18

TUTORIAL CHEMISTRY TEXTS

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Maths *for* Chemists

Volume I

Numbers, Functions and Calculus

by MARTIN C. R. COCKETT *and* GRAHAM DOGGETT

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Volume 1

Numbers, Functions and Calculus

MARTIN COCKETT & GRAHAM DOGGETT
University of York

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Preface

These two introductory texts provide a sound foundation in the key mathematical topics required for degree level chemistry courses. While they are primarily aimed at students with limited backgrounds in mathematics, the texts should prove accessible and useful to all chemistry undergraduates. We have chosen from the outset to place the mathematics in a chemical context – a challenging approach because the context can often make the problem appear more difficult than it actually is. However, it is equally important to convince students of the relevance of mathematics in all branches of chemistry. Our approach links the key mathematical principles with the chemical context by introducing the basic concepts first, and then demonstrates how they translate into a chemical setting.

Historically, physical chemistry has been the target for mathematical support; however, in all branches of chemistry – be they the more traditional areas of inorganic, organic and physical, or the newer areas of biochemistry, analytical and environmental chemistry – mathematical tools are required to build models of varying degrees of complexity, in order to develop a language for providing insight and understanding together with, ideally, some predictive capability.

Since the target student readership possesses a wide range of mathematical experience, we have created a course of study in which selected key topics are treated without going too far into the finer mathematical details. The first two chapters of Volume 1 focus on numbers, algebra and functions in some detail, as these topics form an important foundation for further mathematical developments in calculus, and for working with quantitative models in chemistry. There then follow chapters on limits, differential calculus, differentials and integral calculus. Volume 2 covers power series, complex numbers, and the properties and applications of determinants, matrices and vectors. We avoid discussing the statistical treatment of error analysis, in part because of the limitations imposed by the format of this series of tutorial texts, but also because the procedures used in the processing of experimental results are commonly provided by departments of chemistry as part of their programme of practical chemistry courses. However, the propagation of errors, resulting from the use of formulae, forms part of the chapter on differentials in Volume 1.

Martin Cockett
Graham Doggett
York

TUTORIAL CHEMISTRY TEXTS

This series of books consists of short, single-topic or modular texts, concentrating on the fundamental areas of chemistry taught in undergraduate science courses. Each book provides a concise account of the basic principles underlying a given subject, embodying an independent-learning philosophy and including worked examples. The one topic, one book approach ensures that the series is adaptable to chemistry courses across a variety of institutions.

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Contents

Symbols

$>$	greater than
$\geqslant$	greater than or equal to
$\gg$	much greater than
$<$	less than
$\leqslant$	less than or equal to
$\ll$	much less than
$/$ or $\div$	division
$\neq$	not equal to
$\cong$ or $\approx$	approximately equal to
$\Rightarrow$	implies
$\in$	element of
$\propto$	proportionality
$=$	equality
∞	infinity
$\sum$	summation sign
$\prod$	product sign
$!$	factorial
$\{\}$	braces
$[\,]$	brackets
$(\,)$	parentheses

1
Numbers and Algebra

Numbers of one kind or another permeate all branches of chemistry (and science generally), simply because any measuring device we use to record a characteristic of a system can only yield a number as output. For example, we might measure or determine the:

- Weight of a sample.
- Intensity or frequency of light absorption of a solution.
- Vibration frequency for the HCl molecule.
- Relative molecular mass of a carbohydrate molecule.

Or we might:

- Confirm the identity of an organic species by measuring its boiling point.
- Measure, or deduce, the equilibrium constant of a reversible reaction.
- Wish to count the number of isomeric hydrocarbon species with formula C_4H_{10}.

In some of these examples, we also need to:

- Specify units.
- Estimate the error in the measured property.

Clearly then, the manner in which we interact with the world around us leads us quite naturally to use numbers to interpret our experiences.

In many situations, we routinely handle very large and very small numbers, so disparate in size that it is difficult to have an intuitive feel for order of magnitude. For example:

- The number of coulombs (the basic unit of electrical charge) associated with a single electron is approximately 0.000 000 000 000 000 000 160 2177.
- The equilibrium constant for the electrochemical process

$$Au^{3+}(aq) + Al(s) \rightleftharpoons Au(s) + Al^{3+}(aq)$$

is of the order of 1 followed by 4343 zeros.[1] In chemical terms, we have no problem with this answer, as it indicates that the equilibrium is totally

Decimal numbers are commonly written with a space between every group of three digits after the decimal point (sometimes omitted if there are only four such digits).

towards the right side (which means that the aluminium electrode will be completely consumed and the gold electrode untouched).

These two widely different examples, of a type commonly experienced in chemistry, illustrate why it is so important to feel at ease using numbers of all types and sizes. A familiarity and confidence with numbers is of such fundamental importance in solving quantitative chemical problems that we devote the first two chapters of this book to underpinning these foundations. Our main objective is to supply the necessary tools for constructing models to help in interpreting numerical data, as well as in achieving an understanding of the significance of such data.

Aims

In this introductory chapter, we provide the necessary tools for working with numbers and algebraic symbols, as a necessary prelude to understanding functions and their properties – a key topic of mathematics that impinges directly on all areas of chemistry. By the end of the chapter you should be able to:

- Understand the different types of numbers and the rules for their combination
- Work with the scientific notation for dealing with very large and very small numbers
- Work with numerical and algebraic expressions
- Simplify algebraic expressions by eliminating common factors
- Combine rational expressions by using a common denominator
- Treat units as algebraic entities

1.1 Real Numbers

1.1.1 Integers

Counting numbers have been in use for a very long time, but the recognition of zero as a numeral originated in India over two millennia ago, and only became widely accepted in the West with the advent of the printed book in the 13th century (for further details, see D. Wells, *The Penguin Dictionary of Curious and Interesting Numbers*, Penguin, London, 1987).

One of the earliest skills we learn from childhood is the concept of counting: at first we learn to deal with **natural numbers** (positive, whole numbers), including zero, but we tend to ignore the concept of negative numbers, because they are not generally used to count objects. However, we soon run into difficulties when we have to subtract two numbers, as this process sometimes yields a negative result. The concept of a negative counting number applied to an object can lead us into all sorts of trouble, although it does allow us to account for the notion of debt (you owe me 2 apples is the equivalent of saying "I own −2 apples"). We therefore extend natural numbers to a wider category of number called **integers**, which consist of all positive and negative whole numbers, as well as zero:

$$\ldots, -3, -2, -1, 0, 1, 2, 3, \ldots$$

We use integers in chemistry to specify:

- The atomic number, Z, defined as the number of protons in the nucleus; Z is a positive integer, less than or equal to 109.
- The number of atoms of a given type (positive) in the formula of a chemical species.
- The number of electrons (a positive integer) involved in a redox reaction occurring in an electrochemical cell.
- The quantum numbers required in the mathematical specification of individual atomic orbitals. These can take positive or negative integer values or zero, depending on the choice of orbital.

At the time of writing, the heaviest element to have been isolated is the highly radioactive element meitnerium ($Z = 109$), of which only a few atoms have ever been made. The heaviest naturally occurring element is uranium, $Z = 92$.

1.1.2 Rational Numbers

When we divide one integer by another, we sometimes obtain another integer: For example, $6/-3 = -2$; at other times, however, we obtain a fraction, or **rational number**, of the form $\frac{a}{b}$, where the integers a and b are known as the **numerator** and **denominator**, respectively, for example, $\frac{2}{3}$. The denominator, b, cannot take the value zero because $\frac{a}{0}$ is of indeterminate value.

Rational numbers occur in chemistry:

- In defining the spin quantum number of an electron ($s = 1/2$), and the nuclear spin quantum number, I, of an atomic nucleus; for example, ^{45}Sc has $I = \frac{7}{2}$.
- In specifying the coordinates (0,0,0) and $(\frac{a}{2}, \frac{a}{2}, \frac{a}{2})$, which define the locations of two of the nuclei that generate a body-centred unit cell of side a.

1.1.3 Irrational Numbers

Rational numbers can always be expressed as ratios of integers, but sometimes we encounter numbers which cannot be written in this form. These numbers are known as **irrational numbers** and include:

- **Surds**, of the form $\sqrt{2}$, $\sqrt[3]{2}$, which are obtained from the solution of a quadratic or higher order equation.
- **Transcendental numbers**, which, in contrast to surds, do not derive from the solution to algebraic equations. Examples include π, which

$\sqrt{2}$ is obtained as a solution of the equation $x^2 - 2 = 0$; likewise, $\sqrt[3]{2}$ is obtained as a solution of $x^3 - 2 = 0$.

we know as the ratio of the circumference to diameter of a circle, and e, the base of natural logarithms.

1.1.4 Decimal Numbers

Decimal numbers are so called because they use base 10 for counting.

Decimal numbers occur in:

- Measuring chemical properties, and interpreting chemical data.
- Defining relative atomic masses.
- Specifying the values of fundamental constants.

Decimal numbers consist of two parts separated by a **decimal point**:

- Digits to the left of the decimal point give the integral part of the number in units, tens, hundreds, thousands, *etc*.
- A series of digits to the right of the decimal point specify the fractional (or decimal) part of the number (tenths, hundredths, thousandths, *etc*.).

We can now more easily discuss the distinction between rational and irrational numbers, by considering how they are represented using decimal numbers.

Rational numbers, expressed in decimal form, may have either of the following representations:

- A finite number of digits after the decimal point. For example, $\frac{3}{8}$ becomes 0.375.
- A never-ending number of digits after the decimal point, but with a repeating pattern. For example, $\frac{70}{33}$ becomes 2.121 212 ..., with an infinite repeat pattern of "12".

Irrational numbers, expressed in decimal form have a never-ending number of decimal places in which there is *no* repeat pattern. For example, π is expressed as 3.141 592 653... and e as 2.718 281 82... As irrational numbers like π and e cannot be represented exactly by a finite number of digits, there will always be an error associated with their decimal representation, no matter how many decimal places we include. For example, the important irrational number e, which is the base for natural logarithms (not to be confused with the electron charge), appears widely in chemistry. This number is defined by the infinite sum of terms:

We can represent a sum of terms using a shorthand notation involving the summation symbol Σ. For example, the sum of terms $e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \frac{1}{4!} + \cdots + \frac{1}{n!} + \cdots$ may be written as $\sum_{r=0}^{\infty} \frac{1}{r!}$ where the **counting index**, which we have arbitrarily named r, runs from 0 to ∞. A sum of terms which extends indefinitely is known as an **infinite series**, whilst one which extends to a finite number of terms is known as a **finite series**. Series are discussed in more detail in Chapter 1 of Volume 2.

$$e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \frac{1}{4!} + \cdots + \frac{1}{n!} + \cdots \tag{1.1}$$

where $n!$ is the **factorial** (pronounced "n factorial") of the number n, defined as $n! = 1 \times 2 \times 3 \times 4 \cdots \times n$; for example, $4! = 1 \times 2 \times 3 \times 4$.

The form of equation (1.1) indicates that the value for e keeps becoming larger (but by increasingly smaller amounts) as we include progressively more and more terms in the sum, a feature clearly seen in Table 1.1, where the value for e has been truncated to 18 decimal places.

Table 1.1 An illustration of the effect of successive truncations to the estimated value of e derived from the infinite sum of terms given in equation (1.1)

n	*Successive estimated values for e*
1	2.000 000 000 000 000 000
5	2.716 666 666 666 666 666
10	2.718 281 801 146 384 797
15	2.718 281 828 458 994 464
20	2.718 281 828 459 045 235
25	2.718 281 828 459 045 235
30	2.718 281 828 459 045 235

Although the value of e has converged to 18 decimal places, it is still not exact; the addition of more terms causes the calculated value to change beyond the eighteenth decimal place. Likewise, attempts to calculate π are all based on the use of formulae with an infinite number of terms:

- Perhaps the most astonishing method uses only the number 2 and surds involving sums of 2:

$$\pi = 2 \times \frac{2}{\sqrt{2}} \times \frac{2}{\sqrt{2+2}} \times \frac{2}{\sqrt{2+2+2}} \times \cdots$$

- Another method involves an infinite sum of terms:

$$\frac{\pi}{2} = \frac{1}{1} + \frac{1\times 1}{1\times 3} + \frac{1\times 1\times 2}{1\times 3\times 5} + \frac{1\times 1\times 2\times 3}{1\times 3\times 5\times 7} + \cdots,$$

- A particularly elegant method uses a formula that relates the square of π to the sum of the inverses of the squares of all positive whole numbers:

$$\frac{\pi^2}{6} = 1 + \frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \frac{1}{5^2} \cdots$$

  However, this requires an enormous number of terms to achieve a satisfactory level of precision (see Chapter 1 in Volume 2 for more on infinite series and convergence).

Working with Decimal Numbers

As we have seen above, numbers in decimal form may have a finite, or infinite, number of digits after the decimal point. Thus, for example, we say that the number 1.4623 has four decimal places. However, since the decimal representations of irrational numbers, such as π or the surd $\sqrt{2}$, all have an infinite number of digits, it is necessary, when working with such decimal numbers, to reduce the number of digits to those that are **significant** (often indicated by the shorthand, "sig. figs."). In specifying the number of significant figures of a number displayed in decimal form, all zeros to the left of the first non-zero digit are taken as not significant and are therefore ignored. Thus, for example, both the numbers 0.1456 and 0.000 097 44 have four significant figures.

There are basically two approaches for reducing the number of digits to those deemed significant:

- **Truncation** of the decimal part of the number to an appropriate number of **decimal places** or significant digits. For example, we could truncate π, 3.141 592 653 . . ., to seven significant figures (six decimal places) by dropping all digits after the 2, to yield 3.141 592. For future reference, we refer to the sequence of digits removed as the "tail" which, in this example, is 653 . . .
- **Rounding up** or **rounding down** the decimal part of a number to a given number of decimal places is achieved by some generally accepted rules. The number is first truncated to the required number of decimal places, in the manner described above; attention is then focused on the tail (see above):

  (i) If the leading digit of the tail is greater than 5, then the last digit of the truncated decimal number is increased by unity (rounded up), *e.g.* rounding π to 6 d.p. yields 3.141 593.
  (ii) If the leading digit of the tail is less than 5, then the last digit of the truncated decimal number is left unchanged (the number is rounded down), *e.g.* rounding π to 5 d.p. yields 3.141 59.
  (iii) If the leading digit of the tail is 5, then:

    (a) If this is the only digit, or there are also trailing zeros, *e.g.* 3.7500, then the last digit of the truncated decimal number is rounded up if it is odd or down if it is even. Thus 3.75 is rounded up to 3.8 because the last digit of the truncated number is 7 and therefore odd, but 3.45 is rounded down to 3.4 because the last digit of the truncated number is 4 and therefore even. This somewhat complicated rule ensures that there is no bias in rounding up or down in cases where the leading digit of the tail is 5.
    (b) If any other non-zero digits appear in the tail, then the last digit of the truncated decimal number is rounded up, *e.g.* 3.751 is rounded up to 3.8.

Worked Problem 1.1

Q Compare the results obtained by sequentially rounding 7.455 to an integer with the result obtained using a single act of rounding.

A On applying the rules for rounding, the numbers produced in sequence are 7.46, 7.5, 8. Rounding directly from 7.455, we obtain 7.

Problem 1.1

Give the values of (a) 2.554 455, (b) 1.7232 0508, (c) π and (d) e to:

(i) 5, 4 and 3 decimal places, by a single act of rounding in each case;

(ii) 3 significant figures, using $\pi = 3.141\ 592\ 653$ and $e = 2.718\ 281\ 828$.

Observations on Rounding

Worked Problem 1.1 illustrates that different answers may be produced if the rules are not applied in the accepted way. In particular, sequential rounding is not acceptable, as potential errors may be introduced because more than one rounding is carried out. In general, it is accepted practice to present the result of a chemical calculation by rounding the result to the number of significant figures that are known to be reliable (zeros to the left of the first non-zero digit are not included). Thus, although π is given as 3.142 to four significant figures (three decimal places), $\pi/1000$ is given to four significant figures (and six decimal places) as 0.003142.

Rounding Errors

It should always be borne in mind that, in rounding a number up or down, we are introducing an error: the number thus represented is merely an approximation of the actual number. The conventions discussed above, for truncating and rounding a number, imply that a number obtained by rounding actually represents a range of numbers spanned by the implied error bound. Thus, π expressed to 4 decimal places, 3.1416, represents all numbers between 3.14155 and 3.14165, a feature that we can indicate by writing this rounded form of π as 3.14160 ± 0.00005. Whenever we use rounded numbers, it is prudent to aim to minimize the rounding error by expressing the number to a sufficient number of decimal places. However, we must also be aware that if we subsequently combine our number with other rounded numbers through addition, subtraction, multiplication or division, the errors associated with each number also combine, propagate and generally grow in size through the calculation.

Problem 1.2

(a) Specify whether each of the following numbers are rational or irrational and, where appropriate, give their values to four significant figures. You should assume that any repeat pattern will manifest itself within the given number of decimal places:
(i) 1.378 423 7842; (ii) 1.378 423 7842...; (iii) $\frac{1}{70}$; (iv) $\frac{\pi}{4}$;
(v) 0.005068; (vi) $\frac{e}{10}$.
Note: the number e expressed to 9 decimal places, 2.718 281 828, appears to have a repeating pattern, which might wrongly suggest it is a rational number; however, if we extend to a further 2 decimal places, 2.718 281 828 46, we see that there is no repeating pattern and the number is irrational.

(b) In a titration experiment, the volume delivered by a burette is recorded as 23.3 cm^3. Give the number of significant figures, the number of decimal places and estimates for the maximum and minimum titres.

1.1.5 Combining Numbers

Numbers may be combined using the **arithmetic operations** of addition (+), subtraction (−), multiplication (×) and division (/ or ÷). The type of number (integer, rational, irrational) is not necessarily maintained under combination. Thus, for example, addition of the fractions 1/4 and 3/4 yields an integer, but division of 3 by 4 (both integers) yields the rational number (fraction) 3/4. When a number (say, 8) is multiplied by a fraction (say, 3/4), we say in words that we want the number which is three quarters *of* 8 which, in this case, is 6.

For addition and multiplication the order of operation is unimportant, regardless of the number of numbers being combined. Thus:

$$2 + 3 = 3 + 2$$

and

$$2 \times 3 = 3 \times 2$$

and we say both addition and multiplication are commutative. However, for subtraction and division, the order of operation *is* important, and we say that both are non-commutative:

$$2 - 3 \neq 3 - 2$$

and

$$\frac{2}{3} \neq \frac{3}{2}$$

One consequence of combining operations in an arithmetic expression is that ambiguity may arise in expressing the outcome. In such cases, it is imperative to include brackets (the generic term), where appropriate, to indicate which arithmetic operations should be evaluated first. The order in which arithmetic operations may be combined is described, by convention, by the BODMAS rules of precedence. These state that the order of preference is as follows:

Brackets
Of (multiplication by a fraction)
Division
Multiplication
Addition/Subtraction

For example:

- If we wish to evaluate $2 \times 3 + 5$, the result depends upon whether we perform the addition prior to multiplication or *vice versa*. The BODMAS rules tell us that multiplication takes precedence over addition and so the result should be $6 + 5 = 11$ and not $2 \times 8 = 16$. Using parentheses in this case removes any ambiguity, as we would then write the expression as $(2 \times 3) + 5$.
- If we wish to divide the sum of 15 and 21 by 3, then the expression $15 + 21/3$ yields the unintended result $15 + 7 = 22$, instead of 12, as division takes precedence over addition. Thus, in order to obtain the intended result, we introduce parentheses () to ensure that summation of 15 and 21 takes place before division:

  $$(15 + 21)/3 = 36/3 = 12$$

  Alternatively, this ambiguity is avoided by expressing the quotient in the form:

  $$\frac{15 + 12}{3}$$

  However, as the solidus sign, /, for division is in widespread use, it is important to be aware of possible ambiguity.

Powers or Indices

When a number is repeatedly multiplied by itself in an arithmetic expression, such as $3 \times 3 \times 3$, or $\frac{1}{2}\times\frac{1}{3}\times\frac{1}{4}\times\frac{1}{n}$, the **power** or **index** notation (also often called the **exponent**) is used to write such products in the forms 3^3 and $\left(\frac{3}{2}\right)^4$, respectively. Both numbers are in the general form a^n, where n is the index. If the index, n, is a positive integer, we define the number a^n as a raised to the nth power.

We can define a number of laws for combining numbers written in this form simply by inspecting expressions such as those given above: For example, we can rewrite the expression:

$$\frac{3}{2}\times\frac{3}{2}\times\frac{3}{2}\times\frac{3}{2}=\left(\frac{3}{2}\right)^4$$

as

$$\frac{3}{2}\times\frac{3}{2}\times\frac{3}{2}\times\frac{3}{2}=\left(\frac{3}{2}\right)^3\left(\frac{3}{2}\right)^1=\left(\frac{3}{2}\right)^4$$

and we see that the result is obtained simply by adding the indices of the numbers being combined. This rule is expressed in a general form as:

$$a^n a^m = a^{n+m} \tag{1.2}$$

For rational numbers, of the form $\frac{a}{b}$, raised to a power n, we can rewrite the number as a product of the numerator with a positive index and the denominator with a negative index:

$$\left(\frac{a}{b}\right)^n=\frac{a^n}{b^n}=a^n\times b^{-n}=a^n b^{-n} \tag{1.3}$$

which, in the case of the above example, yields:

$$\left(\frac{3}{2}\right)^4=\frac{3^4}{2^4}=3^4\times 2^{-4}$$

On the other hand, if $b = a$, and their respective powers are different, then the rule gives:

$$\frac{a^n}{a^m}=a^n a^{-m}=a^{n-m} \tag{1.4}$$

The same rules apply for rational indices, as is seen in the following example:

$$\left(\frac{3}{2}\right)^{3/2}=\frac{3^{3/2}}{2^{3/2}}=3^{3/2}\times 2^{-3/2}$$