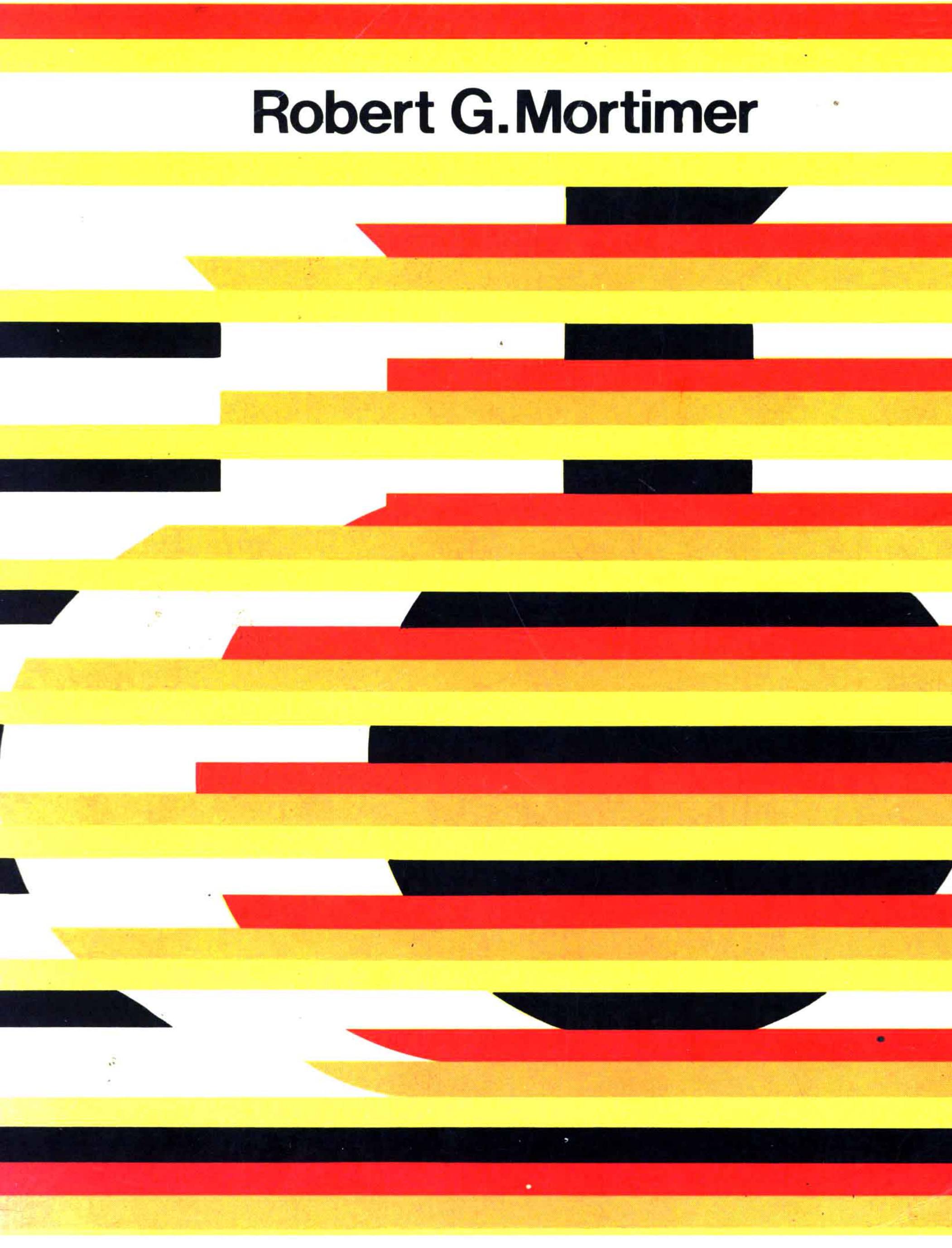
Mathematics for Physical Chemistry

Robert G. Mortimer



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Preface

The purpose of this book is to provide a survey of the mathematics needed for physical chemistry courses at the undergraduate level. Although several kinds of elementary physical chemistry courses exist, all have some mathematics as a prerequisite. However, in nearly two decades of teaching physical chemistry, I have found that only a small minority of students have been introduced to all the mathematical topics needed in physical chemistry, and that most need some practice in applying their mathematical knowledge to the problems of physical chemistry.

Physical chemistry was defined by my first teacher of the subject as "anything that physical chemists are interested in," but a better definition is that physical chemistry is the branch of chemistry which applies the methods and theories of physics to chemical problems. As such, it involves more theory and more mathematics than other branches of chemistry, and in fact contains the theoretical foundation underlying all branches of chemistry.

Students arrive at their first course in physical chemistry with a variety of backgrounds, so I have not tried to write part of the book as a review of familiar topics and part of it as an introduction to new material. I have consciously tried to write all parts of the book so that they can be used for selfstudy by someone not familiar with the material, although of course any book such as this cannot be a substitute for the traditional training in mathematics required by students of chemistry. Solved examples and problems for the reader are interspersed throughout the presentations, and these form an important part of the presentations. As you study any topic in the book, you should follow the solution to each example, and work each problem as you come to it.

The first nine chapters of the book are constructed around a sequence of mathematical topics. Chapter 10 is a discussion of mathematical topics needed in the analysis of experimental data, and Chapter 11 is a brief introduction to computer programming in the BASIC language. Most of the material in at least the first four chapters should be a review for nearly all readers of the book. I have tried to write all of the chapters after the first four so that they can be studied in any sequence, or piecemeal as the need arises. The first section in each chapter (except Chapter 1) contains a list of instructional objectives, which can be used by a reader to determine whether he needs to study that chapter or not.

I hope that this book will serve three functions: (1) as a review or introduction to new topics for those preparing for a course in physical chemistry, (2) as a supplementary text to be used during a physical chemistry course, and (3) as a reference book for graduate students and practicing chemists.

It is a pleasure to acknowledge the help which I have received from James Smith and Gregory Payne of the Macmillan Publishing Co., and from the following persons, who have reviewed all or part of the manuscript:

Sydney Bluestone, Allen Denio, Gerald E. Doeden, Fred H. Dorer, Vojtech Fried, Michael E. Green, Clifford W. Hand, William Z. Plachy, and Daniel Ira Sverdlik. I also wish to express thanks to my teachers of physical chemistry. I have benefited from the instruction of Lowell Tensmeyer, the late Norman Bauer, Robert Mazo, Norman Davidson, Joseph E. Mayer, and Henry Eyring. Thanks are due the Research and Creative Activities Committee of Southwestern College for a summer research grant under which I began this book. Finally, I want to thank my family for exercising a considerable amount of patience while I was working on this book.

Robert G. Mortimer

Contents

CHAPTER ONE

Numbers, Mathematics, and Science—An Introduction to the Book

Section 1-1. GENERAL COMMENTS FROM THE AUTHOR TO THE READER

Mathematics and science have grown up together during the past three or four centuries, and some people, such as Isaac Newton, have made great contributions to both fields. However, there seems to be a gulf between pure mathematics, which is of interest to mathematicians, and applied mathematics, which is an indispensable tool for physicists, chemists, and biologists.

As you can see from the table of contents, this book is organized by mathematical topics. It is, however, not a mathematics book. The rigorous point of view of a trained mathematician is of great value, but I have not taken this point of view. The book presents mathematical concepts and facts without much derivation or rigor, and concentrates on the application of these concepts and facts to problems such as those arising in physical chemistry. Our approach is of course no substitute for a standard course of study in calculus and other areas of mathematics.

Physical chemistry is often the first course, outside of mathematics courses, in which a student encounters applications of mathematics beyond simple algebra and statistics. In my own first course in physical chemistry, it was like a revelation to me to see that chemists actually use calculus in their work, and also to learn that physical theory in a mathematical form underlies all of chemistry. I soon became glad that I was studying both chemistry and mathematics. I hope that you will gain the same feeling in your physical chemistry course, and that this book will assist you.

I have tried to write the book so that the further you go into the book, the more likely you will be to encounter material that is new to you. I have also tried to write the book so that it is not necessary to work through the book from front to back, and you may wish to study the chapters in a sequence of your own design.

Section 1-2. NUMBERS AND MEASUREMENTS

There are several sets into which we can classify numbers. Those which can represent actual measured physical quantities are called *real numbers.* They can range from positive numbers of indefinitely large magnitude to negative numbers of indefinitely large magnitude. Among the real numbers are the integers, 0, ± 1, ± 2, ± 3, etc. Other numbers are said to be *rational numbers.* They are quotients of two integers, such as $\frac{2}{3}$, $\frac{1}{2}$, $\frac{37}{53}$, etc. Of course, the integers are rational numbers. Other numbers are called *algebraic irrational numbers.* They include square roots of rational numbers, cube roots of rational numbers, etc., which are not themselves rational numbers. All of the rest of the real numbers are called *transcendental irrational numbers.* Two commonly encountered transcendental irrational numbers are the ratio of the circumference of a circle to its diameter, called π and given by 3.141592654 . . . , and the base of natural logarithms, called e and given by 2.718281828 . . . . The three dots that follow the given digits indicate that more digits follow. Irrational numbers have the property that if you have some means of finding what the correct digits are, you will never reach a point beyond which all of the remaining digits are zero, or beyond which the digits form a repeating pattern. However, with a rational number, one or the other of these two things will always happen.[1]

Problem 1-1

Take a few simple fractions, such as $\frac{2}{3}$, $\frac{4}{9}$, or $\frac{3}{7}$, and express them as decimal numbers, finding either all the nonzero digits or the repeating pattern of digits. •

The most common use that chemists make of numbers is to report values for measured quantities. A measured quantity can almost never be known with complete accuracy, unless the number is required to be a fairly small integer. It is therefore a good idea to communicate the probable accuracy of a reported measurement.

For example, let us consider the specification of the length of an object, say a piece of glass tubing, which we have measured with a meter stick. We will discuss experimental error in Chapter 10, but let us now assume that we believe our experimental error to be no greater than 0.6 millimeter (mm) and that our measured value is 387.8 mm.

The best way to specify what we believe the length of the glass tubing to be is to say:

$$\text{length} = 387.8 \pm 0.6 \text{ mm}$$

[1] I have been told that early in the twentieth century, the legislature of the state of Indiana, in an effort to simplify things, passed a resolution that henceforth in that state, π should be equal to exactly 3.

If for some reason we cannot include a statement of the probable error, we must at least avoid including digits that are likely to be wrong. That is, we must *round off* the number. Since our error is somewhat less than 1 mm, the correct number is probably closer to 388 mm than to either 387 mm or 389 mm, so we report the length as 388 mm and assert that the three digits given are significant. All this means is that we think the given digits are correct. If we had reported the length as 387.8 mm, the last digit is insignificant. That is, it is probably wrong.

You should always avoid reporting digits that are not significant. When you carry out calculations involving measured quantities, you should always determine how many significant digits your answer can have and round off your result to that number of digits.

When you are multiplying a number of factors together, a good rule of thumb is that your answer will have the same number of significant digits as the factor with the *least* number. The same rule holds for division.

Example 1-1

What is the area of a rectangle whose length is given as 7.78 m and whose width is given as 3.486 m?

Solution

When we use a calculator to find the product of 7.78 m and 3.486 m, we get 27.12108 m^2. We must round this to 27.1 m^2. ●

Example 1-2

Compute the smallest and largest values that the area of the rectangle might have, and determine whether the answer given in Example 1-1 is correctly stated.

Solution

The smallest value that the length might have, assuming the given value to have only significant digits, is 7.775 m, and the largest value that it might have is 7.785 m. The smallest possible value for the width is 3.4855 m and the largest value is 3.4865 m. The minimum value for the area is

$$A(\text{minimum}) = (7.775\text{ m})(3.4855\text{ m}) = 27.0997625\text{ m}^2$$

The maximum value for the area is

$$A(\text{maximum}) = (7.785\text{ m})(3.4865\text{ m}) = 27.1424025\text{ m}^2$$

To get an agreement between these numbers, we must round both of them to 27.1 m^2. The result in Example 1-1 was correctly stated. ●

The rule of thumb for significant digits in addition or subtraction is slightly different: For a digit to be significant, it must arise from a significant digit in every term of the sum or difference.

Example 1-3

Determine the combined length of two objects, one of length 0.783 m and one of length 17.3184 m.

Solution

We add:

$$\begin{array}{rl} 0.783 & \text{m} \\ 17.3184 & \text{m} \\ \hline 18.1014 & \text{m} \end{array}$$

The final 4 is not a significant digit, because the fourth digit after the decimal point in the top number is unknown, and the 4 could be significant only if the fourth digit in the first number were a zero. We must round the answer to 18.101 m. •

Some people round off the insignificant digits at each step of a calculation. However, this can lead to "round-off" error if a number of steps are required in a calculation. A reasonable policy is to carry along at least one insignificant digit during the calculation, and then to round off the insignificant digits at the final answer.

If your only insignificant digit is a 5, you must decide whether to round up to the next larger significant digit or to round down to the next lower significant digit. This problem can usually be avoided by carrying along two or more insignificant digits, but it is possible that a 50 or 500 will occur that must be rounded. It is best to be consistent, and either round up in all such cases, or always round down.

If you are carrying out operations other than additions, subtractions, multiplications, and divisions, you may have trouble in determining which digits are significant. If you must take sines, cosines, logarithms, etc., it may be necessary to do the operation with the smallest and the largest values that the number on which you must operate can have. However, rules of thumb can be found.[2]

Problem 1-2

Calculate the following to the proper numbers of significant digits.

a. $(37.815 + 0.00435)(17.01 + 3.713)$
b. $625[e^{12.1} + \sin(30^\circ)]$
c. 65.718×14.3
d. $17.13 + 14.7651 + 3.123 + 7.654 - 8.123$ •

[2] Donald E. Jones, "Significant Digits in Logarithm–Antilogarithm Interconversions," *J. Chem. Educ.* **49**, 753 (1972).

Scientific Notation. A problem in communication arises if the last significant digit or digits in a number happen to be zeros. For example, say that a certain distance on the surface of the earth happens to be 6300 kilometers (km). That is, the distance is closer to 6300 km than it is to 6299 km or 6301 km. If you report the distance as 6300 km, most people will not assume that the two zeros are significant digits, but that they are included only to show where the decimal point belongs. In other words, they will assume that the distance is only known to lie between 6250 and 6350 km. However, if some leading zeros are necessary to locate a decimal point, everybody recognizes that there are not significant digits. Thus, 0.0000149 cm is a distance expressed with only three significant digits.

The communication difficulty just mentioned can be avoided by the use of *scientific notation*, in which a number is expressed as the product of two factors, one 10 raised to some power, and the other a number lying between 1 and 10. The distance mentioned above would thus be written as 6.300×10^3 km, and there are clearly four significant digits indicated, since the trailing zeros are not required to locate a decimal point. If the number were known only to two significant digits, it would be written as 6.3×10^3.

Scientific notation is convenient if extremely small or extremely large numbers must be written. For example, Avogadro's number, the number of molecules per mole, is much easier to write as 6.0220×10^{23} molecules mol^{-1} than as 602,200,000,000,000,000,000,000, and the charge on an electron is easier to write as 1.602×10^{-19} coulomb than as 0.0000000000000000001602 coulomb.

Problem 1-3

Convert the following numbers to scientific notation (assume that trailing zeros on the right are not significant).

a. 0.000645
b. 67,342,000
c. 0.000002
d. 6432

●

Section 1-3. UNITS OF MEASUREMENT

In Section 1-2, we mentioned measuring the length of an object with a meter stick. Such a measurement would be impossible without a standard definition of the meter (or other unit of length), and for many years science and commerce were hampered by the lack of accurately defined units of measurement. This problem has been largely overcome by accurate measurements and international agreements.

The internationally accepted system of units of measurements is called the *Système International d' Unités*, abbreviated SI. This is an MKS system, which means that length is measured in meters, mass in kilograms, and time

Table 1-1. SI Units*

SI Base Units (quantities with independent definitions)

Physical Quantity	*Name of Unit*	*Symbol*	*Definition*
length	meter	m	1, 650, 763.73 wavelengths in vacuum for a certain spectral line of krypton-86.
mass	kilogram	kg	The mass of a platinum-iridium cylinder kept at the International Bureau of Weights and Measures
time	second	s	The duration of 9, 192, 631, 770 cycles of the radiation of a certain emission of the cesium atom
electric current	ampere	A	The magnitude of current which, when flowing in each of two long parallel wires 1 m apart in free space, results in a force of 2×10^{-7} N per meter of length
temperature	kelvin	K	Absolute zero is 0 K, triple point of water is 273.16 K
luminous intensity	candela	cd	The luminous intensity, in prependicular direction, of surface of 1/600,000 sq m of a black body at temperature of freezing platinum at a pressure of 101325 N/m^2
amount of substance	mole	mol	Amount of substance which contains as many elementary units as there are carbon atoms in 0.012 kg of carbon-12.

Other SI Units

Physical Quantity	*Name of Unit*	*Physical Dimensions*	*Symbol*	*Definition*
force	newton	$kg\ m\ s^{-2}$	N	$1\ N = 1\ kg\ m\ s^{-2}$
energy	joule	$kg\ m^2\ s^{-2}$	J	$1\ J = 1\ kg\ m^2\ s^{-2}$
electrical charge	coulomb	A s	C	$1\ C = 1\ A\ s$
pressure	pascal	$N\ m^{-2}$	Pa	$1\ Pa = 1\ N\ m^{-2}$
magnetic field	tesla	$kg\ s^{-2}\ A^{-1}$	T	$1\ T = 1\ kg\ s^{-2}\ A^{-1} = 1\ weber\ m^{-2}$
luminous flux	lumen	cd sr	lm	1 lm = 1 cd sr (sr = steradian)

* Robert A. Alberty and Farrington Daniels, Physical Chemistry, fifth edition, p. 662, John Wiley and Sons, New York, 1979.

in seconds. These and the four other base units given in Table 1-1 form the heart of the system. Included in the table are also some "derived" units, which owe their definitions to the definitions of the seven base units. In 1960 the international chemical community agreed to use SI units, which had been in use by physicists for some time.[3]

Some non-SI units continue to be used, such as the atmosphere, which is a pressure equal to 101,325 N m^{-2}, and the torr, which is a pressure such that 760 torr equals 1 atmosphere. The Celsius temperature scale also remains in common use among chemists.

Multiples and submultiples of SI units are commonly used.[4] Examples are the millimeter and kilometer. These quantities are denoted by standard prefixes attached to the name of the unit, as listed in Table 1-2. The abbreviation for a multiple or submultiple is obtained by attaching the prefix abbreviation to the unit abbreviation, as in Gm (gigameter), or ns (nanosecond). Note that since the base unit of length is the kilogram, the table would imply the use of things such as the megakilogram. This is not done. We use gigagram instead of megakilogram.

Table 1-2. Prefixes for Multiple and Submultiple Units

Multiple	Prefix	Abbreviation
10^{12}	tera-	T
10^{9}	giga-	G
10^{6}	mega-	M
10^{3}	kilo-	k
1	—	—
10^{-1}	deci-*	d
10^{-2}	centi-*	c
10^{-3}	milli-	m
10^{-6}	micro-	μ
10^{-9}	nano-	n
10^{-12}	pico-	p
10^{-15}	femto-	f
10^{-18}	atto-	a

* The use of the prefixes for 10^{-1} and 10^{-2} is being discouraged, but centimeters will probably not be abandoned for many years to come.

[3] See "Policy for NBS Usage of SI Units," *J. Chem. Educ.* **48**, 569 (1971).

[4] There is a somewhat apocryphal story about Robert A. Millikan, a Nobel-prize-winning physicist who was not noted for false modesty. A rival is supposed to have told Millikan that he had defined a new unit for the quantitative measure of conceit, and had named the new unit the kan. However, 1 kan was an exceedingly large amount of conceit, so that for most purposes the practical unit was to be the millikan.

Any measured quantity is not completely specified until its units are given. If a is a length, one must say

$$a = 10.345 \text{ m} \tag{1.1}$$

not just

$$a = 10.345 \qquad (\textit{not correct})$$

It is permissible to write

$$a/\text{m} = 10.345$$

which means that the length a divided by 1 meter (m) is 10.345, a dimensionless number.

When you make numerical calculations, you should always make certain that you use consistent units for all quantities. Otherwise, you will almost certainly get the wrong answer. This means that (1) you must convert all multiple and submultiple units to the base unit, and (2) you cannot mix different systems of units. For example, you cannot substitute a length in inches into a formula in which the other quantities are in SI units without converting. It is a good idea to write the unit as well as the number, as in Eq. (1.1), even for scratch calculations. This will help you avoid some kinds of mistakes, since you can inspect any equation and see that both sides are measured in the same units.

The Factor-Label Method. This is an elementary method for the routine conversion of a quantity measured in one unit to the same quantity measured in another unit. The method consists of multiplying the quantity by a fraction that is equal to unity in a physical sense, with the numerator and denominator equal to the same quantity expressed in different units. This does not change the quantity physically, but numerically expresses it in another unit, and so changes the number expressing the value of the quantity.

For example, to express 3.00 km in terms of meters, one writes

$$(3.00 \text{ km})\left(\frac{1000 \text{ m}}{1 \text{ km}}\right) = 3000 \text{ m} = 3.00 \times 10^3 \text{ m} \tag{1.2}$$

You can check the units by considering the same unit to "cancel" if it occurs in both the numerator and denominator. Thus, the left-hand side of Eq. (1.2) has units of meters, because the km on the top cancels the km on the bottom.

Example 1-4

Convert the speed of light, $2.9979 \times 10^8 \text{ m s}^{-1}$, to the same quantity in miles per hour. Use the definition of the inch, 1 in. = 0.0254 m (exactly).

Solution

$$2.9979 \times 10^8 \text{ m s}^{-1} \times \frac{1 \text{ in.}}{0.0254 \text{ m}} \times \frac{1 \text{ ft}}{12 \text{ in.}} \times \frac{1 \text{ mi}}{5280 \text{ ft}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ h}}$$

$$= 6.7061 \times 10^8 \text{ mi h}^{-1}$$

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