Doggett & Sutcliffe

# Mathematics for Chemistry

# 化学数学

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# Introduction

## Mathematics in the context of chemistry

Chemistry is a practical subject, so why should mathematics now play such an important role in its understanding? Coulson provided compelling answers to this question in his presidential address to the Institute of Mathematics and its Applications (Coulson, 1973), when he reviewed the reactions of those involved in the development of chemical ideas one hundred years earlier. He reminds us, for example, that in 1878 Frankland wrote: 'I am convinced that further progress of chemistry as an exact science depends very much indeed upon the alliance with mathematics'. This prophetic view was not shared by most chemists of the time; and it was not until the development of the quantum theory in the late 1920s, and the consequent impact on our understanding of spectroscopy and electronic structure, that chemists started to develop the mathematical tools that were relevant to the needs of chemistry. There are many reasons for the growth of this symbiotic relationship, and it is helpful to examine some of them in putting the objectives of this book into the proper context.

The study of chemistry, whilst concerned intimately with the syntheses and reactions of an ever increasing number of compounds, is concerned basically with the discovery of patterns in the way chemical properties of such compounds are interrelated. At the simplest level, for example, the shell model of the atom (a mathematical concept) relates to the framework provided by the Mendeleyev classification of the elements – the detailed understanding of which requires mathematical insight to see how the periodic classification is manifested in the quantum mechanical concept of the orbital model. The point about this development is that the orbital model in turn provides an excellent tool for understanding the nature of atoms and molecules, the microscopic behaviour of which may then be explored with the aid of experimental spectroscopic techniques.

The intrusion of mathematics into chemistry provides the necessary tools for quantitative model building that are required for the prediction, elucidation and rationalization of chemical phenomena. It is very difficult indeed, for example, to recognize and verify the presence of both simple ($Fe^{16+}$) ▷

▷ Goldberg, 1988

▷ Taylor and Williams, 1993

and unusual chemical species like $HC_{3+2n}N$ ($n = 0, 1, 2, 3, 4$) in interstellar space ▷, without the orbital model for atoms and molecules. Furthermore, without the underlying warp of mathematics, and the weft of physics and biology, chemistry would be reduced to a vast catalogue of apparently unrelated facts and observations: instead of quantitative models there would be 'rules of thumb'! It is because of this strong interrelation between mathematics and chemistry (and physics) that we are able to understand the molecular structure of biomolecules such as insulin, through the interpretation of the results obtained from X-ray diffraction. Understanding molecular structure is, of course, a precursor to understanding the chemical behaviour of atoms and molecules.

Other branches of chemistry, whilst less concerned with the determination of molecular structures, are concerned more with the gathering of data by observing chemical species reacting: in these situations, where time is the key variable, the results can only be interpreted and understood with the aid of a knowledge of the form and solution of special kinds of differential equation. The chemical objective here is to interpret the observed results in terms of a mechanism for the reaction, and this necessitates plotting data in the form suggested by the theory in order to recognize the function that relates concentration of a species and time. However, because there are errors present in the data collected, there are problems associated with the handling of these errors when attempting to establish the quantitative relation between concentration and time. The proper treatment of the problems experienced in these kinds of situation involves understanding the ideas of error propagation and statistics – both of which involve using the tools of calculus. In fact, estimating and assessing the consequences of error propagation in some form or other pervades all experimental science.

This book is written to help those for whom mathematics has always been a problem, because the subject has not been studied to the depth required for understanding the infrastructure of chemistry. We hope that it will also help those who have studied mathematics in more depth, but the interrelation between their knowledge and the requirements of chemistry is not fully developed. Typically, although this latter group may have an elementary knowledge of complex numbers and even group theory, the connections with structural, spectroscopic and quantum chemistry are unlikely to have been made. Furthermore, despite their knowledge of mathematics before entering higher education, much of the detail of what has been learnt earlier has become forgotten and unused. In fact, there is often a feeling of anxiety (and associated lack of confidence) in many students when it becomes apparent that important areas of chemistry are going to become inaccessible without some sound working mathematical tools in their baggage.

In view of these well-known problems, we have set ourselves the aim of raising the threshold for the onset of anxiety, by presenting a selection of mathematical ideas and techniques in the form of a tool-kit set within a chemical context. We therefore adopt the deliberate policy of avoiding much formal proof in favour of a more pragmatic approach – simply because the mathematics of chemistry is linked to physical phenomena and, for the most part, the exception to the rule is not the norm.

The material covered in this text splits broadly into the two areas of calculus and linear algebra, prefaced by an introductory tour through some necessary mathematical grammar and symbolism. The fact that the models used in understanding and rationalizing real physical problems can involve the simultaneous use of tools from each of these areas (and also the deployment of other techniques) is recognized from the outset in our choice of topics and is seen, for example, in the ubiquitous and apparently simplest of problems in requiring the best fit of observed data to a linear or quadratic form.

## Organization of the text

The text is organized so that the first three chapters provide a review of elementary principles and notation in algebra, trigonometry and calculus. This review can be regarded as revision or a rapid survival course, depending upon the background of the reader! There is then a reiteration of some of the calculus before further developments and applications are considered within the general contexts of kinetics, thermodynamics and spectroscopy. The remainder of the text is concerned more with topics that come within the area of mathematics termed linear algebra, where time is spent developing techniques involving the matrix and vector notation, in preparation for all kinds of applications (primarily those associated with spectroscopy and bonding theory). The inclusion of these topics is most important as they also provide the tools for dealing with the anisotropy of directional chemical properties associated with, for example, the consequences of electric and magnetic fields interacting with matter. We are quite honest about our general style of approach and choice of content. In no way can we hope to be exhaustive, and we make this clear at the outset. Our basic aim is to provide some useful tools which, in many cases, act like keys for opening doors into other areas of mathematics. Thus, for example, armed with ideas of functions, calculus and complex numbers, it is possible to gain access to the theory of functions of a complex variable as a first step in developing the understanding of the theoretical modelling of scattering processes and advanced spectroscopic methods used in the laboratory – just to highlight two applications.

Throughout the text marginal notes are used for comment, and citations of references, equations, sections, etc. All references cited by author name are collected in the References section at the end of the text. Answers are also included for all the problems given in the text, along with some working and hints. Examples and problems of a chemical nature are used as far as possible, in the knowledge that the detailed chemistry will require students to consult a physical chemistry text. It is almost inevitable that some of the examples will be premature; however, the problems are self-contained and, for their execution, do not rely on a detailed knowledge of the chemistry. In developing the mathematics, we use current widely accepted physical chemistry texts either to illustrate the application of mathematical principles, or to provide additional mathematical commentary. Further examples and problems in the more basic aspects of mathematics may be found in *Foundation Maths* by Croft and Davison.

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Graham Doggett
Brian Sutcliffe
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# Contents

# 1 Numbers, symbols and rules

**Objectives**

This chapter provides

- a working knowledge of some of the very basic building blocks associated with numbers, and the rules determining their manipulation
- confidence in handling numbers with associated units
- a simple introduction to algebra and equations
- an insight into the need for extending the number system to include complex numbers

Mathematics, like much of chemistry, is concerned with numbers, symbols, and rules for their manipulation. Searching for pattern also forms an important part of the rule development. The complexity of the symbolism in mathematics, delineated by particular rules, often obscures meaning and comprehension as, within a given subject area, the background knowledge required is often hierarchical in nature, and the consequent understanding of the working of the mathematics may become difficult – especially if there are gaps in this background knowledge.

The development of ideas in chemistry follows a very similar hierarchical pattern and much of the associated thinking and experience is basically related to working with numbers, symbols and rules. Numbers permeate chemistry in terms of experimentally measured values, or in the appearance of quantum numbers, associated with physical properties. Although symbols are used in chemical equations, according to well-defined rules, several layers of meaning are usually associated with such equations which are, in effect, mathematical statements. In many cases it is the greater familiarity with chemical symbolism that makes it feel more comfortable; however, in many situations, it is the implicit message carried by the symbolism that is important. In the mathematical situation it is therefore more difficult for the chemist to perceive, or even appreciate, the significance of what is not immediately apparent. An example will make this clear: when dealing with numbers or symbols in mathematics or chemistry, the context makes it clear whether order (*commutativity*) is important. Thus $2 \times 3 = 3 \times 2$ or $xy = yx$, if $x$ and $y$ are symbols representing numbers multiplied together (it is common practice to omit the $\times$ sign when there is no ambiguity). The basic rules of handling numbers include commutativity for $+$ and $\times$, which is nearly always assumed. In chemistry, the analogous symbolism has to be read in a different way, because IBr is not the same as IrB (or BIr!). Given the symbols for the elements there are special rules that inform the chemist about how to order these symbols and manipulate them in equations: thus HCN and HNC are recognized as isomers, but for $FeSO_4$ and $FSeO_4$, the latter compound has no sense when interpreted in terms of the rules of valence. Thus, it is clear that in any symbolic approach of classification or definition, the rules for using the symbols must be recognized; also, there may be other factors that need to be understood – both in the mathematical and chemical situations. Many examples of the former will be discussed in this and following chapters; it merely suffices to say that, in the chemical situation, while the equation $C + 2H_2O = CH_4 + O_2$ may make sense in term of conservation of matter, it may not make sense in terms of either kinetics or thermodynamics (or both!). The chemist is aware of the background to the use and misuse of equations in a chemical context; when it comes to the same sort of ideas set out in a mathematical context, it is the background (implicit) assumptions that may be absent or undeveloped. We hope, therefore, that in this introductory chapter on numbers and symbolism, we may prepare the reader for further developments and explorations of areas of mathematics that provide important tools for the chemist. The first section of this chapter is concerned with numbers of different kinds, and the rules for their manipulation; this is followed by sections on algebra and equations before returning to a discussion of an extension of the number system to include complex numbers.

## 1.1 Numbers

### Kinds of numbers

Real numbers come in various kinds: integer, rational, decimal, irrational. *Integers* are the counting numbers (no decimal point) extended to include zero and negative values: thus the *set* $\mathbb{I} = \{\ldots, -1, 0, 1, \ldots\}$ contains all the integers. Integers can be either *odd* or *even*, depending whether or not they are divisible by 2; an integer $p$, not divisible by another integer (apart from $\pm 1$, $\pm p$) is called a *prime* number. *Rational* numbers, or fractions, are of the form $\frac{r}{s}$ or $r/s$ (for example $2/3$) $\triangleright$, where $r, s$ are integers ($s \neq 0$) corresponding to the *numerator* and *denominator*, respectively. Clearly, if $s = 1$, we see that integers are included in the set of rational numbers. A rational number can always be written as a *decimal* number, though not necessarily in terminating form: for example $1/3 = 0.333\ 33 \cdots$. Decimal numbers which have an infinite number of digits after the decimal point, but with no repeating pattern,

$\triangleright$
The symbol / for division is sometimes referred to as a *solidus.*

▷ See Chapter 2.

are termed *irrational* numbers, and some such numbers play an important role in chemistry: for example, $\pi$, $\sqrt{2}$, $e$ (the base for natural logarithms ▷), etc.

A decimal number that can be written as a rational number must possess a finite number of digits after the decimal point or an infinite number with a repeating pattern. Thus, for example, 1.128 can be written as a rational number, since $1.128 = 1.128 \times 1000/1000 = 1128/1000 = 141/125$, after cancelling the common factor of 8 from numerator and denominator. On the other hand, for the number with the repeating pattern of 128, we can proceed as follows: let $x = 1.128\,128\cdots\cdots$, then $1000x - x = 1127$ implies ▷ $x = 1127/999$.

▷ The symbol ⇒ is usually used for *implies*.

> **Problem 1.1**
>
> Write the following decimal numbers in rational number form: $0.005\,5$, $0.055\,555\cdots$, $0.037\,037\cdots$.

The necessity for recognizing the difference between an integer and a decimal number is important within the context of computing, as a decimal number could take twice the storage space of an integer. Thus, a decimal number essentially requires storage locations for the integers before and after the decimal point (but this is not exactly how the number is stored in practice). The storage of irrational numbers presents an especially awkward problem because they must always be truncated to a decimal number with a fixed number of digits after the decimal point: the computer software (and hardware) therefore determines the size of the error in storing such numbers. This problem can be demonstrated on most electronic calculators by displaying the number 2 and then pressing the square root button six times (say). If the squaring button is now pressed six times, then a decimal number close to 2 is usually obtained.

## Relations involving numbers

Apart from magnitude and sign, real numbers can be ordered in an increasing or decreasing sense: so, for example, $-1$ is less than 2, but 2 is greater than $-1$; also $-1$ is greater than $-5$, etc. These ordering relations ▷ are written symbolically as $-1 < 2$, $2 > -1$, $-1 > -5$, respectively. In general terms $x$ is larger than $y$ if $x - y$ is a positive number; if $x < y$ then $x - y$ is a negative number. Thus $-2 < -1$, but $2 > 1$ ▷. If $x$ is very much larger than $y$, then we often write this relation as $x >> y$.

▷ Known as *inequalities*.

▷ Thus multiplying both sides of an inequality by a negative number changes the sense of the inequality.

From a mathematical point of view it is often necessary to discuss collections of numbers, rather than focusing attention on individual numbers. In this sort of situation, which we shall meet first in the discussion of functions, we use the shorthand $\mathbb{R}$ to represent the whole collection (set) of real numbers. From time to time it will be necessary to use other shorthand forms to represent parts (*subsets*) of this complete collection. So, for example, the set of all integers, $\mathbb{I}$, is contained in $\mathbb{R}$, and we write this as $\mathbb{I} \subset \mathbb{R}$ ▷; similarly, we may wish to refer to the subset of all positive numbers.

▷ For an individual integer, $j$, we write this as $j \in \mathbb{I}$ or $j \in \mathbb{R}$, depending upon the context.

## Operations on numbers

The manipulation of expressions containing fractions involves the use of a few simple rules:

### Addition or subtraction

Here all fractions are rewritten with a lowest common denominator (the lowest number into which all denominators will divide).

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Worked example

**1.1** (a) $\frac{1}{6}+\frac{1}{2}-\frac{1}{3}=\frac{1}{6}+\frac{3}{6}-\frac{2}{6}=\frac{1+3-2}{6}=\frac{2}{6}=\frac{1}{3}$.
With practice, it is possible to miss out the first step involving the rewriting of the (three) fractions in terms of the common denominator.

(b) $\frac{2}{3}-\frac{1}{9}+\frac{1}{2}=\frac{12-2+9}{18}=\frac{19}{18}$, where 18 is the lowest common denominator.

(c) $\frac{2}{x}+\frac{1}{3y}=\frac{6y+x}{3xy}$, where $x$ and $y$ are symbols representing arbitrary numbers, neither of which is zero.

### Multiplication

Multiplication of fractions follows the simple rule of taking the product ▷ of the two numerators divided by the product of the two denominators.

▷ Indicated by $\cdot$ or $\times$ (the latter when there is any ambiguity with the sign for the decimal point).

---

Worked example

**1.2** (a) $\frac{2}{3}\cdot\frac{1}{6}=\frac{2}{18}=\frac{1}{9}$, after cancelling the common factor 2 in both numerator and denominator.

(b) $\frac{a}{b}\cdot\frac{c}{d}=\frac{ac}{bd}$.

(c) $\frac{1}{3}\cdot\frac{c}{d}=\frac{c}{3d}$.