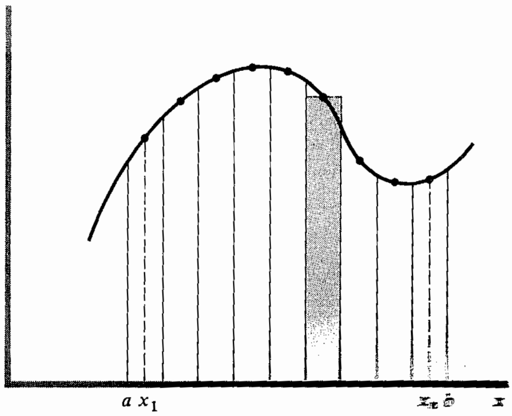

Figure 2.1
Definition of the definite integral.

The motivation for the definition (2.9) is that the quantity on the right side of (2.9) occurs very frequently in physical problems.

Each term in the sum (2.7) is the area of a rectangle of width Δx and height $f(x_i)$. A typical rectangle is indicated by the shading in Fig. 2.1. As the limit $\Delta x \to 0$ is taken, the total area of these n rectangles becomes equal to the area under the curve $f(x)$ between a and b. Thus we can interpret the definite integral as an area. Areas lying below the x axis, where $f(x)$ is negative, make negative contributions to the definite integral.

Use of the definition (2.9) to evaluate an indefinite integral would be tedious. The fundamental theorem of integral calculus (proved in any calculus text; see *Thomas*, sec. 4-9, for example) states that if $y(x)$ is an indefinite integral of $f(x)$ [that is, if y satisfies (2.1)], then

$$\int_a^b f(x)\,dx = y(b) - y(a) \tag{2.10*}$$

For example, if $f(x) = x$, $a = 2$, $b = 6$, we can take $y = \frac{1}{2}x^2$ (or $\frac{1}{2}x^2$ plus some constant) and (2.10) gives $\int_2^6 x\,dx = \frac{1}{2}(6^2) - \frac{1}{2}(2^2) = 16$.

The integration variable x in the definite integral on the left of (2.10) does not appear in the final result (the right side of this equation). It thus does not matter what symbol we use for this variable. If we evaluate $\int_2^6 z\,dz$, we still get 16. In general, $\int_a^b f(x)\,dx = \int_a^b f(z)\,dz$. For this reason the integration variable in a definite integral is called a *dummy variable*. (The integration variable in an indefinite integral is not a dummy variable.) Similarly it doesn't matter what symbol we use for the summation index in (2.8). Replacement of i by j gives exactly the same sum on the right; thus i in (2.8) is a dummy index.

Two identities that readily follow from (2.10) are $\int_a^b f(x)\,dx = -\int_b^a f(x)\,dx$ and $\int_a^b f(x)\,dx + \int_b^c f(x)\,dx = \int_a^c f(x)\,dx$.

An important method for evaluating integrals is a change of variables. For example, suppose we want $\int_2^3 x \exp(x^2)\,dx$. Let $z \equiv x^2$; then $dz = 2x\,dx$, and

$$\int_2^3 xe^{x^2}\,dx = \frac{1}{2}\int_4^9 e^z\,dz = \tfrac{1}{2}e^z\Big|_4^9 = \tfrac{1}{2}(e^9 - e^4) = 4024.2 \tag{2.11}$$

Note that the limits were changed in accord with the substitution $z = x^2$.

From (2.2) and (2.1), it follows that the derivative of an indefinite integral equals the integrand: $(d/dx)\int f(x)\,dx = f(x)$. Note, however, that a definite integral is simply a number and not a function; hence, $(d/dx)\int_a^b f(x)\,dx = 0$.

We can define integration with respect to x for a function of two variables in an analogous manner to (2.2) and (2.9). Thus if $y(x, z)$ is the most general function that satisfies

$$\left[\frac{\partial y(x, z)}{\partial x}\right]_z = f(x, z) \tag{2.12}$$

then the indefinite integral of $f(x, z)$ is

$$\int f(x, z)\,dx = y(x, z) \tag{2.13}$$

For example, if $f(x, z) = xz^3$, then $y(x, z) = \frac{1}{2}x^2z^3 + g(z)$, where g is an arbitrary function of z. If y satisfies (2.12), one can show [in analogy with (2.10)] that a definite integral of $f(x, z)$ is given by

$$\int_a^b f(x, z)\, dx = y(b, z) - y(a, z) \tag{2.14}$$

For example, $\int_2^6 xz^3\, dx = \frac{1}{2}(6^2)z^3 + g(z) - \frac{1}{2}(2^2)z^3 - g(z) = 16z^3$.

Note from (2.14) that the definite integral with respect to x of $f(x, z)$ is a function of z (but not of x). One can show (see *Sokolnikoff and Redheffer*, p. 348) that

$$\frac{d}{dz}\int_a^b f(x, z)\, dx = \int_a^b \frac{\partial f(x, z)}{\partial z}\, dx \tag{2.15}$$

The integrals (2.13) to (2.15) are similar to ordinary integrals of a function $f(x)$ of a single variable in that we regard the second independent variable z in these integrals as constant during the integration process; z acts as a parameter rather than a variable. However, in thermodynamics, we shall frequently have occasion to integrate a function of two (or more) variables in which all the variables are changing during the course of the integration. Such integrals are called line integrals and will be discussed in Sec. 2.4.

2.2 CLASSICAL MECHANICS

Two important concepts in thermodynamics are work and energy. Since these concepts originated in classical mechanics, it is useful to review this subject before we continue with thermodynamics. Some knowledge of classical mechanics is also needed for the study of quantum mechanics.

Classical mechanics (first formulated by the alchemist, theologian, physicist, and mathematician Isaac Newton) deals with the laws of motion of macroscopic bodies whose speeds are small compared with the speed of light c. For objects with speeds not small compared with c, one must use Einstein's *relativistic mechanics.* Since the thermodynamic systems we consider will not be moving at high speeds, we need not worry about relativistic effects. For nonmacroscopic objects (e.g., electrons), one must use *quantum mechanics.* Thermodynamic systems are of macroscopic size, so we shall not need quantum mechanics at this point.

The fundamental equation of classical mechanics is Newton's second law of motion:

$$\mathbf{F} = m\mathbf{a} \tag{2.16*}$$

where m is the mass of a body, $\mathbf{F}$ is the vector sum of all forces acting on it at some instant of time, and $\mathbf{a}$ is the acceleration the body undergoes at that instant of time. Both $\mathbf{F}$ and $\mathbf{a}$ are vectors (as indicated by the boldface type). Vectors have both magnitude and direction. Scalars (for example, m) have only a magnitude. The meaning of acceleration is as follows. We set up a coordinate system with three mutually perpendicular axes x, y, and z. Let $\mathbf{r}$ be the vector from the coordinate origin to the