Mathematics for Physical Chemistry

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For Rhona,
to whom I owe so much.

I advise my students to listen carefully the moment they decide to take no more mathematics courses. They might be able to hear the sound of closing doors.

James Caballero, *CAIP Quarterly* 2 (Fall, 1989)

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PREFACE

From years of advising undergraduate students in the sciences, a favorite quotation of mine is from James Caballero and appears as the epigraph to this book: “I advise my students to listen carefully the moment they decide to take no more mathematics courses. They might be able to hear the sound of closing doors.” This book is written for those students. It is the outgrowth of a collection of MathChapters from my *Physical Chemistry: A Molecular Approach*, which I wrote with John Simon several years ago, and from my *Quantum Chemistry*, which recently was published in its second edition. These MathChapters consist of concise reviews of mathematical topics, discussing only the minimum amount that you need to know to understand subsequent material. From years of publishing scientific texts, my publisher says that physical chemistry is difficult because of the mathematics, but it is impossibly difficult without it. The point of the MathChapters is that by reading these reviews before the mathematics is applied to physical chemistry topics, you will be able to spend less time worrying about the math and more time learning the physical chemistry. A number of people suggested that I expand these MathChapters into a single volume, and this book is the result.

One thing that makes mathematics courses difficult for many science students is that they are taught by professional mathematicians, whose primary interest is to develop mathematics for its own sake, often without regard to applications. Consequently, they appreciate and recognize the need for rigor by carefully specifying each and every condition for the validity of theorems and the use of certain techniques. Most science students simply want to apply mathematics to physical problems and bring a certain degree of physical intuition into their mathematics courses and feel that the rigor is excessive. Unfortunately, this intuition is not always correct. Since the development of calculus in the 17th and 18th centuries, mathematicians have discovered many counterintuitive examples of functions that are supposed to display certain behavior. For example, there is a function that is continuous at every point but has a derivative nowhere. In fact, there is an entire book on mathematical counterexamples, *Counterexamples in Analysis*, by B.R. Gelbaum and J.M.H. Olmsted, published by Dover. These counterexamples rarely arise in physical problems but are of central importance in mathematics. Thus, there is a natural and justifiable dichotomy between the people who teach mathematics and many of the students who take mathematics. I don't know the source of this saying, but it goes, "Applied mathematicians don't understand pure mathematicians and pure mathematicians don't trust applied mathematicians."

There are 23 chapters in the book. Each one is fairly short, with the longest one being 20 pages, and is meant to be read at a single sitting. The material is presented at a practical level with an emphasis on applications to physical problems, although a few theorems along with their conditions are given. Each chapter contains several Examples, which serve to illustrate the techniques that are discussed. No one can learn physical chemistry (nor anything else in the physical sciences for that matter) without doing lots of problems. For this reason, I have included about 30 problems at the end of each chapter. These problems range from filling in gaps to extending the material presented in the chapter, but most illustrate applications to physical problems. All told, there are over 600 problems, and I have provided answers to most of them at the end of the book.

Throughout the book, I encourage you to learn how to use one of a number of general mathematics programs such as *Mathematica*, *Maple*, or *MathCad*, which are collectively called computer algebra systems (CAS). For a comparison of these various CAS, see *http://en.wikipedia.org/wiki/Computer_algebra_system*. These CAS make it easy to do calculations routinely that were formerly a drudgery. Most chemistry departments have a license for one of these programs. These programs not only perform numerical calculations but also can perform algebraic manipulations. They are relatively easy to learn and to use, and every serious science student should know how to use one of them. They allow you to focus on the underlying physical ideas and free you from getting bogged down in algebra. They also allow you to explore the properties of equations by varying parameters and plotting the results. In fact, all the figures in the book were produced by Professor Mervin Hanson of Humboldt State University using *Mathematica*. There are a number of problems that require the use of one of these programs, and many others are made much easier by using one of them.

Another product of the computer age is the availability of websites for most any topic, and that is true for mathematics as well. At one time, most physical chemistry students owned some sort of math handbook such as the *CRC Standard Math Tables*, which contained tables of trigonometric formulas, a table of integrals, and many other tables, but these are all available online nowadays. I have suggested websites for many topics throughout the book. Websites have the distressing habit of disappearing now and then, and I have tried to include only those that I think might still exist when you go to them. If by any chance you can't open one of them, you'll probably find it and many others by going to Google. There is a complete list of the websites that I refer to in the References at the end of the book.

It always amazes me just how many people are involved in the production of a book. Foremost are the reviewers, who frequently save me from promulgating my misunderstandings and misconceptions. I wish to thank Scott Feller of Wabash College, Mervin Hanson of Humboldt State University, Helen Leung and Mark Marshall of Amherst College, and John Taylor of the University of Colorado for very helpful reviews. I also wish to thank Christine Taylor and her crew at Wilsted & Taylor Publishing Services and particularly Jennifer Uhlich, who could not have done a more conscientious or competent job of turning a manuscript into a beautiful-looking and inviting book, and Yvonne Tsang for designing a great-looking book; Jennifer McClain for superb copyediting; and Bill Clark and Gunjan Chandola at ICC Macmillan for one of the best jobs of composition that I have experienced. I also wish to thank Mervin Hanson for rendering and rerendering all the figures in *Mathematica* without one crusty word, Jane Ellis of University Science Books for overseeing many of the production details and for suggesting the cover that ties in so well with the epigraph by James Caballero, and Bruce Armbruster and his wife and associate, Kathy, for being the best publishers around and good friends in addition. Finally, I wish to thank my wife, Carole, for preparing the manuscript in TeX, for reading the entire manuscript, and for being my best critic in general (in all things).

There are bound to be both typographical and conceptual errors in the book, and I would appreciate your letting me know about them so that they can be corrected in subsequent printings. I would also welcome general comments, questions, and suggestions at *mquarrie@mcn.org*, or through the University Science Books website, *www.uscibooks.com*.