Mathematics for Chemists

MATHEMATICS FOR CHEMISTS

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Preface

A sound knowledge of the elementary aspects of many areas of mathematics is indispensible to the study of the quantitative aspects of chemistry. This book presents the mathematics required for the study of chemistry to honours degree level in British universities and polytechnics. The material presented should also be suitable for chemistry majors and first-year graduate students in North American universities. It has evolved from a course of lectures given over the past ten years to first-year students in Molecular and Biological Sciences at the University of Warwick.

Students of chemistry have, in general, a more limited mathematical background than physics or engineering students. This book does not assume that the student has followed an A-level or other post-O-level course in mathematics. Therefore the calculus is developed from first principles. The approach is descriptive rather than formal in that the emphasis is on the application of mathematical techniques rather than on the proving of theorems. Some results are quoted without proof where the derivation is more confusing than illuminating.

Wherever possible, mathematical techniques and ideas have been illustrated with chemical examples. It has often been necessary to present applications without explaining the underlying theory; for a full explanation the reader should consult texts on physical or quantum chemistry such as those included in the bibliography.

The material presented here should prepare the student for the study of quantum mechanics and group theory. A chapter on group theory has not been included because it was felt that the topic could not be adequately covered in one chapter and because many excellent texts on group theory in chemistry are available.

Numerical and statistical methods are becoming increasingly important in the analysis of experimental data. Introductory chapters on these topics have been included to give the student some background before he consults more complete treatments of these subjects.

Several problems, indicated by '(U.W.)', have appeared in University of Warwick examinations. The copyright for these problems is vested in the University of Warwick and the author is grateful for permission to reproduce them here.

The author is grateful to Dr S. P. Liebmann who read much of the manuscript and to Mr M. S. Hunt and Professor P. J. Harrison for reading chapters 13 and 14, respectively.

March 1975

D. M. Hirst

1

Review of Basic Material—Functions, Inequalities

1.1 FUNCTIONS

The concept of a function is probably familiar to you, but since this is fundamental to the material to be presented in this book, it is important that we review the definition.

When we say that *y is a function of x*, we mean that if we take some particular value of x, say x_1, we can find a corresponding value y_1 of y. Thus a function is a rule for associating a number y_1 with each number x_1.

$$x_1 \rightarrow y_1 \tag{1.1}$$

For example, if

$$y = 2x^2 + x + 1 \tag{1.2}$$

then for x = 1, y = 4 and for x = 2, y = 11. This relation gives us a method for associating a value y with each value of x.

x is the *independent variable* because we select a value of x and then associate with it a value of y, the *dependent variable*. In general, we write y = f(x), which means 'y is a function of x' or y = y(x). x is sometimes called the *argument*.

We use a function whenever we express some physical phenomenon in a quantitative manner. For example, when a substance A decays by first-order kinetics, the concentration a at time t is given by

$$a = a_0 e^{-kt} \tag{1.3}$$

where a_0 is the initial concentration and k is a constant.

1.1.1 Graphical representation of functions

A convenient representation of a function is a *graph*, in which we conventionally have right-angled *cartesian co-ordinates* labelled the x-axis (horizontal) and the y-axis (vertical). The x-axis is sometimes called the *abscissa* and the y-axis the *ordinate*. The axes intersect at the origin O. Values of y, y_i are calculated for a series of values of x, x_i and each

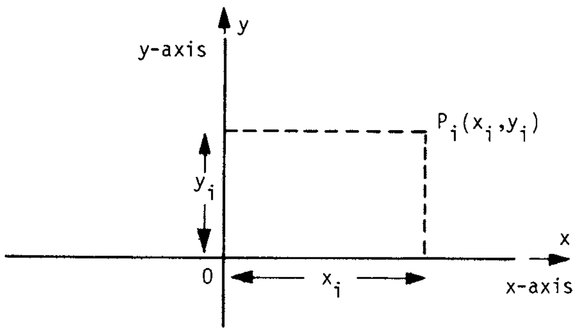

Figure 1.1

pair of values is represented by a point P_i on the graph (figure 1.1). x_i and y_i are known as the *co-ordinates* of the point P_i and are usually written as (x_i, y_i). The points P_i are then joined up to give a smooth curve. Clearly, the more points we plot, the more accurate will be the representation of the function.

1.1.2 Types of function

(i) The linear function

The simplest type of function is the linear function

$$y = mx + b \tag{1.4}$$

whose graph is a straight line (figure 1.2). The *intercept* on the y-axis is the value of y when x is equal to zero and is equal to b. Another important concept is the *slope* of a line. If we take two points on the line with co-ordinates (x_1, y_1) and (x_2, y_2), the slope of the line is defined by

$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1} \tag{1.5}$$

and is, in fact, equal to the tangent of the angle θ between the line and the x-axis. It clearly doesn't matter where the points (x_1, y_1) and (x_2, y_2) are on the line. The slope of the straight line $y = mx + b$ is given by

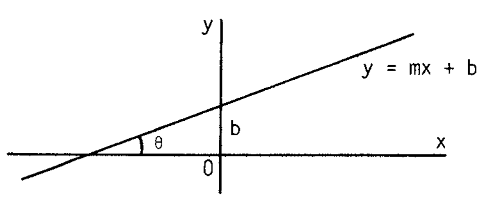

Figure 1.2

$$\text{slope} = \frac{(mx_2 + b) - (mx_1 + b)}{x_2 - x_1} = m \qquad (1.6)$$

Thus for $y = mx + b$, m is the slope and b is the intercept on the y-axis.

Linear graphs are very important in the analysis of chemical data because they are characterised by the two parameters b and m. Also it is easy to see if a set of points lies on a straight line, whereas it is much more difficult to decide if a set of points corresponds to a particular curve. Wherever possible we try to convert a function to a linear form if we wish to draw a graph. For example, the variation of equilibrium constant K with temperature T is given by

$$\ln K = -\frac{\Delta H^o}{RT} + C \qquad (1.7)$$

provided that ΔH^o, the heat of reaction, is independent of T. R is the gas constant and C is a constant. Plotting K against T would give a curve that would be difficult to analyse. However, if we plot the logarithm of K, ln K, against 1/T, we get a straight line of slope $\Delta H^o/R$ from which ΔH^o can be obtained.

(ii) Quadratic function

A *quadratic function* has the general form

$$y = ax^2 + bx + c \qquad (1.8)$$

and its graph is a *parabola* (figure 1.3). We shall define the slope of a curve in the next chapter. If there are real values of x for which $ax^2 + bx + c = 0$, the curve will intersect the x-axis at the values of x given by the formula

$$x = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a} \qquad (1.9)$$

(iii) Single-valued functions

In the two examples above, there is only one value of y_1 for each value of x_1 and we say that the functions are *single valued*. This concept is important in quantum mechanics because wavefunctions are required to be single valued.

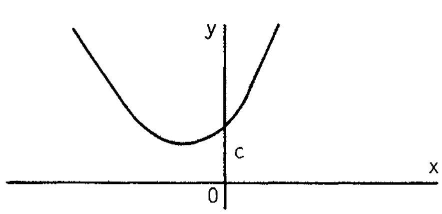

Figure 1.3

(iv) Many-valued functions

If we can associate several values of y with one value of x, then the function is *many valued*. An example of this is $y^2 = x$ for which there are two values of y, $+\sqrt{x_1}$ and $-\sqrt{x_1}$ for each value of x_1.

(v) Regions for which a function is undefined

So far we have assumed that the independent variable x can take any value. However, if we consider $y^2 = x_1$, we see that x can only have positive values or be zero. For the function

$$y = \frac{x}{\sqrt{(x^2 - 16)}} \tag{1.10}$$

x is restricted to being larger than 4 or smaller than −4, as otherwise we would have the square root of a negative number. We must also exclude x = ±4 for which y is infinite. If a function is only defined for a certain range of values of x, this should be specified; for example

$$y = \frac{x}{\sqrt{(x^2 - 16)}} \qquad x < -4 \text{ or } >4 \tag{1.11}$$

(vi) Functions of many variables

In chemistry a quantity frequently depends on two or more variables. For example, the pressure P of a gas depends on the volume V, the temperature T and the number of moles n. For an ideal gas

$$P = \frac{nRT}{V} \tag{1.12}$$

where R is the gas constant. In order to define P, we need values of V, T and n.

(vii) A polynomial

A function such as

$$f(x) = a_0 + a_1x + a_2x^2 + \ldots + a_nx^n = \sum_{i=0}^{n} a_ix^i \tag{1.13}$$

is known as a *polynomial of degree n*. Such a function is defined for all values of x and is finite if x is finite.

(viii) Implicit functions

We can rewrite equation 1.12 in the form

$$V = \frac{nRT}{P} \tag{1.14}$$

that is, we can write V as an *explicit function* of n, T and P. We cannot always do this, as, for example, in the case of the van der Waals equation of state

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{1.15}$$

If, in this case, we wish to regard V as a function of P, T and n, then V is an *implicit function* of these variables.

(ix) Even and odd functions

A useful classification of functions is into even and odd functions. An *even function* of x is one that remains unchanged when the sign of x is reversed; that is

$$f(-x) = f(x) \tag{1.16}$$

whereas an *odd function* changes sign

$$f(-x) = -f(x) \tag{1.17}$$

Examples of even functions are $y = x^2$, $y = \cos x$ (see section 1.1.3) and these functions are symmetrical about the y-axis (figure 1.4a). $y = x$ and $y = \sin x$ are odd functions and are not symmetrical about the y-axis (figure 1.4b).

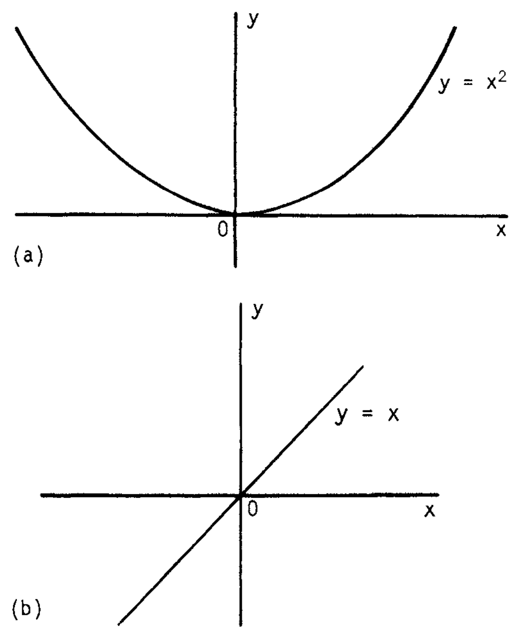

Figure 1.4

(x) Transcendental functions

Certain functions such as trigonometric, exponential and logarithmic functions cannot be expressed *exactly* in terms of algebraic functions. They are called *transcendental functions*. We discuss them in more detail in the following sections.

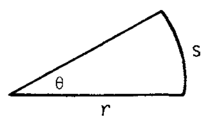

Figure 1.5

1.1.3 Trigonometric functions

We shall review briefly some basic ideas about trigonometric functions. We shall use the *radian* as a measure of angle. If an angle θ subtends a length of arc s of radius r, the angle θ in radians is given by (figure 1.5)

$$\theta = \frac{s}{r} \tag{1.18}$$

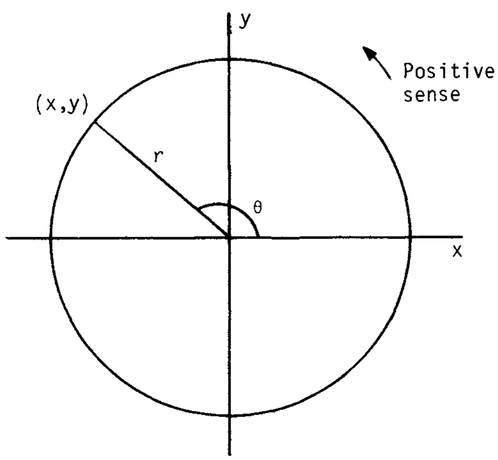

Figure 1.6

Clearly 360° is equivalent to 2π radians and the conversion factor from degrees to radians is $\pi/180$. If we can define an angle in a positive sense as in figure 1.6, the three basic trigonometric functions, sine (sin), cosine (cos) and tangent (tan) are defined by

$$\sin\theta = \frac{y}{r}; \qquad \cos\theta = \frac{x}{r}; \qquad \tan\theta = \frac{y}{x} \tag{1.19}$$

These functions will have different signs in different

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