5 Differentials

In many areas of chemistry (*e.g.* error analysis; thermodynamics) we are concerned with the consequences of small (and, sometimes, not so small) changes in a number of variables and their overall effect upon a property depending on these variables. For example, in thermodynamics, the temperature dependence of the equilibrium constant, K, is usually expressed in the form:

$$K = \mathrm{e}^{-\Delta G^{\circ}/RT}$$

where the change in Gibbs energy, $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$, itself depends upon temperature, both explicitly through the presence of T, and implicitly, as ΔH° and ΔS° are, in general, both temperature dependent. However, if we assume that ΔH° and ΔS° are, to a good approximation, independent of temperature, then for small changes in temperature we obtain the explicit formula relating K and T:

$$K = \mathrm{e}^{-(\Delta H^{\circ} - T\Delta S^{\circ})/RT} = \mathrm{e}^{-(\Delta H^{\circ}/T - \Delta S^{\circ})/R} \tag{5.1}$$

Quite frequently, we are interested in the effect of *small changes* in the temperature on the equilibrium constant. We could, of course, use equation (5.1) to calculate K at two different temperatures for any reaction which satisfies the requirements given above and determine the change in K by subtraction. However, in practice, a much more convenient route makes use of the properties of differentials. This chapter is concerned with exploring what effect small changes in one or more independent variables have on the dependent variable in expressions such as equation (5.1). We shall see that this is particularly useful in determining how errors propagate through expressions relating one property to another. However, before discussing further the importance of differentials in a chemical context, we need to discuss some of the background to the method of differentials.

Aims

By the end of this chapter you should be able to:

- Understand the definition of change defined by the differential and the concept of infinitesimal change
- Understand the difference between the differential dy representing an approximate change in the dependent variable resulting from a small change in the independent variable, and the actual change in the dependent variable, Δy
- Calculate the differentials and the errors in approximating the differential to the actual change in a dependent variable
- Define the differential of a function of more than one variable
- Use differentials to calculate relative and percentage errors in one property deriving from those in other properties

5.1 The Effects of Incremental Change

We recall from Chapter 4 (Figure 4.1) that if Δy is the change in y that accompanies an *incremental* change Δx in x, then:

$$\Delta y = f(x + \Delta x) - f(x) \tag{5.2}$$

For example, if we consider the function $y = f(x) = x^3$, the incremental change in y that accompanies a change in Δx in x is given as:

$$\Delta y = (x + \Delta x)^3 - x^3$$

which, on expanding, yields:

$$\Delta y = 3x^2\Delta x + 3x(\Delta x)^2 + (\Delta x)^3$$

For sufficiently small values of Δx, the power terms in Δx decrease very rapidly in magnitude. Thus, for example, if $\Delta x = 10^{-2}$, then $\Delta x^2 = 10^{-4}$ and $\Delta x^3 = 10^{-6}$. This may be expressed algebraically as:

$$(\Delta x)^3 << (\Delta x)^2 << \Delta x$$

and, if we neglect Δx raised to power 2 or higher, we can approximate the expression for Δy by:

$$\Delta y \approx 3x^2\Delta x$$

The appearance of $3x^2$ in this expression is no accident. If we rewrite the expression for Δy as:

$$\Delta y = \left(\frac{f(x + \Delta x) - f(x)}{\Delta x}\right) \times \Delta x \tag{5.3}$$

then it is clear that, for very small Δx, the term in parentheses is an approximation for the derivative of $f(x)$, which, for the present choice of function, is $3x^2$. We can therefore rewrite the general result in the form $\Delta y \approx f'(x)\Delta x$.

5.1.1 The Concept of Infinitesimal Change

An **infinitesimal** change in x, known as the **differential** dx, gives rise to a corresponding change in y that is well represented by the differential dy:

$$dy = f'(x)dx \tag{5.4}$$

The concept of an infinitesimal change is not soundly based mathematically: we interpret such changes as being very, very small (non-zero) increments in the specified variable.

We can see from the defining equation (5.4), and from Figure 5.1, that $f'(x)$ is the slope of the tangent to the curve $y = f(x)$ at the point P. We can also see that dy represents the change in the dependent variable y that results from a change, Δx, in x, as we move along the tangent to the curve at point P. It is important to stress that, although dy is *not* the same as Δy, for small enough changes in x it is reasonable to assume that the two are equivalent. Consequently, the difference between Δy and dy is simply the error in approximating Δy to dy. However, the same is not true of the differential dx, because, at all times, $\Delta x = dx$.

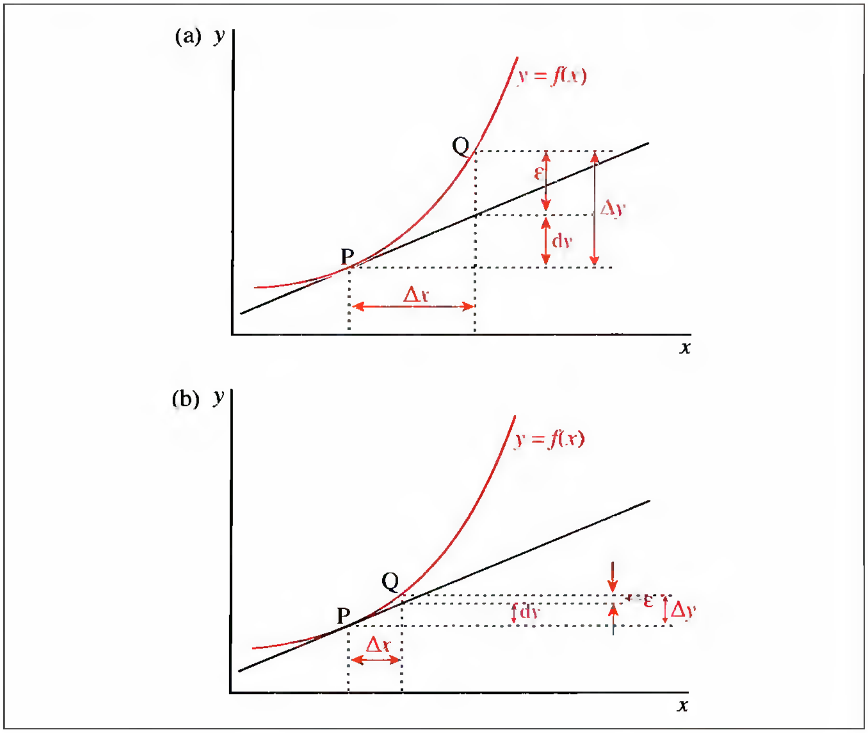

Figure 5.1 (a) The differential dy, for a change Δx in x, for the function $y = f(x)$. The actual change in y is given by $\Delta y = dy + \varepsilon$, where ε is the difference between Δy and dy. (b) As $\Delta x \to 0$, the error ε gets proportionately smaller and Δy becomes increasingly well approximated by dy.

The Origins of the Infinitesimal

The concept of the infinitesimal first arose in 1630 in Fermat's "Method of Finding Maxima & Minima". This work marks the beginning of differential calculus. The ideas introduced by Fermat lead to speculation about how we can evaluate "*just*" *before* or "*just*" *after*. In the 17th century, the infinitesimal was known as the "disappearing" and tangents as "touchings". Leibniz thought them "*useless fictions*", but they were subsequently recognized as being capable of producing extraordinary results. The philosopher Berkeley attacked differentials as "*neither finite quantities, nor quantities infinitely small, not yet nothing. May we not call them the ghosts of departed quantities*". Today, Borowski and Borwein in their Dictionary of Mathematics[1] regard an infinitesimal as "*a paradoxical conception* ··· *largely abandoned in favour of the epsilon-delta treatment of limits,* ··· *but made their reappearance in the formulation of hyper-real numbers*"!

5.1.2 Differentials in Action

The use of the differential is important in the physical sciences because fundamental theorems are sometimes expressed in differential form. In chemistry, for example, the laws of thermodynamics are nearly always expressed in terms of differentials. For example, it is common to work with the following formula as a means of expressing how the molar specific heat capacity at constant pressure, C_p, of a substance varies with temperature, T:

$$C_p = g(T) \text{ where } g(T) = \alpha + \beta T + \gamma T^2 \tag{5.5}$$

The optimum values of the parameters α, β, γ are found by fitting measured values of C_p over a range of temperatures to equation (5.5). Thus, if we know the value of C_p at one temperature, we can evaluate it at another temperature, and thereby determine the effect of that incremental (or decremental) change in temperature, ΔT, upon C_p, given by ΔC_p. Alternatively, we can use the properties of differentials given in equation (5.4) to evaluate the differential of C_p, dC_p, in terms of the differential dT as:

$$dC_p = g'(T)dT = (\beta + 2\gamma T) \times dT \tag{5.6}$$

The parameters in an expression such as equation (5.5) allow the expression to be tailored to fit experiment to some reasonable accuracy.

For small enough changes in T, it is reasonable to make the approximation that the differential dC_p is equivalent to the actual change ΔC_p, and we can use the expression above as a simple one-step route to evaluating the effect of small changes in T upon C_p.

Worked Problem 5.1

Q (a) Find dy and Δy for the function $y = f(x)$, where $f(x) = x^3$, given that $x = 4$ and $\Delta x = -0.1$. (b) Give the approximate and exact values of y at the point $x = 3.9$. (c) Calculate the percentage error in your approximate value from (b).

A (a) $f'(x) = 3x^2 \Rightarrow f'(4) = 48$. It follows that $dy = f'(4)\Delta x = 48 \times -0.1 = -4.8$. The actual change in y is given by $\Delta y = f(3.9) - f(4) = -4.681$.
(b) The actual and approximate values of y at $x = 3.9$ are 59.319 and 59.2, respectively.
(c) The percentage error is given by

$$\frac{59.319 - 59.2}{59.319} \times 100 = 0.201\%.$$

Sometimes, Δy will be smaller than dy, as in Worked Problem 5.1, but sometimes it can be larger: examples include functions whose slope decreases with increasing values of the independent variable, such as $y = f(x) = \ln x$ and $y = \sqrt[n]{x}$ where $n > 1$.

Problem 5.1

For the function $y = x^{1/3}$, find the values of the differential, dy, and the actual change, Δy, when the value of x is increased (a) from 27 to 30 and (b) from 27 to 27.1. Give the percentage error in each case in approximating Δy by dy.

Problem 5.2[2]

The variation of the molar heat capacity at constant pressure for $CH_4(g)$ is described by equation (5.5), with $\alpha = 14.143$ J K^{-1} mol^{-1}, $\beta = 75.495 \times 10^{-3}$ J K^{-2} mol^{-1} and $\gamma = -179.64 \times 10^{-7}$ J K^{-3} mol^{-1}.
(a) Use equation (5.5) to calculate the value of C_p at $T = 500$ K and at $T = 650$ K.
(b) Use equation (5.6) to evaluate dC_p for an incremental change in T, dT, of 150 K at $T = 500$ K. Hence, estimate the value of C_p at $T = 650$ K.
(c) Compare the value for C_p obtained in (b) with the value calculated directly from equation (5.5).

5.2 The Differential of a Function of Two or More Variables

We have seen in equation (5.4) that the differentials dy and dx are related through the derivative d$y = f'(x)$dx, which we can rewrite as:

$$\mathrm{d}y = \frac{\mathrm{d}y}{\mathrm{d}x}\mathrm{d}x \qquad (5.7)$$

We can now extend this principle to define differentials for functions of two or more variables. If $z = f(x, t)$ is a general function of two independent variables x and t, then there are two contributions to the differential dz: one from the change in x and the other from the change in t:

$$\mathrm{d}z = \frac{\partial z}{\partial x}\mathrm{d}x + \frac{\partial z}{\partial t}\mathrm{d}t \qquad (5.8)$$

This result extends readily to functions of n independent variables x_1, x_2, x_3,..., x_n. Thus, if $z = f(x_1, x_2, x_3,..., x_n)$, the differential of z is built up from contributions associated with each independent variable, as a straightforward generalization of the result for two independent variables:

$$\mathrm{d}z = \frac{\partial z}{\partial x_1}\mathrm{d}x_1 + \frac{\partial z}{\partial x_2}\mathrm{d}x_2 + ... + \frac{\partial z}{\partial x_n}\mathrm{d}x_n = \sum_{i=1}^{n}\frac{\partial z}{\partial x_i}\mathrm{d}x_i \qquad (5.9)$$

Examples of functions of two or more variables expressed in differential form are common in thermodynamics. For example, the equation:

$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S$$

relates the consequence of very small changes in the enthalpy, H, and entropy, S, on the Gibbs energy, G (here, G is the dependent variable, and H and S are the independent variables). As we shall see below, the use of differentials helps us to study such effects, if the changes are small. However, for large changes in the defining variables we have to evaluate the overall change in the property with the aid of *integral calculus*, which we meet in Chapters 6 and 7.

Worked Problem 5.2

Q Given the function $z = x^2y + y^2x - 2x + 3$, express dz in terms of dx and dy.

A $\mathrm{d}z = \frac{\partial z}{\partial x}\mathrm{d}x + \frac{\partial z}{\partial y}\mathrm{d}y = (2xy + y^2 - 2)\mathrm{d}x + (x^2 + 2xy)\mathrm{d}y.$

Problem 5.3

If $z = xy/2$, express dz in terms of the differentials of the three independent variables.

Problem 5.4

(a) For a non-reacting system, the internal energy, $U = f(V, T)$, is a function of both V and T. By analogy with equation (5.8), write down an expression for the differential dU in terms of the differentials dV and dT.

(b) In thermodynamics, the expression derived in part (a) is commonly written as:[3]

$$dU = \pi_T dV + C_V dT$$

where π_T and C_V are the internal pressure and specific heat capacity at constant volume. (i) Use your answer to part (a) to find expressions for the internal pressure, π_T, and C_V. (ii) Assuming that $\Delta U \approx \mathrm{d}U$, calculate the change in U that results when a sample of ammonia is heated from 300 K to 302 K and compressed through 100 cm^3, given that $C_V = 27.32$ J K^{-1} and $\pi_T = 840$ J m^{-3} at 300 K. Comment on the relative magnitudes of the two contributions to dU.

5.3 The Propagation of Errors

In many chemical situations we deduce a value for a property of interest by placing experimentally measured values in the right-hand side of an appropriate formula. For example, if we use the ideal gas equation:

$$p = n\frac{RT}{V} \tag{5.10}$$

to calculate the pressure, p, from a knowledge of volume, temperature, amount of substance and the gas constant, R, we might wish to know how the errors in the measured property values (n, T, V) propagate through to errors in the calculation of the pressure, p. If, for simplicity, we assume that n and R are fixed (given) constants, how can we estimate the error, dp, in p that results from errors, dT and dV, in the measurement of T and V, respectively? The answer lies in using equation (5.8) to obtain dp in terms of dV and dT:

$$\mathrm{d}P = \frac{\partial P}{\partial T}\mathrm{d}T + \frac{\partial P}{\partial V}\mathrm{d}V \tag{5.11}$$

If dV and dT are the estimated errors in the measured values of V and T, then we need to know the two partial derivatives, so that we can estimate the error dp in P. However, in this and other instances the differentials themselves do not provide realistic measure of the errors. For example, an absolute error of 10 cm in a measured length is insignificant if we are talking about the shortest distance from Berlin to Moscow, but highly significant if a furniture van driver has enough clearance to pass under a low bridge in a country lane. For this reason, the **relative error**, or the closely related **percentage error**, give much more useful measures of error than absolute errors. Thus, in the context of the ideal gas example, the two kinds of error are defined as follows:

- The relative error in p is given by $\frac{dp}{p}$.
- The percentage error in p is given by $\frac{dp}{p} \times 100$.

Worked Problem 5.3

Q For a right-angled triangle with adjacent sides a, b and hypotenuse c, we have the relation $c = (a^2 + b^2)^{1/2}$. Find the relative and percentage errors in c when $a = 3$ cm, $b = 4$ cm, $da = 0.1$ cm and $db = 0.1$ cm.

Note that we have taken the product of the partial derivatives, $\frac{\partial u}{\partial a}$ and $\frac{\partial u}{\partial b}$, with the derivative $\frac{dc}{du}$. This is perfectly legitimate because $\frac{dc}{du} \equiv \frac{\partial c}{\partial u}$ in the context of the original expression involving two independent variables.

A Using the chain rule, with the substitution $u = a^2 + b^2$, we initially define the partial derivatives of u with respect to a and b, respectively:

$$\frac{\partial u}{\partial a} = 2a; \quad \frac{\partial u}{\partial b} = 2b$$

Differentiating c with respect to the *single* variable, u, gives:

$$\frac{dc}{du} = \frac{1}{2}u^{-1/2}$$

Finally, we use the chain rule to obtain the partial derivatives of c with respect to a and b:

$$\frac{\partial c}{\partial a} = \frac{\partial u}{\partial a} \times \frac{dc}{du} = 2a \times \frac{1}{2}u^{-1/2} = 2a \times \frac{1}{2}(a^2 + b^2)^{-1/2} = a(a^2 + b^2)^{-1/2}$$

$$\frac{\partial c}{\partial b} = \frac{\partial u}{\partial b} \times \frac{dc}{du} = 2b \times \frac{1}{2}u^{-1/2} = 2b \times \frac{1}{2}(a^2 + b^2)^{-1/2} = b(a^2 + b^2)^{-1/2}$$

The differential dc is then given by:

$$dc = \frac{\partial c}{\partial a}da + \frac{\partial c}{\partial b}db = a(a^2 + b^2)^{-1/2}da + b(a^2 + b^2)^{-1/2}db$$

and so:

$$dc = 3(9+16)^{-1/2} \times 0.1 + 4(9+16)^{-1/2} \times 0.1 = 0.06 + 0.08$$
$$= 0.14 \text{ cm}$$

Thus the relative error

$$\frac{dc}{c} = \frac{0.14}{5} = 0.028$$

and the percentage error

$$\frac{dc}{c} \times 100 = 2.8\%.$$

Problem 5.5

The volume, V, of an orthorhombic unit cell with edges of length a, b and c and all internal angles between vertices of 90° is given by $V = abc$.

(a) Find the approximate change in volume, dV, when a, b and c change by da, db and dc, respectively.

(b) Give an expression for the percentage error in V, in terms of the percentage errors in a, b and c.

Problem 5.6

Calcium carbonate crystallizes in several different forms. In aragonite[4] there are four formula units in an orthorhombic primitive unit cell with dimensions $a = 4.94 \times 10^{-10}$ m, $b = 7.94 \times 10^{-10}$ m and $c = 5.72 \times 10^{-10}$ m.

(a) Calculate the mass, M, of a unit cell in kg, using molar atomic masses as follows:
Ca = 40.08 g mol^{-1}; C = 12.01 g mol^{-1}; O = 16.00 g mol^{-1} ($N_A = 6.022 \times 10^{23}$ mol^{-1}).

(b) Calculate the volume, V, of the unit cell, using the values of a, b and c above, and hence determine the density, ρ, of aragonite, using the formula $\rho = M/V$.

(c) Since the values of the unit cell parameters have been given to two decimal places, the error in their values is $\pm 0.005 \times 10^{-10}$ m. Ignoring the effects of the analogous errors associated with the masses of the atoms, give the relative and percentage errors in the volume of the unit cell.

(d) Find the greatest and smallest estimated unit cell volumes, and give the corresponding greatest and smallest estimates of the density (again ignoring errors associated with the relative atomic masses). Using the value of the density calculated in part (b), find the percentage errors and compare your answers to part (c).

Summary of Key Points

Differentials provide a means to quantify the effect of small changes in one or more variables upon a property that depends on those variables. The key points discussed include:

1. An illustration of the use of differentials in the mathematical and chemical context: in particular, many of the fundamental laws of thermodynamics are expressed in terms of differentials.

2. A review of the concept of infinitesimal change, and its relevance in chemistry, in view of the links to the concept of reversability in thermodynamics.

3. The distinction between approximate and exact changes in the dependent variable, resulting from changes in one or more independent variables.

4. The use of differentials in assessing how errors in one or more properties of a system propagate through to errors in a property that is related to those properties.

5. How differentials associated with each variable in a function of two or more variables contribute to the differential associated with the dependent variable.

References

1. E. J. Borowski and J. M. Borwein, *Collins Dictionary of Mathematics*, Harper Collins, New York, 1989, p. 294.
2. The data for Problem 5.2 were taken from R. A. Alberty and R. J. Silbey, *Physical Chemistry*, Wiley, New York, 1992, p. 52.
3. See, for example, P. W. Atkins, *Physical Chemistry*, 5th edn., Oxford University Press, Oxford, 1994, p. 98.
4. See H. D. Megaw, *Crystal Structures: A Working Approach*, Saunders, Philadelphia, 1973, p. 247.

6 Integration

In the earlier chapters on arithmetic, algebra and functions, we saw examples of actions for which there was another action available to reverse the first action: such a reversing action is called an **inverse**. Some examples of mathematical actions and their inverses are listed below:

Start	*→ Action*	*→ Result*	*→ Inverse action*	*→ Result*
2	Add 3	5	Subtract 3	2
x^2	Subtract $2x$	$x^2 - 2x$	Add $2x$	x^2
$(x - 1)$	Multiply by x^3	$(x - 1)x^3$	Divide by x^3	$(x - 1)$
x	Logarithm	$\ln x$	Exponential $\exp(\ln x)$	x
$x^3 - x^2+1$	Differentiate	$3x^2 - 2x$	Integrate	$x^3 - x^2+C$

Division by x^3 requires that $x \neq 0$.

The final example listed above proposes that the inverse to the operation of differentiation is known as **integration**. The field of mathematics which deals with integration is known as integral calculus and, in common with differential calculus, plays a vital role in underpinning many key areas of chemistry.

A differentiation/integration cycle involving a chosen initial function will lead to the appearance of an unspecified constant, C (as we shall see later on).

Aims

In this chapter we define and discuss integration from two perspectives: one in which integration acts as the inverse, or reverse, of differentiation and the other in which integration provides a means to finding the area under a curve. By the end of the chapter you should be able to:

- Understand the concept of integration as the reverse of differentiation
- Find the indefinite integral of a number of simple functions from first principles

- Integrate standard functions by rule
- Understand why the results of integration are not unique, unless constraints are placed on the integrated function
- Apply the integration by parts and substitution methods to integrate more complicated functions
- Understand the concept of the definite integral and be able evaluate a wide range of definite integrals using the methods discussed above

6.1 Reversing the Effects of Differentiation

Integration is used frequently in kinetics, thermodynamics, quantum mechanics and other areas of chemistry, where we build models based on changing quantities. Thus, if we know the rate of change of a property, y (the dependent variable), with respect to x (the independent variable), in the form of $\mathrm{d}y/\mathrm{d}x$, then integral calculus provides us with the tools for obtaining the form of y as a function of x. We see that integration reverses the effects of differentiation.

Consider, for example, a car undergoing a journey with an initial speed u and moving with a constant acceleration a. The speed, v, and distance, s, travelled after time t are given by:

$$v = u + at \text{ and } s = ut + \frac{1}{2}at^2 \tag{6.1}$$

The rate of change of distance with time yields the speed, v at time, t:

$$\frac{\mathrm{d}s}{\mathrm{d}t} = u + at = v \tag{6.2}$$

However, the reverse process, in going from speed to distance, involves integration of the **rate equation** (6.2). In chemistry, the concept of rate is central to an understanding of chemical kinetics, in which we have to deal with analogous rate equations which typically involve the rate of change of concentration, rather than the rate of change of distance. For example, in a first-order chemical reaction, where the rate of loss of the reactant is proportional to the concentration of the reactant, the rate equation takes the form:

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}] \tag{6.3}$$

where k, the constant of proportionality, is defined as the rate constant. The concentration of the reactant at a given time is found by integrating the rate equation (6.3), and the relationship between the differentiated and integrated forms of the rate equation is given schematically by:

$$-\frac{d[A]}{dt} = k[A]$$

differentiate ↑ ↓ *integrate*

$$[A] = [A]_0 e^{-kt}$$

where $[A]_0$ is the initial concentration of reactant A. We will discuss the integration methods required for obtaining the solution of this type of problem in some detail when we discuss differential equations in Chapter 7.

6.2 The Definite Integral

6.2.1 Finding the Area Under a Curve: The Origin of Integral Calculus

The concept of integration emerges when we attempt to determine the area bounded by a plot of a function $f(x)$ (where $f(x) > 0$) and the x axis, within an **interval** $x = a$ to $x = b$ (written alternatively as $[a,b]$). Clearly, if the plot gives a straight line, such as for the functions $y = 4$ or $y = 2x + 3$, shown in Figure 6.1, then measuring the area is straightforward, as the two areas are rectangular and trapezoidal in shape, respectively. However, for areas bounded by a curve and three straight lines, the problem is more difficult. The three situations are shown in Figure 6.1.

The area of a trapezium is given by half the sum of the parallel sides, multiplied by the distance between them.

The solution to the general problem of determining the area under a curve arises directly from differential calculus, the concept of limits, and the infinitesimal. Seventeenth century mathematicians began to think of the area, not as a whole, but as made up of a series of rectangles, of width Δx, placed side by side, and which, together, cover the interval $[a,b]$ (see Figure 6.2).

With this construction, there are two ways of estimating the area under the curve. First, the interval $[a,b]$ is divided into n subintervals of width $\Delta x = (b - a)/n$. The area of each rectangle is obtained by multiplying its width, Δx, by its height on the left vertical side, as shown in Figure 6.3a.

In this case, the total area is given by:

$$A_1(n) = f(a)\Delta x + f(a + \Delta x)\Delta x + f(a + 2\Delta x)\Delta x + \ldots$$

$$\ldots + f(a + [n - 1]\Delta x)\Delta x = \sum_{k=0}^{n-1} f(a + k\Delta x)\Delta x \qquad (6.4)$$

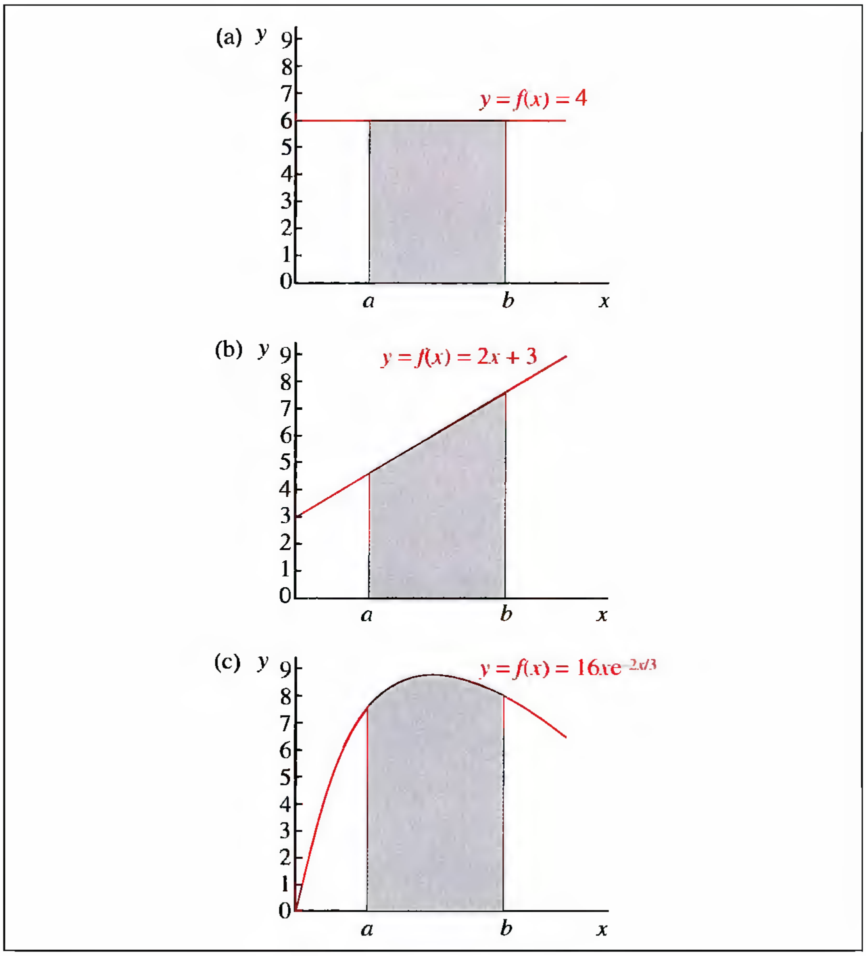

Figure 6.1 Plots of the three functions (a) $y = 4$, (b) $y = 2x + 3$ and (c) $y = 16xe^{-2x/3}$. Evaluating the area bound by the straight line functions and the x-axis in the interval $x = a$ to $x = b$ in (a) and (b) is straightforward but, in (c), where the plot is a curve, we need to make use of the definite integral

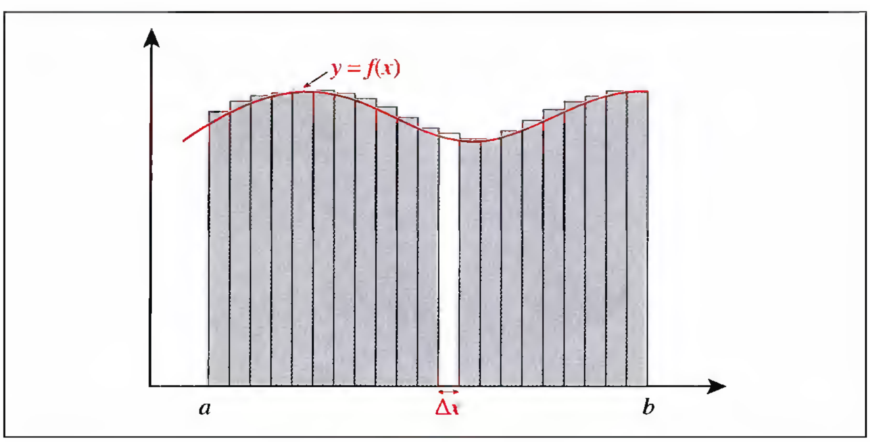

Figure 6.2 Approximating the area under a curve by a contiguous sequence of rectangles of width Δx