

Media Reviews

Crime Scene to Court: The Essentials of Forensic Science. Edited by Peter White. The Royal Society of Chemistry: Cambridge, UK. 1998. ISBN 0-85404-539-2. Softcover, xxiv + 360 pp. Price 19.95 pounds.

When I was much younger than I am now, I read the collected works of Sir Arthur Conan Doyle. For months I lived and breathed Sherlock Holmes, trying to learn the tricks of the trade and understand the basis of being a good detective. After all, a crime scene can inform only if you know what you are looking for. Is the criminal left or right handed? What color is his or her hair? For that matter, is the criminal male or female? Clues, such as the striking pattern of a chisel used to open a window and the relative height of the chisel marks, can tell a detective a great deal.

It is, of course, unrealistic to expect a book on the "Essentials of Forensic Science" to match the feats of the great detective. This is not a literary piece and is not written to entertain the reader. Indeed, it is written for the well, that is the problem that I had with this book. I could never understand who the audience was supposed to be. In the preface, the editor lists prospective readers: the general public with an interest in forensics, police, post- and undergraduate forensic science and law students, forensic scientists and crime scene examiners starting their careers, and people who are not connected with a forensic profession but appear as expert witnesses. Whew! That is a remarkably broad and diverse group of people and I must add that I don't belong to any of these groups, except maybe the first one. But in trying to appeal to and satisfy the knowledge demands of this group, the authors, in my opinion, fail to satisfy the needs of any of them. For example, take the description of infrared spectroscopy:

"With this technique, individual fibre fragments are squashed into a film through which infrared light is passed. The ways in which the chemical structure of the film reacts with the infrared light is ... recorded in the form of a printed graph in which the various peaks can be used to determine the chemical identity of the material."

I have absolutely no doubt that the contributor who wrote this description understands infrared spectroscopy. But for whom is it written? For the forensic scientist, this strikes me as a very poor explanation of both the intricacies of the method and the diversity of the results that can be obtained, along with its broad applicability. If it is written for the lawyer or the lay public, what understanding have they gained by reading it? Only that the technique can identify various materials. But there is nothing to assure us that it *truly* can do so, other than the expert opinion of the author.

This is just one example, but one that typifies the treatment of detail in many chapters. Either I want to know a lot more or a lot less, but I don't want to be stranded in the middle! This inability to properly identify a target audience persists throughout the book. The book might be expanded with discussions of real cases with real evidence and real descriptions. It might be contracted to a much simpler publication. In its present form, though, it serves none of its possible audiences even adequately.

While this book represents a good attempt to explain a complex subject, it needs to focus much more clearly on an

intended audience. The expertise that the various authors bring to bear in their respective chapters could then be truly appreciated.

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Advanced Inorganic Chemistry, Sixth Edition. By F. Albert Cotton, Geoffrey Wilkinson, Carlos A. Murillo, and Manfred Bochmann. John Wiley & Sons, Inc.: New York, 1999. Figures, tables. xv + 1355 pp. 18.5 × 26.0 cm. \$89.95, 58.50 pounds sterling. ISBN 0-471-19957-5.

In the Spring of 1952 a 21-year-old student from Philadelphia, Pennsylvania (A.B., Temple University, 1951) enrolled in a first-year graduate course in inorganic chemistry at Harvard University. The young (30-year-old) British assistant professor found it difficult, if not impossible, to find a satisfactory textbook for his course. Among recently published books Nevil Vincent Sidgwick's massive, two-volume *The Chemical Elements and Their Compounds* (Oxford University Press: Oxford, 1950; 1628 pp), although a gold mine of information, was hardly appealing as a text. The only available option was Harry Julius Emeléus and J. S. Anderson's *Modern Aspects of Inorganic Chemistry* (Van Nostrand: Princeton, NJ, 1938 and 1952), which was not really a text but rather a collection of reviews of interesting new areas. Early in 1952 Therald Moeller's *Inorganic Chemistry: An Advanced Textbook* (Wiley: New York) appeared, but although its treatment of general principles and the descriptive chemistry of the main group elements were adequate, only about 7% (ca. 65 of 910 pages) were devoted to the transition elements.

Therefore the professor and the student, who had already chosen him as his Ph.D. mentor, decided that as soon as they were in a position to do so, they would write a balanced textbook of inorganic chemistry for senior and first-year graduate students at American universities—a decision that would profoundly affect the teaching of inorganic chemistry for an entire generation of students. The professor's name? Geoff (later Sir Geoffrey) Wilkinson, the late 1973 Nobel chemistry laureate and Sir Edward Frankland Professor of Chemistry at London's Imperial College of Science, Technology, and Medicine. The student's name? Al Cotton, later W. T. Doherty-Welch Foundation Distinguished Professor of Chemistry and Director of the Laboratory for Molecular Structure and Bonding at Texas A&M University as well as recipient of numerous prestigious awards, including the Priestley Medal (1998), the American Chemical Society's highest award. And the rest, as they say, is history.

The book was written, as were all later editions, with the authors an ocean apart. Yet, although each possessed different approaches to his own research, the two authors had a spontaneous harmony in their writing. Also, because each edited what the other had written, there was little, if any, variation in style from one chapter to another. An entire decade was to elapse before *Advanced Inorganic Chemistry: A Comprehensive Text* (Wiley: 1962, 925 pp) was to appear. The



F.A.Cotton and G.Wilkinson at a meeting in Ettal, Germany in 1974.

book was the first inorganic text, at any level, to present an introduction to ligand field theory (LFT), which by that time had become very prominent in the research literature and hence should have been discussed in inorganic chemistry courses. It was a systematically organized work dealing with all the elements from hydrogen to the actinides, with a reasonable allotment of space to each. The concepts of LFT were not only expounded but also brought to bear on the magnetic and spectroscopic properties of each of the transition elements as its chemistry was discussed. Other innovations included tables of oxidation states and stereochemistries of each metallic element, with examples of each and with a strong emphasis on structural chemistry in general. These, and other methods of treating the subject that were new at the time, have continued to shape the coverage in all subsequent editions.

Cotton and Wilkinson's text has evolved during the more than three and a half decades since its inception, while the authors learned more about the field as it underwent a veritable renaissance. The first edition contained a good deal of bonding theory, notably LFT, that has since been deleted because it is now discussed in lower level courses. It gave only a few references to the secondary literature such as reviews and monographs. Because of the rapid growth of the subject, references to the primary literature were first introduced in the second edition (1966), and this practice has continued to the present. The second through sixth editions contain a total of about 13,000 references, including about 4100 in the sixth. With the third edition (1972) the authors adopted a policy of presenting new references only for new material, a policy that they have continued. (With the exception of three earlier references in tables or figures, the references in the sixth edition range from 1987 to 1998). Thus, through the years, the various editions of this phenomenally successful and popular text present an extensive historical record of when and where new facts and new ideas were first reported.

After the appearance of the second edition, the book firmly established itself as the standard text for advanced inorganic courses. Although the second, third, and fourth (1980) editions were translated into seven, four, and four foreign languages, respectively, the first and fifth (1988) editions were never translated, probably because of the emerging dominance of English as the *lingua franca* of science beginning in the 1960s.

The first edition was a true textbook, admirably suited for teaching. To accommodate new descriptive material, however,

the authors had to eliminate more and more theoretical background to the point where only a minimum is present in the sixth edition, which is as much a reference book as a textbook. Cotton and Wilkinson were forced to make this change in character in order to adhere to a double goal to which they were irrevocably committed—to make each edition a book that would prepare the reader to understand the contemporaneous research literature and to keep it within one volume, albeit a hefty one. By the time that the fifth edition appeared, the book had become so thick and hefty that Al Cotton joked that for \$2 extra it would be available in a special binding with wheels and a pull-strap like airline luggage!

The sixth edition involves significant changes. Because of the ever-accelerating rate of the growth of the inorganic research literature, Cotton and Wilkinson found the writing of the fourth (1980) and fifth (1988) editions to be more and more laborious. As they began to plan the latest edition during 1993 or 1994, they decided to include two additional co-authors, both former students, to reduce their burden of research and composition. Cotton chose Carlos Murillo, Professor of Chemistry at the University of Costa Rica and Adjunct Professor of Chemistry at Texas A&M University, and Wilkinson chose Manfred Bochmann, Professor of Chemistry at the University of Leeds in the United Kingdom. They divided the responsibilities for the first draft into four approximately equal portions. Fortunately, Sir Geoffrey was able to finish written drafts of all his chapters only days before his unexpected death of cardiac arrest on September 26, 1996 at the age of 75 years.

Cotton and Wilkinson also decided to ask Russell N. Grimes, Professor of Chemistry at the University of Virginia, Charlottesville, to revise the chapter on boron, which has been almost completely rewritten and rearranged. In Cotton's words, "This vast and idiosyncratic subject had always been a *bête noire* to both of us, and we had passed it back and forth between us from one edition to the next like a hot potato."

Because this text is well known to chemical educators and research chemists alike, I shall concern myself here primarily with the differences between the fifth and sixth editions. Like its predecessors, this latest edition is organized according to the periodic table of the elements. The fifth edition employed the older Roman numeral group numbers with the newer Arabic numeral group numbers in parentheses, but the new edition uses the latter designations exclusively. The authors have eliminated several of the broad topical chapters previously included, e.g., "Bioinorganic Chemistry" or "Organometallic Chemistry," and have enlarged coverage of the individual elements or groups by dealing with this chemistry on an element-by-element basis. However, this change does not necessarily correspond to a reduction in space devoted to important topics, e.g., more rather than less space is now allotted to the biochemistry of iron. In arrangement of material, the latest edition is more like the third edition than the fourth or fifth editions, but the amount of material is much greater. Although a few of the chapters remain relatively unchanged, in general the text shows evidence of judicious rearrangement and careful rewriting of chapters and of material within sections.

Part 1, "Survey of Principles," the shortest part (45 pp), has been condensed from two chapters ("Concepts in Stereochemistry and Bonding" and "Introduction to Ligands and Complexes," 81 pp) to one, "Some Cross-Cutting Topics,"

that are best treated generically, such as the new sections on relativistic effects, Zintl compounds, chemical vapor deposition, and inorganic materials. Part 2, "The Chemistry of the Main Group Elements" (579 pp), has been increased slightly from 534 pp. Part 3, "The Chemistry of the Transition Elements," the longest part, has been increased by 35% from 393 to 532 pages.

Part 4, "The Role of Organometallic Chemistry in Catalysis" (128 pp), now consists of two chapters, "Fundamental Reaction Steps of Transition Metal Catalyzed Reactions" (62 pp) and "Homogeneous Catalysis by Transition Metal Complexes" (66 pp). It replaces the much longer earlier part, "Survey of Selected Areas" (366 pp), which consisted of nine chapters: "Transition Metal Carbon Monoxide Compounds" (31 pp), "Metal-to-Metal Bonds and Metal Atom Clusters" (45 pp), "Transition Metal Compounds with Bonds to Hydrogen" (25 pp), "Compounds with Transition Metal Single, Double, and Triple Bonds to Carbon" (30 pp), "Compounds of Transition Metals Alkenes, Alkynes, and Delocalized Hydrocarbon Systems" (34 pp), "Oxidative-Addition and Migration (Insertion) Reactions" (38 pp), "Homogeneous Catalytic Synthesis of Organic Chemicals by Transition Metal Complexes" (59 pp), "Reaction Mechanisms of Transition Metal Complexes" (52 pp), and "Bioinorganic Chemistry" (42 pp).

Most of the corresponding chapters in the two editions are of similar length. Notable exceptions are the chapters on "Carbon" (50 pp vs. 31 pp in the fifth edition), "The Group 14 Elements" (51 pp vs. 40 pp), "Survey of Transition Elements" (59 pp vs. 24 pp), "The Elements of the First Transition Series" (185 pp vs 127 pp), and "The Elements of the Second and Third Transition Series," the longest chapter in both editions (231 pp vs 179 pp). New separate sections are devoted to fullerenes, nitrogen fluoride oxide, zinc enzymes, biological aspects of chromium chemistry, bioinorganic chemistry of iron, nickel in biological systems, organometallic nickel complexes, biochemistry of copper, low and very low formal oxidation states, organosilver compounds, subvalent silver compounds and silver clusters, gold clusters, and organogold compounds.

Once again, the book is liberally provided with numbered figures (329), tables (123), structural formulas (762), bottom-of-page references (3298, many cite several articles), and additional references at the end of chapters (144, some with annotations) as well as countless unnumbered equations. The five useful appendices (31 pp) remain unchanged except for the addition of a table of conversion factors. Considering the immense size and scope of the book, however, the index (29 double-column pages, reduced from 45 double-column pages in the fifth edition) seems inadequate. However, inasmuch as the book is arranged according to the periodic system, finding specific material is not difficult.

Again, the authors have spared no pains in revising what has been a balanced, comprehensive, up-to-date, and most successful text. Many of the figures and graphs have been redrawn, and the use of larger and darker type for section headings make this edition more legible and attractive than the previous one. Without allowing the size of the book to get out of hand (the sixth edition is 100 pages shorter than the fifth edition!), they have significantly increased the amount of factual material and still attained their goal of providing "the [senior or first-year graduate] student with the background

necessary to comprehend current research literature in inorganic and certain aspects of organometallic chemistry." For this pedagogical triumph they deserve our profound thanks. And, furthermore, in view of the huge amount of well-organized and cutting-edge material in this text, its reasonable price makes it a "best buy."

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Beginning Group Theory for Chemistry. By Paul H Walton. Workbooks in Chemistry Series, Oxford University Press: Oxford, England. 144 pp, & pound;16.95.

Group theory is an "all or nothing" topic within university chemistry courses: students either fail completely to get through its rather abstract nature or, alternatively, score very highly on problem-oriented exam questions. Any book that can transform the former into the latter will be welcomed by staff and students alike, and in general the Walton workbook will help do this. In content it is midway between two other established texts. It has the textual, explanatory component of Davidson's *Group Theory for Chemists* combined with the "self-learning through problems" method initially adopted by Vincent in his book *Molecular Symmetry and Group Theory*. In combining the two approaches, Walton has produced a book that contains sufficient explanatory material to act as a textbook to support a traditional lecture course, while giving students the chance to evaluate their understanding through regular self-assessment questions, supported by model answers which follow immediately. Additional problems at the end of each chapter that require the students to apply their acquired knowledge would have been useful, but this does not markedly detract from the format, as these can be found in other widely available texts.

After a brief Introduction, Chapter 2 deals with symmetry operations and point groups. Provided students have purchased model kits, this topic should not prove too difficult and the chapter follows traditional lines. Chapters 3 and 4 discuss groups and their representations, and form the interface between symmetry (and its application in vibrational spectroscopy) and bonding. This is usually the point at which students become lost, and the correct balance is important. It is also the most difficult task facing anyone teaching group theory and is inevitably the most contentious. The idea of "a group" is introduced using the analogy of soldiers on parade who can turn about, left, or right; this is an uncomplicated way of showing how operations can combine. The jump to replacing operations by integers requires the student to guess valid representations and, as this can be a little hit or miss, it may frustrate the unlucky guesser. Asking students to demonstrate that a certain collection of integers is a faithful representation of the operations would take students to the same point a little quicker.

Chapter 4 covers matrices, characters, and their use as representations and is a chapter that the author suggests (but does not recommend) nonmathematically minded students can omit. I can't agree with this. Matrices are the mathematical link between symmetry operations and groups and are not so difficult they cannot be explained with some simple examples. What is more difficult is for students who have ignored this

chapter to take at face value a series of statements which define *basis*, *reducible* and *irreducible representations*, and *characters* at the outset of Chapter 5, which is entitled "The Heart of Group Theory." I can't help feeling that this latter crucial chapter is lost before it is begun without Chapter 4. Chapter 4 also introduces the idea of *chi per unshifted atom* and I find it surprising that, in a book that asks students to verify their understanding through regular self-assessments, this important concept is dismissed with the phrase "*these equations can be easily verified by writing out the appropriate full matrix*" but without further discussion. Perhaps it is in anticipation of many students omitting this chapter, but when the same concept reappears later in the book, its origin must be a puzzle to many.

Notwithstanding the above comments, Chapter 5 describes the use of the reduction formula in a clear manner which students will find particularly helpful. It is then used to derive irreducible representations for the hydrogen 1s orbitals in H₂O, which immediately makes a link with MO theory and places a rather abstract concept into a chemical context. Chapter 6 continues the applications theme and describes the use of group theory in the analysis of vibrational spectra. In so far as it reinforces the use of the reduction formula, this chapter is well presented. This is followed by the use of projection operators to describe the form of the various vibrational modes and here I am less sure how well this fits into a beginners' course. It is helpful to show how a pictorial view of stretching–bending modes can be derived, but in simple cases (e.g., the symmetric and antisymmetric stretching modes for H₂O) the A₁ and B₂ symmetries are easy to demonstrate by other means. I can't see much point in extending this to degenerate cases where the choice of generating coordinate is, as the author quite rightly says, *beyond this text*. This then leaves the student with a knowledge of the methodology but not the ability to apply it generally. I think this is a question of where one draws the line defining a beginners' course, and for those courses that emphasize the use of projection operators, what is incorporated in the workbook is of value.

The issue of relevance continues through the latter part of the chapter, where selection rules for IR and Raman spectroscopy are demonstrated using direct products. The same discussion applies here as to projection operations, but whatever one's view on this I can't understand why the basic rules are not more clearly spelled out: IR modes have the same symmetry as T_x , T_y , or T_z and Raman active modes the symmetry of one of the binary terms. In practice, this is what is actually used.

The workbook concludes with a more detailed look at the application of group theory to molecular orbital problems and much the same comments apply to this chapter as to that on vibrational spectroscopy. The generation of reducible representations and their combination in the correct manner to form MOs is clearly explained, but the shortcut that the symmetries of orbitals on the central atom can be read directly from the character table lies buried in Chapter 5. It seems a general weakness of the workbook that these key shortcuts are not highlighted more forcefully. Projection operators again figure heavily in this chapter, both for terminal atom SALC combinations and for molecules without a central atom. There is nothing wrong with this, other than its value in a beginners' book. Personally, I find that reasonably good pictorial representations can be arrived at simply by using the nodal

patterns for linear arrays of orbitals, and increasing the number of nodes symmetrically as energy increases, cyclic arrays being derived from these by joining the ends of the appropriate linear array (there are very useful diagrams in, for example, *Inorganic Chemistry* by Purcell and Kotz). While such an approach is not as rigorous as the projection operator method, it is far easier for students to assimilate.

Overall, it is easier to be critical of a book than to praise it, and this review might sound more negative than intended. No book is read by students in isolation and without recourse to lecture material. As a book that students can work through to support lectures it has much to commend it and, as the author points out, group theory is one of those topics where practice does indeed make perfect. The book is logically arranged and contains a good balance of background, vibrational spectroscopy, and bonding. It is not unreasonably priced at about £16 and I shall certainly be asking our bookstore to stock it. I will also recommend it to my students as a book they should consider using as part of their learning strategy.

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Energy Levels in Atoms and Molecules. By W. G. Richards and P. R. Scott. Oxford University Press: Oxford, UK, 1994; 96 pp, 246 mm × 189 mm, softcover ISBN 0-19-855804-X, £ 6.99.

I enjoyed reading this well-written and easy-to-read book, one of the Oxford Primer Series. It is constructed somewhat like a collection of lecture notes; all topics are treated at a level appropriate to senior undergraduates or postgraduate students.

Energy levels in atoms are treated first, starting with the photoelectric effect, wave–particle duality, units and measurements, and the electromagnetic spectrum. Energy levels of the hydrogen atom are used to introduce wave mechanics, quantum numbers, hydrogen wave functions, electron spin, Pauli principle, the periodic table, Hund's rule, and ionization energies. The energy levels of atoms are discussed with coupling of angular momenta, Russell–Saunders coupling, term symbols, and closed electron shells. This is followed by a discussion of some simple atoms, helium as a model for photochemistry, spin–orbit coupling, and *jj* coupling.

The second chapter concentrates on diatomic molecules. It deals with the orbital and LCAO approximations, bonding and antibonding molecular orbitals, molecular orbital diagrams, molecular electronic energy levels, vibrational energy levels, rotational energy levels including the effects of nuclear spin, excitation energies, and populations.

The third chapter extends the discussion to polyatomic molecules. It deals with orbitals in polyatomic molecules, water, molecular shape, sp³ and other hybridizations, delocalization in benzene, excited states in organic compounds, Walsh diagrams, transition metal complexes in their ground and excited states, Rydberg states, photoelectron spectroscopy, vibrational energy levels and characteristic frequencies, rotational energy levels, and inversion in ammonia.

Energy levels in NMR are discussed in the final chapter, which includes the effect of magnetic fields on atomic energy levels, basic principles of NMR, chemical shifts, spin-spin

coupling, rate processes, double resonance, NMR of solids, relaxation times, basic principles of ESR, hyperfine structure, and the g value.

This final chapter on NMR seems somewhat out of place compared to the remaining subject matter. Perhaps it would be more appropriate to include a chapter on "Energy Levels Between Spin States," with a general description of spin resonance methods such as NMR, ESR, Mossbauer, MuSR, etc. Only magnetic field effects are discussed; an additional discussion of electric field effects would have made this section more complete. Another significant omission is the energy levels due to magnetic exchange between metal atoms. My enjoyment of the book was marred by several typographical errors. Those that seem to affect the logic of the discussion are given below.

Appendix—typographical errors

Page 22, 6th line: The term symbols should be $^2P_{3/2}$ and $^2P_{1/2}$ and not $^2S_{3/2}$ and $^2S_{1/2}$.

Page 31, 7th line: The equation should be $p = 1s_A - 1s_B$

Page 49: Figure 3.3 depicting the sp^2 hybridization in ethene should be modified to show the correct geometry.

Page 55: The end of second paragraph says, thus for BH_2 : It should be for BH_2^+ .

Page 57, 5th paragraph: It is wrong to use the symbols t_{2g} and e_g for tetrahedral geometry. These should be simply t_2 and e .

Page 62: Table 3.3 gives no indication as to which vibration is being referred to. For example C=C-H has a frequency of $2260\text{--}2100\text{ cm}^{-1}$. This molecular unit has three vibrations; the authors should be more specific. C-O at $1780\text{--}1660\text{ cm}^{-1}$ is incorrect.

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