CHAPTER 1

Introduction: A Physical Chemists's Toolbox

"Indocti discant, amentque meminisse periti."
Charles Jean Hénault (1685–1770) in *Nouvel Abrégé Chronologique de l'Histoire de France jusqu'à la Mort de Louis XIV*

Jack Sherman: "Dr. Pauling, how does one get good ideas?"

Linus Pauling: "Well, I guess one must have many ideas, and throw away the bad ones."
Linus Carl Pauling (1901–1994)

"Never give in. Never give in. Never, never, never, never give in."
Sir Winston Churchill (1874–1965) at Harrow School, 29 October 1941

This compendium, "vademecum," or toolbox is an abbreviated introduction to, or review of, theory and experiment in physics and chemistry. The term "vade mecum" or "go with me" was the first tentative title for this book; it was associated with the learned and boring Baedeker® guidebooks for travel in the early 1900s: These Baedekers have been replaced with heavily illustrated and less boring Dorling–Kindersley® guides. Most students in 2011 who know some Latin would ask "vade mecum?" go with me? where? why?

The intended audience for this toolbox is the beginning researcher, who often has difficulty in reconciling recent or past classroom knowledge in the undergraduate or first-year graduate curriculum with the topics and research problems current in research laboratories in the twenty-first century. While several excellent and specialized monographs exist for all the topics

The Physical Chemist's Toolbox, Robert M. Metzger.

discussed in this book, to my knowledge there is no single compact book that covers adequately the disparate techniques needed for scientific advances in the twenty-first century. In particular, there is a need to find "What will this or that technique do for my research problem?" The aim of this toolbox is thus fourfold:

1. Summarize the theory common to chemistry and physics (Chapters 2–6).
2. Introduce topics and techniques that lead to instrumentation (Chapters 7–9).
3. Discuss the advanced instrumentation available in research (Chapters 10 and 11).
4. Travel a path from crystals to nanoparticles to single molecules (Chapter 12).

The book is interspersed with problems to do: some trivial, some difficult. This expedient can keep the volume more compact, and it becomes a useful pedagogical tool. This book tries to be a mathematically deep, yet brief and useful compendium of several topics, which can and *should* be covered by more specialized books, courses, and review articles.

Throughout, the aim is to bring the novice up to speed. The teaching of chemistry leaned rather heavily toward mathematical and physical rigor in the 1960s, but this fervor was lost, as chemical, physical, and biochemical complexity eluded simple mathematical precision. Alas, chemical and biological phenomena are usually determined by small but significant differences between two very large quantities, whose accurate calculation is often difficult!

Lamentably, the recent educational trend has been to train what could be called one-dimensional scientists, very good in one subfield but blissfully unaware of the rest. It is sad that we no longer produce those broadly trained scientists of past generations, who were willing to delve into new problems far from their original interest: I am thinking of Hans Bethe, Peter Debye, Enrico Fermi, Linus Pauling, or Edward Teller. This toolbox tries to adhere to this older and broader tradition, redress the temporary malady, and help restore the universality of scientific inquiry.

To the instructor: This toolbox could form the basis of a one-year graduate course in physical chemistry and/or analytical chemistry, perhaps team-taught; it should be taught with mandatory problem sets (students will connect the dots by doing the suggested problems) and with recourse to traditional texts that cover, for example, quantum mechanics or statistical mechanics in much greater detail. I am reminded of the very successful one-year team-taught courses such as "Western Civilization" at Stanford University in the 1960s! I have taught the toolbox several times at the University of Alabama as a one-semester course, but found the pace exhausting.

To the many students who took my course: Thanks for being so patient.

To Chemistry and Physics departments: The toolbox could become a valuable resource for all entering graduate students, so maybe students, even in areas far from physical chemistry, should be encouraged to buy it and work at it on their own.

To the student: (1) Do the problems; (2) read around in specialized reference texts that may be suggested either in this toolbox or by your instructor(s); (3) discover whether the toolbox could be developed in new directions.

To myself: To adapt Tom Lehrer's (1928–) famous quip, I am embarrassed to realize that at my present age Mozart had been dead for 36 years.

Alan MacDiarmid (1927–2007) once said "Chemistry is about people": In this spirit, full names and birth and death dates are given to all the scientists quoted in this book; such brief historical data may help illuminate how and when science was done. I have resisted mentioning who was a Nobel prize winner: too many to list, and some worthy scientists—for example, Mendeleyeff, Eyring, Edison, Slater, and Tesla—were not honored. I owe a deep debt of gratitude to many people who have educated me over several decades, as live teachers and silent authors. In particular, I am indebted to Professor Willard Frank Libby (1908–1980), who taught us undergraduates at UCLA to love current research problems and led us into quite a few wild-goose chases; Professor Harden Marsden McConnell (1927–), who led us at Caltech and Stanford by example to see what are the interesting problems and what are "trivial" problems; Professor Linus Carl Pauling (1901–1994), who taught me electrical and magnetic susceptibilities with his incomparable photographic recall of data and dates, and with his insight and humanity about current events; Dr. Richard Edward Marsh (1922–) and Professor Paul Gravis Simpson (1937–1978), who taught me crystallography; Professor Michel Boudart (1925–), who introduced me to heterogeneous catalysis; Mr. William D. Good (1937–1978), who taught me combustion calorimetry; Professor Sukant Kishore Tripathy (1952–2000), who introduced me to Langmuir–Blodgett films; and finally, Professor Richard Phillips Feynman (1918–1983), who taught me about the Schwartzschild singularity and event horizons and who was a source of deep inspiration, pleasant conversations, and mischievous fun. Thanks are also due to two persons who helped me greatly in my academic career and taught me a thing or two about what good science really means: Professor Andrew Peter Stefani (1927–) of the University of Mississippi and Professor Michael Patrick Cava (1926–2010) of the University of Alabama. Professor Carolyn J. Cassady (University of Alabama) kindly allowed me to use an experiment she had devised for students of mass spectrometry.

The following books have inspired me: (1) *Principles of Modern Physics* by Robert B. Leighton, (2) *Theoretical Physics* by Georg Joos, (3) *The Feynman Lectures on Physics* by Richard P. Feynman, and (4) *Principles of Instrumental Analysis* by Doug Skoog, James Holler, and Stanley Crouch. In this twenty-first century, much help was obtained on-line from Wikipedia, but "*caveat emptor*"!

Writing is teaching but also learning; Marcus Porcius Cato (234–149 BC), who was echoing Solon (630–560 BC), said "I dare to say again: '*senesco discens plurima*.'"

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Dr. Ralph H. Young (Eastman Kodak Co.), and Adam Csoeke-Peck (Brentwood, California). The errors that remain are all mine; *errare humanum est, sed perseverare diabolicum* [Lucius Anneus Seneca (ca. 4 BC–AD 66)]. To the reader who finds errors, my apologies: I will try to correct the errors for the next edition; echoing what Akira Kurosawa (1910–1998) said in 1989, when he received an honorary Oscar for lifetime achievements in cinematography: "So sorry, [I] hope to do better next time."