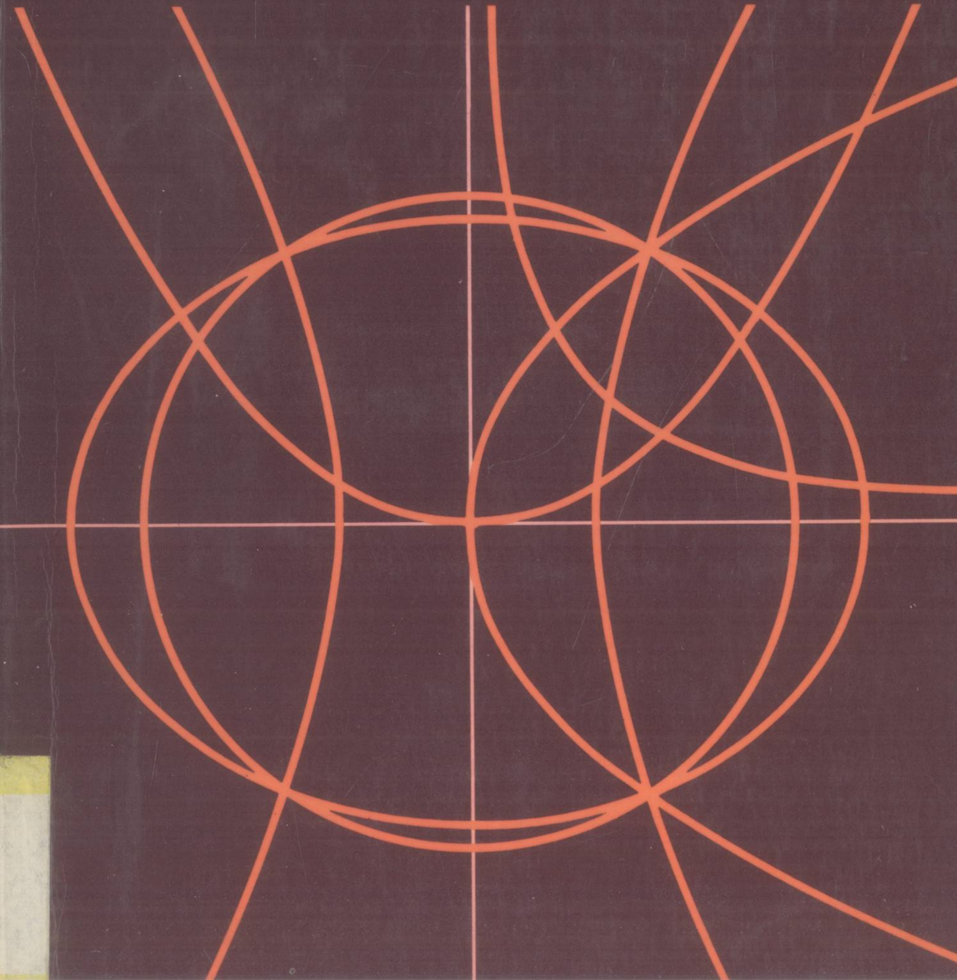
Mathematics for Chemists

P.G. FRANCIS



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Preface

This text is concerned with those aspects of mathematics that are necessary for first-degree students of chemistry. It is written from the point of view that an element of mathematical rigour is essential for a proper appreciation of the scope and limitations of mathematical methods, and that the connection between physical principles and their mathematical formulation requires at least as much study as the mathematical principles themselves. It is written with chemistry students particularly in mind because that subject provides a point of view that differs in some respects from that of students of other scientific disciplines. Chemists in particular need insight into three-dimensional geometry and an appreciation of problems involving many variables. It is also a subject that draws particular benefit from having available two rigorous disciplines, those of mathematics and of thermodynamics. The benefit of rigour is that it provides a degree of certainty which is valuable in a subject of such complexity as is provided by the behaviour of real chemical systems. As an experimental science, we attempt in chemistry to understand and to predict behaviour by combining precise experimental measurement with such rigorous theory as may be at the time available; these seldom provide a complete picture but do enable areas of uncertainty to be identified. Mathematical rigour has been provided for us by generations of professional mathematicians, who continue to give support and advice both in the application of established techniques and in the development of new approaches. Experimental scientists have added to this a rigour of a different kind, which is based upon a small number of premises, or axioms, deduced from seemingly disconnected experimental observations. These provide the experimental laws of thermodynamics and quantum theory whose justification lies in the absence of disagreement with experiment. When these are expressed in mathematical terms we can add mathematical rigour to produce theoretical structures in which only the basic premises, often corresponding to a simplified physical model, leave room for uncertainty. These

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considerations are reflected in this text by frequent reference to physical principles, by the inclusion of a number of mathematical proofs and by the inclusion of a discussion of the treatment of experimental data.

It is assumed that the reader has previous mathematical knowledge extending to the elementary applications of calculus. The subject matter is developed during each chapter, so that an initial reading of only the earlier sections in each chapter is possible. The later sections contain brief outlines of the principles and scope of more advanced techniques and are intended to point the way to more specialized texts.

The examples are, in the main, given with their solutions; this is in order that the text may be used as a reference source, for which purpose worked examples are more valuable than exercises. Readers are strongly recommended to attempt their own solutions to these examples before consulting the one that is given.

A proper acknowledgement of the many sources from which the author has drawn cannot be justly be made for a text in which the material was largely developed during the last two- or three-hundred years. It is a subject on which many admirable texts have been written, the only justification for adding to their number being changes in emphasis.

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CHAPTER 1

Algebraic and geometrical methods

1.1 Natural numbers

Quantitative measurements in science are usually made in terms of appropriate, but arbitrary, units (Section 1.2), so that the numerical values obtained depend on the size of the units and are not significant in themselves. Only when there is a natural unit, such as the gas constant R, do numerical values assume absolute significance; for example, the heat capacity at constant volume of an ideal monatomic gas at a high enough temperature is $3R/2$, where the number 3 corresponds to the three degrees of freedom of the particles.

There are some pure numbers, however, that arise naturally, the ones most commonly met in science being π and e. These can be regarded as the mathematical equivalent of natural units and occur so often in scientific formulae and equations that we consider how they originate.

Our first natural number, π, could be defined as the ratio of circumference to diameter for a circle. This ratio is a pure number that is independent of the size of the circle, and it is also used as the natural measure of angle. The definition of angle is

$$\text{angle} = (\text{length of arc})/\text{radius}, \tag{1.1a}$$

and for a given angle, this has a numerical value that is independent of any conventional scale of measurement. The circumference of a complete circle of radius r being $2\pi r$, the angle corresponding to a full rotation is $2\pi r/r = 2\pi$ natural units of angle, this unit being called the radian. We also have the conventional definition of such a full rotation

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as 360 degrees (360°), so that

$$\pi \text{ radian} = 180°.$$

The definition of angle in two dimensions as (arc length)/radius can be extended into three dimensions; if we take a conical segment from a sphere we can define a three-dimensional solid angle as

$$\text{solid angle} = (\text{area of segment of spherical surface})/(\text{radius})^2. \tag{1.1b}$$

For a complete sphere of surface area $4\pi r^2$,

$$\text{complete solid angle} = 4\pi r^2/r^2 = 4\pi,$$

and since this expression does not contain r it is also a pure number that is independent of the size of the sphere. The unit of solid angle is called a steradian. It is a useful geometrical concept that (area)/(radius)^2 is constant for a given solid angle, and this is used in Section 5.7.

Our second natural number, e, arises in a different way. It is useful to divide the mathematical methods used in science into two categories, geometrical methods and analytical methods. The above definition of π is geometrical and belongs in the field of diagrams and models. The second category is algebraic and numerical, and does not depend on our ability to construct models and diagrams. Analytical methods are developed by strictly logical deductions from first principles, called axioms. This is generally the more powerful of the two mathematical methods and, as such, is the one preferred by mathematicians and is often the one needed to solve the more difficult problems. Geometrical methods, on the other hand, often seem simpler but are sometimes deceptively so. The wise rule is to use geometrical methods with care and to defer to analytical methods when in doubt.

This division into geometrical methods and analytical methods is arbitrary since they are parts of the same whole and a combination of the two is frequently used in practice. Sometimes the connection between the two methods is not obvious, an example being provided by the trigonometric functions $\sin\theta$, $\cos\theta$, $\tan\theta$, ... The geometrical definition of $\sin\theta$ is

$$\sin\theta = \frac{\text{opposite side}}{\text{hypotenuse}} \quad \text{in a right-angled triangle,} \tag{1.2}$$

whereas the analytical definition is

$$\sin\theta = \theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \frac{\theta^7}{7!} + \cdots. \tag{1.3}$$

We can see that these two definitions are the same in a particular case by taking the angle θ to be, say, $90^\circ = \pi/2$ radian. Then $\sin\theta = 1$ by the geometrical definition, and if we put $\theta = \pi/2 = 1.5708$ into the series (1.3) it is easily shown that successive terms become rapidly smaller and smaller, and that the sum tends towards a limit of 1.000.

The fact that the two definitions of $\sin\theta$ are always the same can be proved only by means of extensive analytical argument. One way is to use the definition of $\cos\theta$ as the series

$$\cos\theta = 1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - \frac{\theta^6}{6!} + \ldots . \qquad (1.4)$$

This is then the derivative (Chapter 2) of $\sin\theta$. The derivative is used to define the slope of the tangent to a curve, and the angle between two straight lines can be obtained as the inverse of the cosine series. In this way, geometry can be developed by the analytical approach leading eventually to showing that (1.2) and (1.3) are equivalent to each other.

As mentioned above, our second natural number, e, belongs in analytical methods. It is defined by the series

$$\mathrm{e}^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots, \qquad (1.5)$$

so that when $x = 1$,

$$\mathrm{e} = 1 + 1 + \frac{1}{2!} + \frac{1}{3!} + \ldots = 2.71828\ldots. \qquad (1.6)$$

This arises naturally in science because e^x, and only e^x, gives exactly the same quantity when it is differentiated (Chapter 2). This corresponds to the quite common situation where the rate of change of a quantity is proportional to the quantity itself, as in first-order reaction kinetics. More fundamentally, exponential relations arise as a result of the simple probability that determines the Boltzmann distribution which underlies many physical phenomena (Section 2.8).

Putting $x = 0$ in (1.5) gives $\mathrm{e}^0 = 1$. This is a particular case of the general rule that any quantity raised to the power of zero is unity, which follows from the laws of indices:

$$a^x a^y = a^{(x+y)} \qquad \text{and} \qquad a^{-x} = 1/a^x,$$

so that

$$a^{(x-y)} = a^x/a^y,$$

and when $x = y$,

$$a^0 = 1.$$

1.2 Units and dimensional analysis

The units used in the SI system are given in the appendix together with numerical values of the fundamental physical constants and conversion factors. Notice that the symbols for units are written only in the singular, or they cannot be cleanly cancelled and we would also have absurdities such as 0.99 g but 1.01 gms. This need not conflict with colloquial usage; we may speak of a temperature difference of 10 kelvins but this is written as 10 K.

Algebraic symbols are used to denote physical quantities, such as p for pressure; the symbol denotes the quantity, not the units. A particular value of the quantity is then the product of a pure number and its units, and this product follows the normal rules of algebra. Thus 2 atm is the product of the pure number 2 and the unit atm, so that if $p = 2$ atm we have $p/\text{atm} = 2$, or a quantity divided by its units is a pure number. An important particular case is when taking logarithms; since the definition of a logarithm only applies to pure numbers, the value of any quantity must first be divided by its units, such as $\ln(p/\text{atm})$. The value obtained will then depend on the units being used since, for example,

$$\begin{aligned}\ln(p/\text{atm}) &= \ln(p/101.325\,\text{kPa})\\ &= \ln(p/\text{kPa}) - \ln(101.325)\\ &= \ln(p/\text{kPa}) - 4.618.\end{aligned}$$

The dimensions of a physical quantity are defined as the appropriate combination of powers of the fundamentals mass (M), length (L) and time (T); thus velocity has dimensions LT^{-1} and force (mass × acceleration) has dimensions MLT^{-2}. The dimensions are precisely analogous to the SI units of kilogram, metre and second, so that force has units of kg m s^{-2}.

Dimensional analysis is a method of checking and predicting relations between physical quantities based simply on the principle that the dimensions must balance in any equation. A standard example of the technique is to predict the form for Stokes's law for the drag on a sphere moving in a viscous fluid. Since

$$\text{force} = \text{mass} \times \text{acceleration}$$

it has dimensions MLT^{-2}. The viscosity η of a fluid is defined by

$$\begin{aligned}\eta &= \frac{\text{force per unit area}}{\text{velocity gradient}}\\ &= \frac{\text{force}}{\text{area}} \times \frac{\text{distance}}{\text{velocity}}\end{aligned}$$

with dimensions

$$\frac{\mathrm{M}\cancel{\mathrm{L}}}{\mathrm{T}^{\cancel{2}}} \times \frac{1}{\cancel{\mathrm{L}}^{2}} \times \cancel{\mathrm{L}} \times \frac{\cancel{\mathrm{T}}}{\mathrm{L}} = \mathrm{ML}^{-1}\mathrm{T}^{-1}.$$

We then assume that the drag (resisting force) on the sphere will depend on the size of the sphere (radius a), its velocity (v) and on the viscosity of the fluid. Dependence on temperature will be taken care of through change in the viscosity of the fluid. The relation that is assumed is written as

$$\text{force} = ka^{\alpha}v^{\beta}\eta^{\gamma}$$

and dimensional analysis will enable us to find the numbers α, β and γ. The assumed relation is rewritten in terms of the dimensions (or units) of the quantities, thus

$$\mathrm{MLT}^{-2} = \mathrm{L}^{\alpha}(\mathrm{LT}^{-1})^{\beta}(\mathrm{ML}^{-1}\mathrm{T}^{-1})^{\gamma}.$$

Finally, we equate powers of each of the primary dimensions M, L and T to obtain

$$\begin{aligned} &\text{for } M, & \gamma &= 1,\\ &\text{for L}, & \alpha+\beta-\gamma &= 1,\\ &\text{for T}, & -\beta-\gamma &= -2, \end{aligned}$$

so that $\alpha = \beta = \gamma = 1$ and the required equation is

$$\text{force} = ka\eta v.$$

Physical, rather than dimensional, arguments are needed to show that the proportionality constant k is 6π.

The same principle can be applied when using the practical SI units of kilogram (kg), metre (m) and second (s), so that in any equation connecting physical variables the units must cancel on the two sides of the equation. This has two valuable and practical uses: unless the units cancel, the equation being used is wrong; and when we wish to change to other units, we can do so by a simple algebraic method called quantity calculus. The latter is based on the principle that multiplication by unity leaves any quantity unchanged, and we can construct 'unity brackets' by writing, as a fraction, the new units over the old using appropriate conversion factors. As a simple example, if we write (1 week/7 days) this has the value unity. To convert, say, 42 days into weeks we multiply by the appropriate unity bracket and cancel the units:

$$42\text{ days} = 42\,\cancel{\text{days}} \times \frac{1\text{ week}}{7\,\cancel{\text{days}}} = 6\text{ weeks}.$$

Example 1.1
The gas constant R in the equation $pV = nRT$ has the units needed for the equation

$$R = \frac{pV}{nT}$$

to have the same units on both sides. Thus if the pressure p is in atmospheres (atm), volume V in dm^3 (also called litres), and temperature T in kelvins (K), and amount of substance, n in moles (mol)

$$R = 0.08205 \text{ litre atm mol}^{-1}\,\mathrm{K}^{-1}.$$

If we wish to use SI units instead, we make use of unity brackets based on the conversion factors

$$\begin{aligned} 1\,\mathrm{atm} &= 101.325\,\mathrm{kPa}, \\ 1\,\mathrm{J} &= 1\,\mathrm{N\,m}, \\ 1\,\mathrm{dm}^3 &= 10^{-3}\,\mathrm{m}^3, \\ 1\,\mathrm{Pa} &= 1\,\mathrm{N\,m}^{-2}, \end{aligned}$$

so that, using four significant figures,

$$R = \frac{0.082057\,\cancel{\mathrm{dm}^3}\,\cancel{\mathrm{atm}}}{\mathrm{mol\,K}} \times \frac{10^{-3}\,\cancel{\mathrm{m}^3}}{\cancel{\mathrm{dm}^3}} \times \frac{101.325 \times 10^3\,\cancel{\mathrm{Pa}}}{\cancel{\mathrm{atm}}} \times \frac{\cancel{\mathrm{N}}}{\cancel{\mathrm{Pa}}\,\cancel{\mathrm{m}^2}} \times \frac{\mathrm{J}}{\cancel{\mathrm{N}}\,\cancel{\mathrm{m}}}$$

$$= 8.3144\,\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}.$$

Example 1.2
Show that Planck's constant has the dimensions of momentum × length.

From the appendix,

$$h = 6.624 \times 10^{-34}\,\mathrm{J\,s}.$$

The units of momentum × length are those of mass × velocity × length. The unity brackets are based on the conversion factors

$$\begin{aligned} 1\,\mathrm{J} &= 1\,\mathrm{N\,m}, \\ 1\,\mathrm{N} &= 1\,\mathrm{kg\,m\,s}^{-2}, \end{aligned}$$

so that the units of momentum × length are

$$\mathrm{kg} \times \frac{\mathrm{m}}{\mathrm{s}} \times \mathrm{m} = \frac{\cancel{\mathrm{kg}}\,\cancel{\mathrm{m}^2}}{\cancel{\mathrm{s}}} \times \frac{\cancel{\mathrm{N}}\,\mathrm{s}^{\cancel{2}}}{\cancel{\mathrm{kg}}\,\cancel{\mathrm{m}}} \times \frac{\mathrm{J}}{\cancel{\mathrm{N}}\,\cancel{\mathrm{m}}} = \mathrm{J\,s}$$

Example 1.3

Suppose that we are given that the spacing between the lines in the microwave spectrum of HCl is 20.7 cm^{-1} and that we need to calculate the moment of inertia I, but can remember only that the spacing is $2B$ where B is either $h^2/8\pi^2 I$ or $h/8\pi^2 Ic$. This difficulty can be resolved by adopting the strongly recommended rule that we substitute into formulae not just numerical values but the units as well.

We have that either

$$I = \frac{h^2}{8\pi^2} \times \frac{\mathrm{cm}}{10.35} \qquad \text{or} \qquad I = \frac{h}{8\pi^2 c} \times \frac{\mathrm{cm}}{10.35},$$

where $h = 6.626 \times 10^{-34}\ \mathrm{J\,s}$ and $c = 2.998 \times 10^{8}\ \mathrm{m\,s^{-1}}$, so that either

$$I = \frac{(6.626 \times 10^{-34})^2\, \cancel{\mathrm{J}^2}\, \cancel{\mathrm{s}^2}\, \mathrm{cm}}{8\pi^2 \times 10.35} \times \frac{\cancel{\mathrm{N}^2}\, \mathrm{m}^2}{\cancel{\mathrm{J}^2}} \times \frac{\mathrm{kg}^2\, \mathrm{m}^2}{\cancel{\mathrm{N}^2}\, \mathrm{s}^{\cancel{4}2}} \times \frac{\mathrm{m}}{10^2\ \mathrm{cm}}$$

giving units of $\mathrm{kg^2\,m^3\,s^{-2}}$, or

$$I = \frac{6.626 \times 10^{-34}\, \cancel{\mathrm{J}}\, \cancel{\mathrm{s}}\, \cancel{\mathrm{cm}}\, \cancel{\mathrm{s}}}{8\pi^2 \times 2.998 \times 10^{8}\, \cancel{\mathrm{m}} \times 10.35} \times \frac{\cancel{\mathrm{N}}\, \mathrm{m}}{\cancel{\mathrm{J}}} \times \frac{\mathrm{kg}\, \mathrm{m}}{\cancel{\mathrm{N}}\, \cancel{\mathrm{s}^2}} \times \frac{\cancel{\mathrm{m}}}{10^2\, \cancel{\mathrm{cm}}}$$

$$= 2.70 \times 10^{-47}\ \mathrm{kg\,m^2}.$$

The second expression gives the correct units for the moment of inertia.

Example 1.4

Show that a diver at a depth of 66 ft of sea water (density 1.03 $\mathrm{g\,cm^{-3}}$) is under a pressure of about 3 atm.

The pressure exerted by a column of liquid of density ρ and height h is given by

$$p = \rho g h = \frac{1.03\, \cancel{\mathrm{g}}}{\cancel{\mathrm{cm}^3}} \times \frac{9.81\, \cancel{\mathrm{m}}}{\cancel{\mathrm{s}^2}} \times 66\, \cancel{\mathrm{ft}} \times \frac{\cancel{\mathrm{kg}}}{10^3\, \cancel{\mathrm{g}}} \times \frac{\cancel{\mathrm{N}}\, \cancel{\mathrm{s}^2}}{\cancel{\mathrm{kg}}\, \cancel{\mathrm{m}}} \times \frac{12\, \cancel{\mathrm{in}}}{\cancel{\mathrm{ft}}}$$

$$\times \frac{2.54\, \cancel{\mathrm{cm}}}{\cancel{\mathrm{in}}} \times \frac{10^4\, \cancel{\mathrm{cm}^2}}{\cancel{\mathrm{m}^2}} \times \frac{\mathrm{Pa}\, \cancel{\mathrm{m}^2}}{\cancel{\mathrm{N}}}$$

$$= 2.033 \times 10^{5}\ \mathrm{Pa} = 203.3\ \mathrm{kPa}.$$

Thus the water exerts a pressure of about 2 × 101 kPa (2 atm), and so the total pressure on the diver is about 3 atm.

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