3 Integration

3.1 THE INDEFINITE INTEGRAL

The derivative and the differential were introduced in Chapter 2. There, given a function, the problem was to find its derivative. In this chapter the objective is to perform the inverse operation, namely, given the derivative of a function, find the function. The function in question is the integral of the given function. It is defined by the expression*

$$f(x) = \int f'(x)\,\mathrm{d}x. \tag{1}$$

As an example, consider the function $f'(x) = x^3$. The prime on $f(x)$ indicates that this function $\mathrm{d}f(x)/\mathrm{d}x$ is the derivative of the function searched. Given the rules of differentiation [Eq. (2-15)], the function might be expected to have the form $\frac{1}{4}x^4$. This result is correct, although it should be noted that the addition of any constant to the function $\frac{1}{4}x^4$ does not change the value of the derivative, as the derivative of a constant is equal to zero. It must therefore be concluded that the indefinite integral is given by

$$\int x^3\,\mathrm{d}x = \frac{1}{4}x^4 + C. \tag{2}$$

The constant C is the constant of integration introduced in the applications presented in Chapter 1 [Eqs. (1-20) and (1-24)]. There it was indicated that the determination of this constant requires additional information, namely, the initial or boundary conditions associated with the physical problem involved. Integrals of this type are, therefore, called indefinite integrals.

*The notation $f(x) = \int \mathrm{d}x f'(x)$ is often employed. It is, however, ambiguous in some cases and should be avoided.

3.2 INTEGRATION FORMULAS

The general rules for obtaining an indefinite integral can be summarized as follows:

$$\text{(i)} \quad \int \mathrm{d}u = u + C, \tag{3}$$

$$\text{(ii)} \quad \int (\mathrm{d}u + \mathrm{d}v + \cdots + \mathrm{d}z) = \int \mathrm{d}u + \int \mathrm{d}v + \cdots + \int \mathrm{d}z, \tag{4}$$

$$\text{(iii)} \quad \int a\,\mathrm{d}u = a \int \mathrm{d}u \tag{5}$$

and

$$\text{(iv)} \quad \int u^n\,\mathrm{d}u = \frac{u^{n+1}}{n+1} + C, \quad \text{if } n \neq -1, \tag{6}$$

where a is a constant and n is an integer. Rule (iv) is the general power formula of integration. It is obviously the inverse of Eq. (2-15).

Some other formulas for integration can be summarized as follows:

$$\int x^{-1}\,\mathrm{d}x = \ln x + C \tag{7}$$

$$\int e^x\,\mathrm{d}x = e^x + C \tag{8}$$

$$\int \sin x\,\mathrm{d}x = -\cos x + C \tag{9}$$

$$\int \cos x\,\mathrm{d}x = \sin x + C \tag{10}$$

$$\int \sec^2 x\,\mathrm{d}x = \tan x + C \tag{11}$$

$$\int \sinh x\,\mathrm{d}x = \cosh x + C \tag{12}$$

$$\int \cosh x\,\mathrm{d}x = \sinh x + C \tag{13}$$

$$\int \frac{\mathrm{d}x}{1+x^2} = \tan^{-1} x + C \tag{14}$$

$$\int \frac{dx}{\sqrt{1-x^2}} = sin^{-1} x + C \tag{15}$$

Many others are available in standard integral tables* and computer programs.†

3.3 METHODS OF INTEGRATION

3.3.1 Integration by substitution

Very often integrals can be evaluated by introducing a new variable. The variable of integration x is replaced by a new variable, say z, where the two are related by a well chosen formula. Thus, the explicit substitution $x = \phi(z)$ and $dx = (d\phi/dz)dz$ can be made to simplify the desired integration. As an example, consider the integral

$$\int \frac{x^3\, dx}{\sqrt{x^2-a^2}}, \tag{16}$$

where a is a constant. Let $x^2 - a^2 = z^2$; and, with $dx = z\, dz/x$, the integral takes the form

$$\int \frac{(z^2+a^2)z\, dz}{z} = \frac{1}{3}(x^2-a^2)^{3/2} + a^2(x^2-a^2)^{1/2} + C. \tag{17}$$

The expressions, $\sqrt{x^2-a^2}$, $\sqrt{x^2+a^2}$ and $\sqrt{a^2-x^2}$ occur often in the integrand. The substitution of a new independent variable for the radical should be made whenever the integrand contains a factor which is an odd integral power of x. Otherwise, the radical will reappear after the substitution.

Trigonometric substitutions are often useful in evaluating integrals. Among the many possibilities, if the integrand involves the expression $x^2 + a^2$, the substitution $x = a\, tan\, \varphi$ should be tried. Similarly, in the cases of $x^2 - a^2$ or $a^2 - x^2$, the independent variable x should be replaced by $a\, sec\, \varphi$ or $a\, sin\, \varphi$, respectively. As an example of the latter case, consider the integral

$$I = \int \frac{dx}{(a^2-x^2)^{3/2}}. \tag{18}$$

*B. O. Peirce, *A Short Table of Integrals*, Ginn and Company, Boston, 1929.
I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series and Products*, Academic Press, New York, 1965.

†*Mathematica*, Wolfram Research, Inc., Champaign, Ill., 1997.

The substitutions $x = a\, sin\, \varphi$ and $dx = a\, cos\, \varphi\, d\varphi$ yield

$$I = \int \frac{a\, cos\, \varphi\, d\varphi}{(a^2 - a^2\, sin^2\, \varphi)^{3/2}} = \frac{1}{a^2}\int \frac{cos\, \varphi\, d\varphi}{cos^3 \varphi}$$
$$= \frac{1}{a^2}\int sec^2 \varphi\, d\varphi = \frac{1}{a^2}\, tan\, \varphi + C$$
$$= \frac{x}{a^2\sqrt{a^2 - x^2}} + C. \tag{19}$$

3.3.2 Integration by parts

This method is the direct result of Eq. (2-22) for the differential of a product,

$$d(uv) = u\, dv + v\, du. \tag{20}$$

Therefore,

$$\int u\, dv = uv - \int v\, du, \tag{21}$$

which is the basic formula for integration by parts. This method is very useful, although it is not always clear how to break up the integrand. As an example, consider the integral

$$I_1 = \int xe^{-x}\, dx. \tag{22}$$

With the choice $dv = e^{-x}\, dx$ and $u = x$, $v = -e^{-x}$ and, of course, $du = dx$. Eq. (22) then yields

$$I_1 = -xe^{-x} + \int e^{-x}\, dx = -(1 + x)e^{-x} + C. \tag{23}$$

It should be apparent that in integrating $dv = e^{-x}\, dx$ it is not necessary to add the constant of integration, as the final result is not changed by its inclusion.

The above example can be generalized. The integral

$$I_n = \int x^n e^{-x}\, dx, \tag{24}$$

where n is a positive integer, can be reduced to Eq. (23) by successive integration by parts. Thus,

$$I_n = -x^n e^{-x} + n\int x^{n-1} e^{-x}\, dx = -x^n e^{-x} + nI_{n-1}, \tag{25}$$

a result which is given in all integral tables.

3.3.3 Integration of partial fractions

Another common method of integration involves partial fractions. First, it should be noted that every rational algebraic fraction can be integrated directly. A rational algebraic fraction is the ratio of two polynomials. If the polynomial in the numerator is of a lower degree than that of the denominator, or can be made so by division, the resulting fraction can be written as the sum of fractions whose numerators are constants and whose denominators are the factors of the original denominator. Fortunately, in many cases the denominator can be broken up into real linear factors, none of which is repeated. As an example, consider the integral

$$\int \frac{x+3}{x^3-x}\,\mathrm{d}x. \tag{26}$$

The integrand can be written in the form

$$\frac{x+3}{x(x+1)(x-1)} = \frac{A}{x} + \frac{B}{x+1} + \frac{D}{x-1}, \tag{27}$$

where A, B and D are constants. Expressing the right-hand side of Eq. (27) over a common denominator yields the relation

$$x+3 = -A + (D-B)x + (A+B+D)x^2 \tag{28}$$

and by equating coefficients of the various powers of x, $A = -3$, $B = 1$ and $D = 2$. The proposed integral is then given by

$$\int \frac{x+3}{x^3-x}\,\mathrm{d}x = -3\int \frac{\mathrm{d}x}{x} + \int \frac{\mathrm{d}x}{x+1} + 2\int \frac{\mathrm{d}x}{x-1} \tag{29}$$

$$= -3\,ln\,x + ln(x+1) + 2\,ln(x-1) + C$$

$$= ln\,\frac{(x+1)(x-1)^2}{x^3} + C. \tag{30}$$

Integrals involving partial fractions occur often in chemical kinetics. For example, the differential equation which represents a second-order reaction is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a-x)(b-x), \tag{31}$$

where k is the rate constant and a and b are the initial concentrations of the two reactants. In Eq. (31) the independent variable x represents the concentration of product formed at time t. After separation of variables, Eq. (31) becomes

$$\frac{\mathrm{d}x}{(a-x)(b-x)} = k\,\mathrm{d}t. \tag{32}$$

In the general case in which $a \neq b$ the integration of the left-hand side of Eq. (32) can be carried out with the use of partial fractions. Then, the integrand is broken up in the form

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)}, \tag{33}$$

with $A = 1/(b-a)$ and $B = -1/(b-a)$. The integral of Eq. (31) can then be expressed as

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{(b-a)}[-ln(a-x) + ln(b-x)] + C = kt. \tag{34}$$

The initial condition $x = 0$ at $t = 0$ leads to the value of the integration constant, *viz.*

$$C = \frac{1}{(b-a)}(ln\, b - ln\, a) = \frac{1}{(a-b)}\, ln\, \frac{a}{b}, \tag{35}$$

and the resulting expression for the concentration of product at time t,

$$x = \frac{ab(1 - e^{kt(a-b)})}{b - ae^{kt(a-b)}}. \tag{36}$$

The integration method illustrated above becomes somewhat more complicated if the denominator contains repeated linear factors. Thus, if the denominator contains a factor such as $(x-a)^n$, n identical factors would result which could of course be combined. To avoid this problem it is assumed that $1/(x-a)^n$ can be replaced by

$$\frac{A}{x-a} + \frac{B}{(x-a)^2} + \cdots + \frac{N}{(x-a)^n}. \tag{37}$$

The constants appearing in the numerator are then evaluated as before.

The differential equation for a chemical reaction of third order is of the general form

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x), \tag{38}$$

where a, b and c are the initial concentrations of the three reactants. It can be integrated directly by application of the method just illustrated. In the special case in which two of the reactants have the same initial concentration, say $b = c$, Eq. (38) becomes

$$\frac{dx}{dt} = k(a-x)(b-x)^2 \tag{39}$$

and the integral to be evaluated is

$$\int \frac{dx}{(a-x)(b-x)^2} \, . \tag{40}$$

As the factor $b - x$ appears twice in the denominator, the partial fractions must be developed as given by Eq. (37), namely

$$\frac{1}{(a-x)(b-x)^2} = \frac{A}{a-x} + \frac{B}{b-x} + \frac{D}{(b-x)^2} \, . \tag{41}$$

The constants in the numerator are found to be $A = 1/(a-b)^2$, $B = -1/(a-b)^2$ and $D = 1/(a-b)$, yielding

$$\int \frac{dx}{(a-x)(b-x)^2} = \frac{1}{(a-b)^2} ln \frac{b-x}{a-x} + \frac{1}{(a-b)(b-x)} = kt + C. \tag{42}$$

The evaluation of the constant of integration is achieved by applying the initial condition $x = 0$ at $t = 0$.

3.4 DEFINITE INTEGRALS

3.4.1 Definition

Let $f(x)$ be a function whose integral is $F(x)$ and a and b two values of x. The change in the integral, $F(b) - F(a)$, is called the definite integral of $f(x)$ between the limits a and b. It is represented by

$$\int_a^b f(x)\,dx = [F(x)]_a^b = F(b) - F(a) \tag{43}$$

and it is evident that the constant of integration cancels.

All definite integrals have the following two properties:

$$\text{(i)} \int_a^b f(x)\,dx = -\int_b^a f(x)\,dx \tag{44}$$

and

$$\text{(ii)} \int_a^b f(x)\,dx = \int_a^c f(x)\,dx + \int_c^b f(x)\,dx. \tag{45}$$

Relation (ii) is useful in the case of a discontinuity, *e.g.* a missing point at c, which usually lies between a and b.

3.4.2 Plane area

For simplicity, assume that a continuous function $f(x)$ is divided into n equal intervals of width Δx (see Fig. 1). Each rectangle of width Δx at a given point $f(x)$ has an area of $f(x)\Delta x$. Therefore, the definition of the area $\mathcal{A}$ bounded by the curve $y = f(x)$, the x axis and the limits $x = a$ and $x = b$ is given by

$$\mathcal{A} = \lim_{\Delta x \to 0} \sum_{k=1}^{n} f(x_k)\Delta x_k \ . \tag{46}$$

Thus, if Δx_k is taken to be sufficiently small, and the number of rectangles correspondingly large, the sum of the areas of the rectangles will approximate, to the desired degree of accuracy, the value of the area $\mathcal{A}$. Thus, as the widths Δx_k approach zero, the number of them, n, must approach infinity. It should be noted here that the intervals Δx_k have been assumed to be constant over the range a,b. It is not necessary from a fundamental point of view to divide the abscissa in equal steps Δx_k, although in most numerical calculations it is essential, as shown in Chapter 13.

Assuming that the required limit exists and that it can be calculated, the fundamental theorem of the integral calculus can be stated as follows.

$$\lim_{\Delta x \to 0} \sum_{k=1}^{n} f(x_k)\Delta x_k = \int_a^b f(x)\,\mathrm{d}x \tag{47}$$

and the desired area is given by

$$\mathcal{A} = \int_a^b f(x)\,\mathrm{d}x. \tag{48}$$

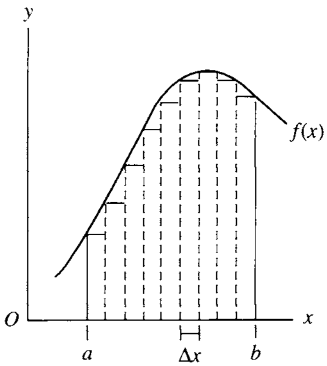

Fig. 1 The integral from $x = a$ to $x = b$.

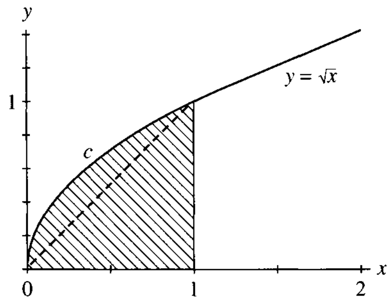

Fig. 2 The area under the curve c [Eq. (48)] and the length of the curve c [Eq. (54)].

As an example, consider the parabola $y = \sqrt{x}$ shown in Fig. 2. The area in the first quadrant under the curve between $x = 0$ and $x = 1$ is equal to

$$\int_0^1 x^{1/2}\,\mathrm{d}x = \left[\frac{2}{3}x^{3/2}\right]_0^1 = \frac{2}{3}, \tag{49}$$

as shown by the shaded area in Fig. 2. If the curve in this figure were cut into equal horizontal "slices" of width dy, the same area could be calculated as

$$\int_0^1 \mathrm{d}y - \int_0^1 y^2\,\mathrm{d}y = 1 - \frac{1}{3} = \frac{2}{3}, \tag{50}$$

where the first term corresponds to the square of unit area.

3.4.3 Line integrals

In Section 2.7 it was shown [see Eq. (2-23)] that a given element ds along a curve is given by

$$\mathrm{d}s = \sqrt{1 + \left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2}\,\mathrm{d}x. \tag{51}$$

Thus,

$$s = \int_a^b {}_c\,\mathrm{d}s = \int_a^b \sqrt{1 + \left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2}\,\mathrm{d}x. \tag{52}$$

The symbol $\int_a^b {}_c\,\mathrm{d}s$ indicates that the integral is taken along the curve c from the point a to the point b. If the variables x and y are related *via* a parameter t, the length of the curve can also be evaluated from the equivalent relation

$$s = \int_{t_a}^{t_b} \sqrt{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2}\, dt \tag{53}$$

where t_a and t_b are the values of t at points a and b, respectively.

As an example, consider the passage from the origin to the point (1,1), as shown in Fig. 2. Obviously, the length of a straight line between these two points, the dotted line, is equal to $\sqrt{2} = 1.414$. However, from Eq. (52) the length of the curve defined by the parabola $y = \sqrt{x}$ between these same two points is given by

$$\int_0^1 \sqrt{1 + \frac{1}{4x}}\, dx = \frac{1}{4}\left[z\sqrt{1+z^2} + ln\left(z + \sqrt{1+z^2}\right)\right]_0^2 = 1.478, \tag{54}$$

where the substitution $z = 2\sqrt{x}$ has been made to simplify the integration. It should be noted that the upper limit to the integral is at $x = 1$, where $z = 2$.

The method illustrated here for determining the length of a given curve can be extended to evaluate the surface of a solid. It is particularly useful in engineering applications to determine, for example, the surface generated by the revolution of a given contour.

3.4.4 Fido and his master

To illustrate some of the principles outlined above, consider the following story. A jogger leaves a point taken as the origin in Fig. 3 at a constant speed equal to v. His dog, Fido, is at that moment at the point $x = a$. As the jogger continues in the y direction, Fido runs twice as fast, at a speed $2v$, always headed towards his master. The problem is then to find the equation that represents Fido's trajectory and the time at which he meets his master. The answers to these two questions are indicated in Fig. 3. The solution is as follows.

The distance along the y axis covered by the jogger at time t is $y = vt$. Thus, the slope of the curve followed by Fido is given by

$$\frac{dy}{dx} = -\frac{vt - y}{x}. \tag{55}$$

At the same time Fido has traveled a distance $s = 2vt$ along the curve. Therefore, replacing vt by $s/2$ in Eq. (55) and rearranging, yields

$$x\frac{dy}{dx} = y - \frac{s}{2}. \tag{56}$$

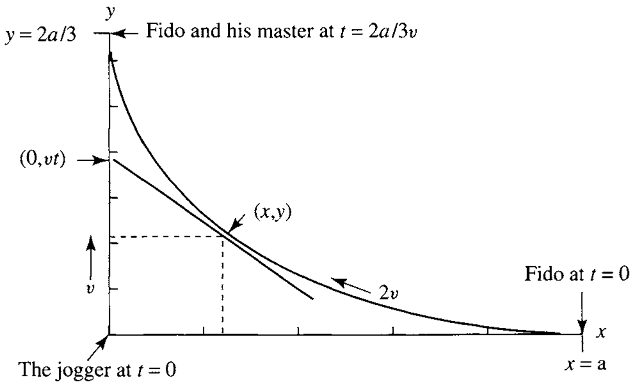

Fig. 3 Fido and his master.

With the use of Eq. (51) and the derivative of Eq. (56),

$$\frac{\mathrm{d}s}{\mathrm{d}x} = -2x\frac{\mathrm{d}^2y}{\mathrm{d}x^2} = -\sqrt{1+\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2}, \tag{57}$$

where the negative sign is chosen on the radical because the distance covered by Fido increases as x decreases. Equation (57) can be rewritten as a first order differential equation for $y' \equiv \mathrm{d}y/\mathrm{d}x$. The variables are separable, *viz.*

$$\frac{\mathrm{d}y'}{\sqrt{1+y'^2}} = \frac{\mathrm{d}x}{2x}. \tag{58}$$

The integration of the left-hand side of Eq. (58) can be carried out with the aid of the substitution $y' = tan\,\theta$ (as suggested in Section 3.3.1), and the tabulated integral $\int sec\,\theta \mathrm{d}\theta = ln(tan\,\theta + sec\,\theta) + C$. The result is

$$ln\left(y' + \sqrt{1+y'^2}\right) + C = \tfrac{1}{2}\,ln\,x. \tag{59}$$

If the initial condition $y' = 0$ at $t = 0$ (where $x = a$) is imposed, the constant of integration is $C = \frac{1}{2}\,ln\,a$, and the solution becomes

$$\sqrt{1+y'^2} = \sqrt{\frac{x}{a}} - y'. \tag{60}$$

Here, again, the variables can be separated. If the left-hand side of Eq. (60) is multiplied and divided by $y' - \sqrt{1 + y'^2}$, the relation

$$y' - \sqrt{1 + y'^2} = -\sqrt{\frac{a}{x}} \tag{61}$$

is easily obtained. Elimination of the radical $\sqrt{1 + y'^2}$ between Eqs. (60) and (61) leads to

$$y' \equiv \frac{\mathrm{d}y}{\mathrm{d}x} = \frac{1}{2}\left(\sqrt{\frac{x}{a}} - \sqrt{\frac{a}{x}}\right), \tag{62}$$

which integrates to

$$y = \frac{x^{3/2}}{3\sqrt{a}} - \sqrt{ax} + \frac{2a}{3}. \tag{63}$$

The boundary condition $x = a$ at $y = 0$ has been employed to evaluate the second integration constant. It is Eq. (63) that describes Fido's path, as shown in Fig. 3. At $x = 0$ he "catches up" with his master, who has jogged a distance equal to $2a/3$ in time $2a/3v$.

3.4.5 The Gaussian and its moments

A very important example of integration by substitution, is that of the function of Gauss,* $exp(-z^2)$, which is shown in Fig. 4. In practical applications this function can be written in the form

$$f(z) = \mathcal{N} e^{-\alpha z^2}, \tag{64}$$

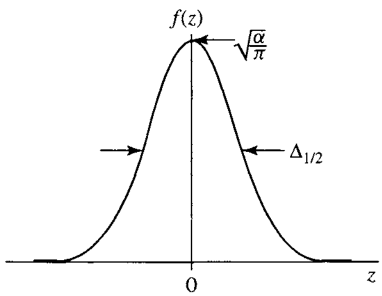

Fig. 4 The Gaussian function.

*Carl Friedrich Gauss, German astronomer and mathematician (1777–1855).

where α is a constant and the factor $\mathcal{N}$ is chosen to normalize the function. The latter can be evaluated by application of the normalization condition

$$\int_{-\infty}^{+\infty} f(z)\,\mathrm{d}z = 1. \tag{65}$$

Then,*

$$\mathcal{N}\int_{-\infty}^{+\infty} e^{-\alpha z^2}\,\mathrm{d}z = \mathcal{N}\cdot 2I_0 = 1 \tag{66}$$

with the definition of the integrals

$$I_n \equiv \int_0^{\infty} z^n e^{-\alpha z^2}\,\mathrm{d}z \tag{67}$$

for $n = 0, 1, 2, \ldots$. Clearly, the integral I_0 has the same value for any choice of symbol for the independent variable, say x or y. Thus,

$$I_0^2 = \int_0^{+\infty} e^{-\alpha x^2}\,\mathrm{d}x \cdot \int_0^{+\infty} e^{-\alpha y^2}\,\mathrm{d}y = \int_0^{+\infty}\int_0^{+\infty} e^{-\alpha(x^2+y^2)}\,\mathrm{d}x\,\mathrm{d}y. \tag{68}$$

Equation (68) can be converted to polar coordinates with the substitutions $x = r\cos\theta$ and $y = r\sin\theta$. The result is given by

$$I_0^2 = \int_0^{+\infty}\int_0^{\pi/2} e^{-\alpha r^2} r\,\mathrm{d}\theta\,\mathrm{d}r = \frac{\pi}{4\alpha} \tag{69}$$

and from Eq. (66) $\mathcal{N} = \sqrt{\alpha/\pi}$. The normalized Gaussian function of Eq. (64) is then

$$f(z) = \sqrt{\frac{\alpha}{\pi}}e^{-\alpha z^2}. \tag{70}$$

In certain applications it is of interest to express the width of the Gaussian distribution at half its value at the maximum. Thus, as the maximum value is $f(0) = \sqrt{\alpha/\pi}$, the value of z at half of this value is $\sqrt{\ln 2/\alpha}$ and the width at half-height is given by

$$\Delta_{1/2} = 2\sqrt{\frac{\ln 2}{\alpha}}, \tag{71}$$

as indicated in Fig. 4. The quantity $\Delta_{1/2}$ is referred to by spectroscopists as the "FWHM" for full width at half-maximum.

*Note that $f(x)$ is an even function (Section 1.2); $\int_{-\infty}^{+\infty} f(z)\,\mathrm{d}z = 2\int_0^{+\infty} f(z)\,\mathrm{d}z$.

A more general distribution can be expressed by a series of so-called moments, which are defined by

$$M(n) \equiv \int_{-\infty}^{+\infty} z^n f(z)\, \mathrm{d}z. \tag{72}$$

In the present example $f(z)$ is an even function, as given by Eq. (70). Hence, all moments with odd values of n vanish and the distribution is symmetric with respect to the origin. The first moment in this case is given by

$$\begin{aligned} M(1) &= \int_{-\infty}^{+\infty} zf(z)\, \mathrm{d}z = \int_{-\infty}^{0} zf(z)\, \mathrm{d}z + \int_{0}^{+\infty} zf(z)\, \mathrm{d}z \\ &= -\int_{0}^{-\infty} zf(z)\, \mathrm{d}z + \int_{0}^{+\infty} zf(z)\, \mathrm{d}z = 0. \end{aligned} \tag{73}$$

The second moment is

$$M(2) \equiv \int_{-\infty}^{+\infty} z^2 f(z)\, \mathrm{d}z = 2\int_{0}^{+\infty} z^2 f(z)\, \mathrm{d}z, \tag{74}$$

which, with $f(z)$ given by Eq. (70), becomes

$$M(2) = 2\int_{0}^{+\infty} z^2 e^{-\alpha z^2}\, \mathrm{d}z = \frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}}. \tag{75}$$

The integral in Eq. (75) can be evaluated by parts (see problem 4).

3.5 INTEGRATING FACTORS

The concept of the total differential was introduced in Section 2.12. It is of importance in many physical problems and in particular in thermodynamics. In this application it is often necessary to integrate an expression of the form

$$\delta z = M(x, y)\, \mathrm{d}x + N(x, y)\, \mathrm{d}y \tag{76}$$

to determine the function $z(x,y)$ evaluated at two points, x_1,y_1 and x_2,y_2. In general this integration requires the knowledge of a relation between x and y, *i.e.* $y = f(x)$. Such a function specifies the path between the two points, and the integral becomes a line integral. As shown in Section 3.4.3, the value of the integral then depends on the chosen path.*

*If a differential such as given in Eq. (76) is not exact, it is represented by δz, following the custom in thermodynamics [see Eq. (2-47)].

If the differential dz is exact, according to the chain rule it is given by Eq. (2-45), *viz.*

$$dz = \left(\frac{\partial z}{\partial x}\right) dx + \left(\frac{\partial z}{\partial y}\right) dy, \tag{77}$$

with

$$M(x, y) = \frac{\partial z}{\partial x} \text{ and } N(x, y) = \frac{\partial z}{\partial y}. \tag{78}$$

It is evident that $z(x,y)$ can be found even if the functional relation between x and y is unknown. In this case, then, the integral is independent of the path, as it depends only on the values of x and y at the two limits.

In thermodynamic applications the integral is often taken around a closed path. That is, the initial and final points in the x,y plane are identical. In this case the integral is equal to zero if the differential involved is exact, and different from zero if it is not. In mechanics the former condition defines what is called a conservative system (see Section 4.14).

Equation (76) can be written as

$$dz = \mu(x, y)\delta z = \mu(x, y)M(x, y)\, dx + \mu(x, y)N(x, y)\, dy, \tag{79}$$

where $\mu(x, y)$ is an integrating factor. It should be noted that the integrating factor is not unique, as there is an infinite choice. In general, it is sufficient to find one suitable factor for the problem at hand.

An example is provided by the differential $y\, dx - x\, dy$, which is not exact. It is therefore written in the form

$$\delta z = y\, dx - x\, dy. \tag{80}$$

However, if this expression is multiplied by $1/y^2$, it becomes

$$\frac{y\, dx - x\, dy}{y^2} = d\left(\frac{x}{y}\right), \tag{81}$$

which is an exact differential. Clearly, $1/y^2$ can be identified as an integrating factor.

In thermodynamics the first law is often written in the form (see Section 2.13)

$$dE = \delta q + \delta w, \tag{82}$$

where dE is the (exact) differential of the internal energy of a system, while δq and δw are the (inexact) differentials of the heat and work, respectively. To illustrate the roles of exact and inexact differentials consider the work done by the reversible expansion or compression of a gas, as given by the expression

$$\delta w = -P\,\mathrm{d}V. \tag{83}$$

Equation (82) then yields

$$\delta q = \mathrm{d}E + P\mathrm{d}V. \tag{84}$$

However, as $E = f(V,T)$,

$$\mathrm{d}E = \left(\frac{\partial E}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial E}{\partial T}\right)_V \mathrm{d}T \tag{85}$$

and

$$\delta q = \left(\frac{\partial E}{\partial T}\right)_V \mathrm{d}T + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \mathrm{d}V. \tag{86}$$

In this form Eq. (86) cannot be integrated without a relation between P and V, because the second term on the right-hand side involves both variables. However, in the special case in which the gas is ideal, $PV = RT$ for one mole and $(\partial E/\partial V)_T = 0$ (see problem 6). The latter relation implies the absence of intermolecular forces. Then, Eq. (86) becomes

$$\delta q = \left(\frac{\partial E}{\partial T}\right)_V \mathrm{d}T + \frac{RT\,\mathrm{d}V}{V} = \tilde{C}_V\,\mathrm{d}T + \frac{RT\,\mathrm{d}V}{V}, \tag{87}$$

where the definition of the heat capacity per mole at constant volume, $\tilde{C}_V = (\partial E/\partial T)_V$ has been introduced. While Eq. (87) can be integrated if the temperature is held constant, a more general relation is obtained by dividing by T. Thus, Eq. (87) becomes

$$\frac{\delta q}{T} = \frac{\tilde{C}_V}{T}\mathrm{d}T + \frac{R\,\mathrm{d}V}{V}. \tag{88}$$

Clearly, the differential obtained, namely, $\mathrm{d}S \equiv \delta q/T$ is exact and S, the entropy, is a thermodynamic state function, that is, it is independent of the path of integration. While Eq. (88) was obtained with the assumption of an ideal gas, the result is general if reversible conditions are applied.

With the definition of the entropy, the substitution $\delta q = T\,\mathrm{d}S$ can be made in Eq. (84); then,

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V. \tag{89}$$

This result leads to one of Maxwell's relations [Eq. (2-53)]. The three remaining relations are found by analogous derivations.

3.6 TABLES OF INTEGRALS

Many tables of indefinite and definite integrals have been published. They range from collections of certain common integrals presented in appendices to most elementary calculus books, the famous Peirce tables, to compendia such as that by Gradshteyn and Ryzhik. More recently, many integrals have become available in analytical form in computer programs. One of the most complete lists is included in *Mathematica* (see footnote in Section 3.2).

Consider, as an example, the calculation of the mean-square speed of an ensemble of molecules which obey the Maxwell–Boltzmann distribution law.* This quantity is given by

$$\overline{u^2} = 4\pi(m/2\pi kT)^{3/2} \int_0^\infty e^{-mu^2/2kT} u^4 \, du, \tag{91}$$

where u is the speed of a molecule of mass m, k is the Boltzmann constant and T the absolute temperature. While this integral can be evaluated by successive integration by parts (Section 3.3.2), it is much easier to employ the standard integral. It is given in the tables in the form†

$$\int_0^\infty x^{2n} e^{-ax^2} \, dx = \frac{(2n-1)!!}{2(2a)^n} \sqrt{\frac{\pi}{a}}, \tag{92}$$

where n is a positive integer and $a > 0$. Comparison of Eqs. (91) and (92) allows the identifications $x = u$ and $a = m/2kT$ to be made. With $n = 2$, the integral in Eq. (91) becomes $3(\pi/2)^{1/2}(kT/m)^{5/2}$, leading to $\overline{u^2} = 3kT/m$. It should be pointed out, however, that most relatively simple integrals which can be evaluated by the methods outlined in Section 3.3 are not included in the standard tables.

When all else fails, recourse to numerical methods is indicated. Some of the classic methods of numerical integration are described in Chapter 13. However, it should be emphasized that numerical methods are to be used as a last resort. Not only are they subject to errors (often not easily evaluated), but they do not yield analytical results that can be employed in further derivations (see p. 45).

*Ludwig Boltzmann, Austrian physicist (1844–1906).

†The notation $(2n - 1)!! = 1 \cdot 3 \cdot 5 \cdot 7 \cdots$ is often employed in integration tables.

PROBLEMS

1. Evaluate the following indefinite integrals:

$$\int \frac{(\sqrt{x}-1)^2}{\sqrt{x}}\,dx \qquad \text{Ans. } \frac{2}{3}x^{3/2} - 2x + 2\sqrt{x} + C$$

$$\int sin^3 x\,dx \qquad \text{Ans. } \frac{1}{3}cos^3 x - cos\, x + C$$

$$\int \frac{\sqrt{x}\,dx}{1+x} \qquad \text{Ans. } 2\sqrt{x} - 2\,tan^{-1}\sqrt{x} + C$$

$$\int \frac{x^3+2}{x^3-x}\,dx \qquad \text{Ans. } x - 2\,ln\,x + \frac{1}{2}ln(x+1) + \frac{3}{2}ln(x-1) + C$$

2. Verify Eq. (54).

3. Verify all of the steps in the solution to the problem of Fido and his master.

4. Calculate the second moment of a Gaussian function as given by Eq. (75).

5. Show that y^{-2} is an integrating factor for the differential given by Eq. (82).

6. Demonstrate that $(\partial E/\partial V)_T = 0$ for an ideal gas.

7. Evaluate the following definite integrals:

$$\int_0^{\pi/3} x\,sin\,x\,dx \qquad \text{Ans. } 0.342$$

$$\int_{-\infty}^{\infty} \frac{x\,dx}{(x^2+1)^2} \qquad \text{Ans. } 0$$

$$\int_0^{\infty} \frac{x\,dx}{(x^2+1)^2} \qquad \text{Ans. } \frac{1}{2}$$

$$\int_{-1}^{+1} \frac{dx}{\sqrt{4-x^2}} \qquad \text{Ans. } \pi/3$$

$$\int_0^1 xe^{-x^2}\,dx \qquad \text{Ans. } \frac{1}{2}(1-e^{-1})$$

8. Verify Eq. (92) for $n = 1$.

9. Show that the FWHM of a Gaussian is given by Eq. (71).

10. Derive an expression for I_1/I_0, where $I_0 = \int_0^{\pi} e^{-a\cos\theta} \sin\theta \, d\theta$ and $I_1 = \int_0^{\pi} \cos\theta e^{-a\cos\theta} \sin\theta \, d\theta$.

Ans.* $\mathcal{L}(a) \equiv \coth a - \frac{1}{a}$

11. Show that $\mathcal{L}(a) \approx \frac{a}{3}$ if $a \ll 1$.†

*The function $\mathcal{L}(a)$ is known as the Langevin function, after Paul Langevin, French physicist (1872–1946). The magnetic susceptibility of a paramagnetic substance can be expressed as $\mathcal{L}(\mu_m \mathcal{B}/kT)$, where μ_m is the magnetic moment, $\mathcal{B}$ the magnetic flux, k the Boltzmann constant and T the absolute temperature.

†At ordinary temperatures the magnetic susceptibility is given approximately by $\mu_m \mathcal{B}/3kT$. This relation was determined experimentally by Pierre Curie, French physicist (1859–1906).