MATHEMATICAL TECHNIQUES IN CHEMISTRY

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Preface

This book was motivated by the fact that students, both upper-division undergraduates and beginning graduate students with whom I have had contact, showed a surprising lack of manipulative ability or knowledge (or both?) of the basic mathematics deemed essential for an understanding of many problems in chemistry. Such problems span virtually the entire range of chemistry and are therefore not restricted to those encountered by physical chemists. Ideas in elementary molecular orbital theory, enzyme kinetics, complex solution equilibria, thermodynamics, wave mechanics, ligand field theory, and the kinetic theory of gases all require mathematics of one sort or another for their full expression. None of these areas can be said to be the domain of physical or theoretical chemists alone; for example, molecular orbital theory is fast becoming a standard part of curricula and general usage, and developments in recent years of valence-shell electron calculations by such workers as J. A. Pople[1] leave no doubt that the intended readers of their literature are practicing organic and inorganic chemists. These readers and others less theoretically inclined, both in academia and in industry, will have to aquaint themselves with basic mathematical notions such as basis sets, orthonormal functions, and coordinate transformations if they are going to cope successfully with these important papers.[2] The day when an organic chemist can arrive at the laboratory, run his reactions, take his melting points and infrared spectra, and go home at 5:00 pm is drawing to a close.

[1]See, for example, J. A. Pople et al., *J. Am. Chem. Soc.*, 92, 2191 (1970); 93, 289 (1971); and other papers in the series.

[2]As an example of the sort of applied use to which molecular orbital theory is being put, read J. M. George, L. B. Kier, and J. R. Hoyland, "Theoretical Considerations of Alpha and Beta Adrenergic Activity," *Mol. Pharm.*, 7, 328 (1971), as well as the monograph L. B. Kier, *Molecular Orbital Theory in Drug Research*, Academic Press, New York, 1971.

It is not entirely the student's fault for his weakness in handling many of these mathematical ideas because little of the mathematics presented in classrooms is directed toward applications. To be fair, it could hardly be otherwise. Mathematics instructors have enough on their hands just presenting the basic concepts of their subject without having to worry about whether they should provide numerous applications to physics, chemistry, engineering, or indeed to all three. Physics instructors recognized the truth of this situation long ago, so that for quite a while a course in mathematical methods in physics has been a permanent feature of undergraduate and graduate physics curricula.[3] Very few departments of chemistry have a similar offering; it is hoped that in the future the number offering such a course will increase.

If recent trends in the educational literature are any sign at all, the time for this and the time when mathematics and physical science departments start paying more attention to each other are fast drawing near. G. Matthews and M. Seed, in an article entitled "The Co-existence in Schools of Mathematics and Science," point out that the most important step is for mathematics and science instructors (at the secondary and the college levels) to actually meet and discuss common problems.[4] The late Professor C. A. Coulson, who has probably done more than anyone to render lucid the complex mathematical ideas in quantum chemistry, has pointed out that practicing chemists must recognize that the relation between mathematics and chemistry has changed drastically over the past few decades.[5] Several other articles in the recent educational literature have outlined newly instituted programs in applied mathematics that should be of value to undergraduate students majoring in the sciences. One article has even made a plea that a course in applied mathematics would be of great value to pure mathematicians![6] All humor aside, the point here is that mathematics is a form of communication just as language is, and that it should be regarded as such in the science classroom, at least as far as the practical variety of mathematics is concerned. Professor K. J. Laidler, upon accepting the Chemical Education Award of the Chemical Institute of Canada, has made this and other points very strongly, and I agree with him one hundred percent.[7]

This book should really be of use to a great variety of people in chemistry since the level of presentation nowhere approaches that of the famous

[3]Texts have scarcely changed in 50 years: compare any present-day text on the subject with the old classic E. Madelung, *Die Mathematischen Hilfsmittel des Physikers*, Julius Springer, Berlin, 1922.
[4]G. Matthews and M. Seed, *Int. J. Math. Educ. Sci. Tech.*, **1**, 21 (1970).
[5]C. A. Coulson, *Chem. Brit.*, **10**, 16 (1974).
[6]M. J. Davies, *Int. J. Math. Educ. Sci. Tech.*, **3**, 71 (1972).
[7]K. J. Laidler, *J. Chem. Educ.*, **51**, 696 (1974).

monographs on mathematical methods, and since the book emphasizes applications in chemistry. To that vast sea of workers in chemical industry (clinical and pharmaceutical chemistry, polymer chemistry, paper, wood and waste chemistry, materials science and other branches of chemical engineering, etc.), who have been away from university training for some time and who feel the need for a review of basic mathematical concepts, this book should be of some help. On the academic scene, the book is intended principally for undergraduate students who are pursuing a major's degree in chemistry and who have already completed at least one-half year or preferably an entire year of a standard course in the calculus. Beginning graduate students who have had a particularly brief mathematical education should also find the book useful. Although there are in existence many excellent books on mathematical methods (see the Annotated Bibliography at the end of this volume), most of these are directed toward physicists or to "scientists" in general. In this volume the applications are drawn entirely from various branches of chemistry. Without entering into any futile polemics, this amounts to an operational definition of chemistry and not to any preconceived notions as to what constitutes physics and what constitutes chemistry. Until such time in the future when the structure of Western physical science will have reached the point where departmental outlines disappear and students are taught "science" instead of physics or chemistry, it will still be possible to justify the existence of separate mathematical techniques courses.

For the benefit of instructors, the author has found that in his lectures the material contained in Chapters 1–4 and part of Chapter 5 can just barely be covered in one quarter. At institutions where classes are conducted on a semester schedule an additional chapter could probably be covered. The instructor can select such material from Chapter 6 ("Matrices, Vectors, and Tensors") and Chapter 7 ("Special Functions") as he feels is appropriate for his course. In these chapters, as in the preceding ones, material that can be skipped without seriously impairing the continuity of the text is marked with an asterisk. Such sections could be covered in fast classes or could be recommended to the more motivated members of class.

At the end of every chapter there is an extensive set of exercises; the beginning chapters, in particular, that presumably every user of this book will read, contain especially large doses of problems. The problems are graded into three levels: drill problems and problems that can be attempted by all readers, somewhat harder problems, which are marked by an asterisk, and challenging problems, which are intended only for very good students and very good classes and which are marked with a double asterisk. Some of the problems are of a purely mathematical type, but many are applications to various situations in chemistry. The author has a personal bias against including answers to exercises in a textbook; real learning should not be a test of willpower.

A matter for concern here is whether a user of this book needs an extensive knowledge of chemistry before he is able to work through the material and attempt many of the problems. It is assumed that all readers have more or less mastered the equivalent of a one-year standard course of freshman chemistry for science majors—a course in which the qualitative concepts of free energy, rate of a reaction, discrete energy states of atoms and molecules, and equations of state for gases have been introduced—and that with careful study a reader can apply the chemistry he already knows and the mathematics he is then acquiring to the solution of ostensibly new problems. In the classroom it is the responsibility of every instructor, of course, to exercise judicious judgment in the selection of homework problems for the class. With an exceptional class this is not apt to be a serious problem, and an instructor may wish to assign some problems from outside the text. A solutions manual is available to instructors from the publisher.

A final comment should be made regarding the selection of subjects that are covered in the book. Two large areas have been omitted: statistics and probability, and group theory. The first was passed over because it was felt that mastery of this topic was of less priority than of many others for undergraduate students. For many workers in industry who continually handle large amounts of data, statistics and probability are of very great importance, but some selection was necessary to keep the book a manageable size. The second was omitted because I felt incapable of approaching the excellence of treatment given by Professor F. Albert Cotton in his book *Chemical Applications of Group Theory* (2nd ed., Wiley-Interscience, New York, 1971). Of the subjects that have been included in the present volume, those contained in the first three chapters are drawn from traditional areas up through the calculus; these are topics that are required almost immediately in one's study of chemistry. The subjects of the last four chapters are more in the line of special, albeit important, topics.

In writing this book, the author has benefited directly or indirectly from numerous people. Professor James V. and Dr. Lidia M. Quagliano provided constant companionship and encouragement, particularly during the early stages of preparation. My longtime friend and colleague Professor Dennis J. Diestler consented to read Chapter 6 and was his usual zealous and critical self. Several of the more subtle and sophisticated mathematical points that are only hinted at in the book were discussed with Dr. Thomas P. Dence. Many thanks finally go to Mrs. Georgia M. Chuhay and to the rest of the editorial and technical staff at John Wiley & Sons, Inc., for expert assistance in the preparation of the manuscript.

Feedback and constructive comments are welcomed from instructors and students and particularly from readers in industry and elsewhere who have used the text, regarding any aspect of the book as a whole. It is expected that this work contains the customary faults of any first-edition work, and the author assumes full responsibility for them. "Now go, write it before them in a table, and note it in a book, that it may be for the time to come for ever and ever [Isaiah 30:8]."...or until I write the second edition!

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September 1975

Contents

ONE

Algebra and Elementary Notions of Functions

Dol Common: "Yes, sir. I studie here the mathematiques, And distillation."

BEN JONSON

1 VARIOUS FUNCTIONS; COORDINATE SYSTEMS; GRAPHING

Algebra, indeed most of mathematics, is built upon the concept of the *function*. The concept of function was unknown to Classical and Arabian mathematicians. It is a product of Western culture and could only take form after François Viète (1540–1603), a French lawyer with important connections at the courts of Henry III and Henry IV, had first introduced in a systematic way general letters instead of numbers into algebra.[1] Briefly, a function is a prescription for taking elements from X, called the *domain* of the function, into *unique* elements of Y, called the *range* of the function (see Figure 1.1). Each element x in X is an *argument* of the function, and each element y in Y corresponding to an x is the *value* of the function. Some mathematicians prefer to use the term *mapping* on occasion in place of function.

Although X and Y are usually sets of real numbers, in some cases they may not be. Mathematicians have constructed several different algebraic systems that usually have most or all of the following properties in common.

[1]D. J. Struik (ed.), *A Source Book in Mathematics*, 1200–1800, Harvard University Press, Cambridge, Mass. 1969, p. 74. There is much historically interesting material in this book.

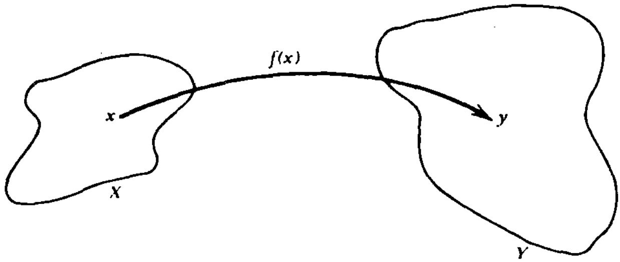

Fig. 1.1 A function or mapping.

1. Two operations analogous to addition and multiplication defined.
2. Existence of a zero and a unity.
3. Associativity: $a+(b+c)=(a+b)+c$, and $a\times(b\times c)=(a\times b)\times c$.
4. Commutativity: $a+b=b+a$, and $a\times b=b\times a$.
5. Distributivity: $a\times(b+c)=(a\times b)+(a\times c)$.
6. Closure: if a, $b\in X$, then $(a+b)$, $(a\times b)\in X$ (the symbol $\in$ means "is a member of").

Some of the above properties may be relaxed; multiplication in the algebra of matrices or of quaternions,[2] for example, is noncommutative. More on this is presented in Chapter 6.

Functions may take many forms; we distinguish two main types following Chrystal (see pp. 281–282, Volume I of his two-volume work listed in the Annotated Bibliography).

1. Algebraic: all arguments are involved in only addition, subtraction, multiplication, division, and being raised to a power.
2. Transcendental: one or more arguments appear as exponents, or as arguments of infinite series.

This definition of a transcendental function may seem unclear now; in Chapter 4 you will see how the logarithmic and the trigonometric functions are best understood in terms of infinite series. With this in mind, the following common examples of algebraic and transcendental functions should be familiar to you. By convention the dependent variable is regarded

[2]Hypercomplex numbers invented by the Irish physicist William Rowan Hamilton (1805–1865) around 1840. Vectors are an offshoot of quaternions, but with the rules for multiplication formulated slightly differently, a fact which caused scientists and mathematicians to square off against each other during the latter half of the nineteenth century. Hamilton was a child genius; in 1827, while still a college student, he was appointed Professor of Astronomy at Trinity College in Dublin.

as the variable placed to the left of the equals sign; the independent variable under consideration is on the right and has been underlined.

Algebraic	Transcendental
$P=\dfrac{nRT}{\underline{V}}$	$\Delta G^0=-RT\ln \underline{K}$
$[H^+]=\underline{1\times10^{-2}M}$	$\lambda=\dfrac{2d}{n}\sin \underline{\theta}$
$\Delta S_{sys}=q\left(\dfrac{1}{T_1}-\dfrac{1}{\underline{T_2}}\right)$	$\psi_{1s}=\dfrac{1}{\sqrt{\pi a_0{}^3}}\exp(-\underline{r}/a_0)$

In this book we use the accepted notation ln to stand for logarithms to the base *e* (natural or Napierian logarithms).

Great convenience results when some of the properties of a mapping are represented pictorially as a *graph*. You should become intimately familiar with the graphs of several common functions (see Figure 1.2) and with a few of the not-so-common functions.

In the graphs in Figure 1.2 the coordinate system used is the familiar rectangular Cartesian coordinate system. However, many other types of coordinate systems are possible: oblique Cartesian coordinates, semilogarithmic coordinates, polar coordinates, spherical polar coordinates, confocal elliptical coordinates, etc. You will meet some of these in later sections of the book. One value of a graph, of course, is that it allows you to estimate slopes, intercepts, and approximate points where two or more curves intersect.

An important point to realize is that it is possible to transpose a function originally graphed in one coordinate system into an equivalent function graphed in another coordinate system, provided one applies certain definite algebraic transformations to the original function. Thus consider the equation

$$\sqrt{x^2+y^2}=\frac{y}{\sqrt{x^2+y^2}}$$

which may be rearranged to give the equation

$$\left(y-\tfrac{1}{2}\right)^2+x^2=\left(\tfrac{1}{2}\right)^2.$$

If we now permit multivalued functions, then the graph is a circle of radius $\frac{1}{2}$ and origin at $(0,\frac{1}{2})$ as shown in Figure 1.3*a*.

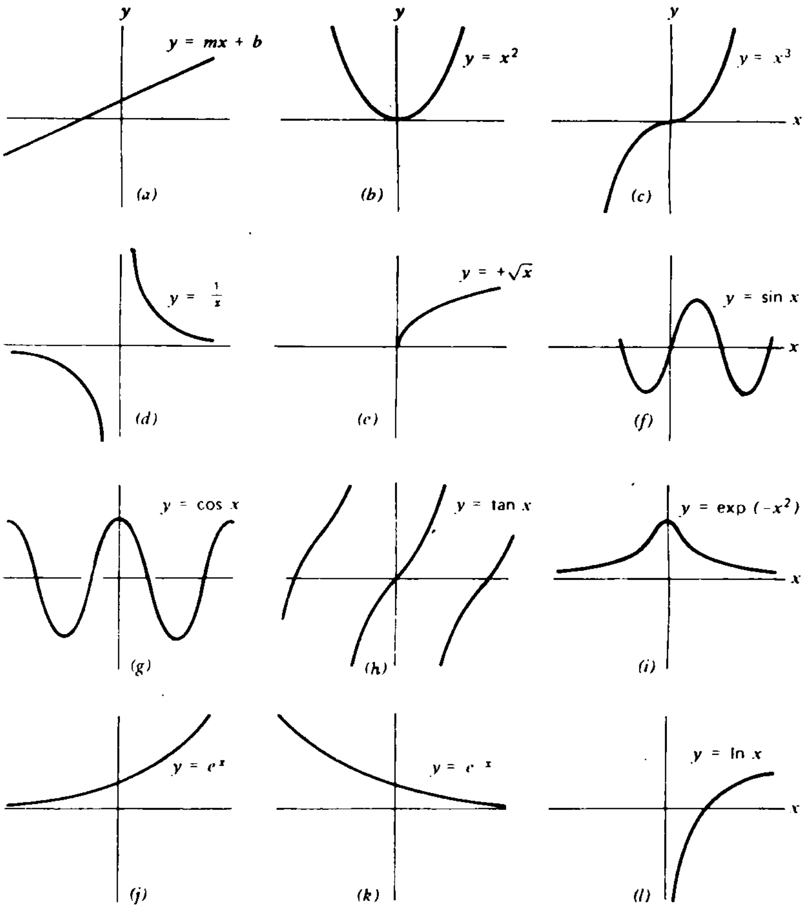

Fig. 1.2 Graphs of some common functions.

On the other hand, polar coordinates r, θ may be defined with reference to a right triangle (Figure 1.4) to yield the set of transformation equations

$$\boxed{\begin{aligned} x &= r\cos\theta \\ y &= r\sin\theta \end{aligned}},$$

and if these relations are substituted into the equation above, the result becomes $r = \sin\theta$. At this point we can do one of two things: either erect a

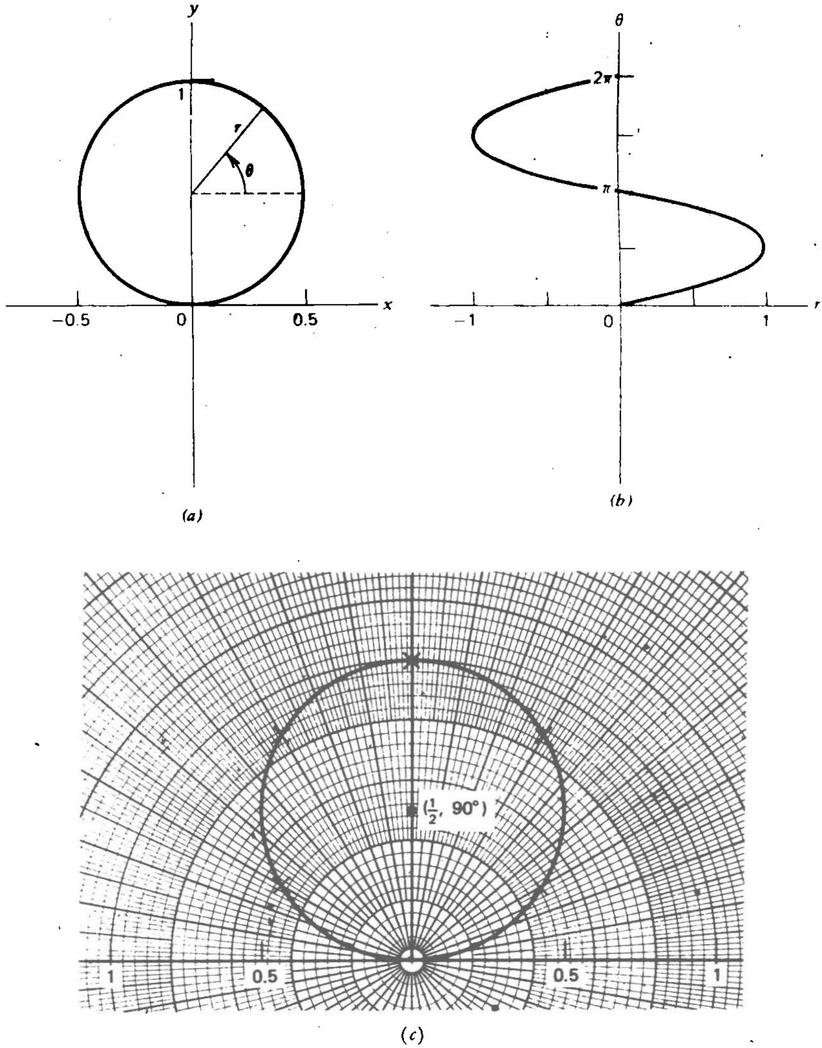

Fig. 1.3 Graph of a function and its equivalent in (*a*) rectangular Cartesian coordinates; in (*b*) polar coordinates, plotted on rectangular axes; and in (*c*) polar coordinates, plotted on polar coordinate axes.