



Figure 2. Experimental (upper trace) and calculated (lower trace) off-resonance  $^1\text{H}$  decoupled  $^{13}\text{C}$  nmr spectra of the methine carbons of indan with  $\nu_2$  at low field from the proton resonances: (a)  $\Delta\nu = -230$  Hz; (b)  $\Delta\nu = -290$  Hz.

established.<sup>8,9</sup> The different fine structure in the doublets of the undecoupled  $\text{C}_\alpha$  and  $\text{C}_\beta$  resonance<sup>8</sup> (Figure 1a) becomes more distinct on off-resonance decoupling (Figure 1b,c), thus enabling a better differentiation. This is of special interest in cases with small  $^1\text{H}$  chemical shift differences (less than 10 Hz), where normal off-resonance decoupling fails because condition 3 is violated and where the fingerprints in the single resonance spectrum disappear.<sup>8</sup> Even more important, calculations (see below) show that fingerprints in the off-resonance  $^{13}\text{C},\{^1\text{H}\}$  nmr spectra are also observed for zero chemical shift between  $\text{H}_\alpha$  and  $\text{H}_\beta$ . Furthermore, since part of the Overhauser enhancement<sup>12</sup> is retained during partial decoupling, the fingerprint method becomes more sensitive than in the undecoupled  $^{13}\text{C}$  nmr spectrum.

As shown in Figure 2, the fingerprints reappear after the decoupler frequency has been swept through the proton resonances. This corresponds to a reversal of the  $^1\text{H}$  chemical shifts and demonstrates that the technique does not depend on the  $^1\text{H}$  assignment.

To provide a firm basis for the interpretation of our

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(9) H. Günther, G. Jikeli, H. Schmickler, and J. Prestien, *Angew. Chem.*, **85**, 826 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 762 (1973). Two other groups<sup>10,11</sup> have measured the indane spectrum independently; they give, however, the reverse assignment.

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(11) G. W. Buchanan and R. H. Wightman, *Can. J. Chem.*, **51**, 2357 (1973).

(12) K. F. Kuhlmann and D. M. Grant, *J. Amer. Chem. Soc.*, **90**, 7355 (1968).

experimental findings, we have calculated theoretical off-resonance decoupled spectra using the well-known double-resonance Hamiltonian<sup>13</sup>

$$\mathcal{H} = \sum_i (\nu_i - \nu_2) \mathbf{I}_z(i) + \sum_{i < j} J_{ij} \mathbf{I}(i) \mathbf{I}(j) - \sum_i \gamma H_2 \mathbf{I}_x(i) \quad (2)$$

With a decoupler power of  $\gamma H_2 = 3000$  Hz (obtained by calibration using eq 1 and  $J_R$  in the  $^{13}\text{CHCl}_3$  resonance), the  $^{13}\text{C},^1\text{H}$  coupling constants of benzene,<sup>15</sup> and the relevant  $^1\text{H}$  nmr data of indan,<sup>16</sup> the spectra given in Figure 1e-g were obtained in excellent agreement with experiment (Figure 1b-d).<sup>17</sup>

As an application of the new technique, the  $\text{C}_\alpha$  and  $\text{C}_\beta$  resonances for benzocycloalkenes up to benzocyclooctene were assigned by inspection of the off-resonance  $^1\text{H}$ -decoupled  $^{13}\text{C}$  nmr spectra after the fingerprints for  $\text{C}_\alpha$  and  $\text{C}_\beta$  had been clearly identified by the indan experiment and the calculations (Figure 1). The results<sup>9</sup> show that the assignment given by Maciel, *et al.*,<sup>10</sup> and by Buchanan and Wightman<sup>11</sup> must be reversed.

Taking advantage of the increasing number of  $^{13}\text{C},^1\text{H}$  and  $^1\text{H},^1\text{H}$  coupling constants available, typical splitting patterns in off-resonance  $^{13}\text{C},\{^1\text{H}\}$  nmr spectra existing in other cases may be identified easily with the help of calculated spectra, thus leading to a facile  $^{13}\text{C}$  nmr assignment of high sensitivity. Alternatively, for a class of structurally similar compounds, the experimental spectra of one member with established  $^{13}\text{C}$  chemical shifts may be used for fingerprint identification.

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(13) E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969. For the calculations the program YBEDOS, based on the first part of the program LAOCOON II<sup>14</sup> was written; copies are available upon request.

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(15) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967).

(16) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **92**, 1605 (1970). The  $^1\text{H}$  assignment based on long-range coupling given there was confirmed by the spectrum of indane-5-d.

(17) A close inspection of the fine structure in each carbon resonance (Figures 1 and 2) reveals that each multiplet is changed to its mirror image upon reversal of the proton chemical shift, *i.e.*, upon sign change for  $\Delta\nu$ ;  $^1\text{H}$  resonances may thus be assigned.

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## Book Reviews\*

**Comprehensive Biochemistry.** Edited by M. FLORKIN and E. H. STOTZ. **Volume 30. A History of Biochemistry.** By M. FLORKIN (University of Liege). Elsevier Publishing Co., New York, N. Y. 1972. xviii + 343 pp. \$27.75.

According to the author, this book is "intended to retrace the long process of evolution in the science of biochemistry framed in a

conceptual background and in a manner not recorded in recent treatises." He has accomplished this in an interesting and informative manner.

The central themes of the historical development are the "matter-of-life" and the "forces-of-life." The first is concerned with the chemistry and mechanism of metabolic processes and the second

with bioenergetics. By limiting the discussions to these two seminal topics of biochemistry, the author has managed to sift adeptly through the almost prohibitive amount of historical material and write a readable narrative.

In the period called proto-biochemistry, the main contributors of ideas were the Greeks who postulated the existence of elements, the composition and decomposition of matter, and dynamic permanence. The first experimentalists were the alchemists who developed chemical processes such as distillation and sublimation and paved the way for the preparation of pure substances. The iatrochemists provided a more rational view of the chemistry of life processes, especially of respiration and digestion.

The speculative ideas and theories of the Greeks underwent careful scrutiny during the ensuing age of chemical revolution. Led by Lavoisier, Dalton, and Liebig, a new system of theoretical and experimental chemistry emerged. Experimentation with animals and development of vivisection techniques gave birth to physiological chemistry. Their results put an end to Liebig's theory of direct assimilation and showed that the processes of composition and decomposition were common to both animals and humans. The careful studies of Schwann then proved that the main unit of metabolic reactions was the cell.

The "forces-of-life" topic was discussed even by the Greeks. In its evolution, it has been called "vital force," "unknown in nature" and "vital principle." After the enunciation of the principle of conservation of energy and the development of the calorimeter, it was established that body heat resulted from metabolic reactions. Later it was to be shown that redox reactions produced the energy which is stored in ATP.

Another important landmark in the history of biochemistry was the discovery of enzymes, their chemical identification, and the delineation of their role in metabolic processes.

Finally, the biochemist, with the aid of the electron microscope, found his way into the cell. The idea of compartmentalization was evolved. Further historical developments will be discussed in Volumes 31, 32, and 33.

One of the main problems of writing a historical narrative is the proper choice of events and of persons whose contributions are most significant. I believe it has been done in this book. The author has included both positive and negative ideas, experiments that have led to erroneous conclusions, and others that have forged ahead the biochemical concepts. For students of the history of science and the historically minded biochemist, this book should prove appealing.

Gloria C. Toralbala, *H. H. Lehman College  
City University of New York*

**Electrodeics.** By HENRY H. BAUER (University of Kentucky). John Wiley and Sons, New York, N. Y. 1973. x + 131 pp. \$11.95.

After a long dry spell during which few books on the fundamentals of modern electrochemistry appeared, a number of texts and monographs in this area, of differing length and viewpoint, have been published recently. Professor Bauer's little book is designed, in the words of the series editor, "to acquaint a general audience with the present state of knowledge" in electrodeics, the study of electrode reactions. While this aim is perhaps overambitious for such a large field and such a concise treatment, the author is surprisingly successful in covering a large amount of material in a clear and generally nonmathematical treatment.

The book covers electrode potentials, kinetics of electrode reactions, the electrical double layer and adsorption, and electrochemical measurements at mercury and solid electrodes. The emphasis is on processes occurring at the electrode surface (about half of the book is devoted to adsorption and double-layer effects) rather than on techniques or electrode reaction mechanisms. Some very important topics, such as cyclic voltammetry, coulometric methods, bulk electrolysis, and electrochemistry in aprotic solvents, are hardly mentioned. Perhaps the book's strongest point is the author's insight into the real-world problems of making electrochemical measurements and his critical comments on techniques and definitions. While this book cannot by itself teach the field of electrodeics, Professor Bauer has provided a very useful guidebook to the area, with numerous references to more complete treatments, which should be of great assistance to newcomers in this field.

Allen J. Bard, *The University of Texas—Austin*

**Modern Petroleum Technology.** Fourth Edition. Edited by G. D. HOBSON (Imperial College of Science and Technology, London) and W. POHL. John Wiley & Sons, New York and Toronto. 1973. xiii + 996 pp. \$45.00.

The stated purpose of this book is "to provide a sound and comprehensive introduction to the scientific and technical aspects of the oil industry, in a form which will be intelligible and useful to the student, to the newer recruits to the industry, and to the oil man who wants to gain a sound understanding of those branches of the industry other than his own." The authors have achieved their purpose. All technical aspects of the petroleum industry are covered, from the origin of petroleum to the transportation of products. In line with the usual definition of the petroleum industry, petrochemicals are excluded.

In view of the introductory nature of each chapter, an expert on any subject is unlikely to find anything useful in his specialty. In fact, he may find statements that he disagrees with. (For this reviewer, there are misstatements in the area of petroleum processing.) However, any such errors are in matters of detail that would be of little consequence to most neophytes.

Each chapter of the book includes a bibliography of source material, but the book is not referenced. Accordingly, a reader who wants more information on a specific point must search for sources himself. In this sense, then, "Modern Petroleum Technology" is not a reference book.

R. J. Hengstebeck, *Amoco Oil Company*

**Mass Spectrometry of Inorganic and Organometallic Compounds.** By M. R. LITZOW (Union Carbide Corp.) and T. R. SPAULDING (The City University, London). Elsevier Scientific Publishing Co., New York, N. Y. 1973. xv + 620 pp. \$51.50.

This book is divided into two unequal parts, a broad introduction to mass spectrometry in general and a rather comprehensive review of mass spectrometric studies conducted on inorganic and organometallic systems up to the end of 1970.

The first section of this book (Chapters 1–3) occupies 15% of the text and was written "to enable the chemist with no working knowledge of mass spectrometry to understand the technique and its limitations." Included in the presentation is a discussion of the various instrumental components such as the ion source (electron impact, field-emission, and photoionization), mass analyzer (single-focusing, double-focusing, time-of-flight, and quadrupole), ion detector, and sample inlet system. Unfortunately no mention is made of two new techniques, field-desorption and chemical ionization mass spectrometry. The omission of material on field-desorption is particularly disappointing since this method of ionization has been shown to be extremely useful for the mass analysis of non-volatile samples.

Chapters 2 and 3 contain a discussion of such topics as resolution, ion types (molecular, fragment, multiply charged, metastable, and negative), isotopic abundance, precise mass measurement, ionization and appearance potentials, and the determination of bond dissociation energies and heats of formation of ions. All of these topics have been treated in more detail in a number of other excellent texts. Apparently, however, the present authors felt that the convenience of having both research related and introductory material under the same cover outweighed the disadvantage associated with the high price of the final product.

The second part of the book is a review of the results obtained in mass spectrometric studies on both the inorganic and organometallic compounds of the main group (Chapters 4–10) and transition elements (Chapter 11). Since over 1500 papers are referenced, this section should prove to be indispensable to those who seek to use mass spectrometry as a tool for the structure elucidation and characterization of nonorganic compounds.

Donald F. Hunt, *University of Virginia*

**Laboratory Techniques in Food Analysis.** By D. PEARSON (University of Reading, Weybridge, Surrey). John Wiley & Sons, New York, N. Y. 1973. 315 pp. \$21.50.

The continuing expansion of the food industry and the growing complexity of the production, processing, and delivery of food to the consumer has created a requirement for individuals with specialized knowledge.

One of these new professionals is the food technologist. In order for these individuals to receive the proper training and knowledge to carry out their new responsibilities, teaching materials must be developed dealing with the specialized area of food technology. Dr. Pearson has compiled this book on techniques used in food analysis, to help meet this important need.

The volume includes ten chapters, a short list of abbreviations, seven appendices, a list of atomic weights of the elements, a short logarithm table, and a subject index. Chapter One discusses the concept of quality control as it applies to the food industry. Chap-

ter Two presents a general discussion of methods of food analysis. Chapters Three to Ten are each devoted to the analysis of a specific class of foods or related substances including: food additives; trace elements; oil values and rancidity; dairy products; flesh foods; flour, baking powder, and self-raising flour; sugar and fruit products and miscellaneous items. The topics of the seven appendices are entitled: notes on food legislation, notes on spectrometry, factors for food energy calculations, control of carcinogenic substances, preparation of indicators, factors for solutions in volumetric analysis and the SI system of units.

All analytical methods are presented in sufficient detail to allow their performance or a specific reference given to a standard procedure. Recommended procedures are presented; however, references to alternative procedures are included. Numerous references are presented at the end of each chapter. Although only a few figures are presented (43), they are well drawn and are of great value in illustrating the analytical procedures.

In general, I feel Dr. Pearson has achieved his principal aim and has prepared a text which will prove of great value in the training of food technologists and will also be of value to practicing food technologists in solving problems of food analysis.

Donald F. Logsdon, Jr., *U. S. Air Force Academy*

**Topics in Inorganic and General Chemistry. Volume 15. The Actinide Elements.** By K. W. BAGNALL (University of Manchester). Edited by P. L. ROBINSON (University of Durham). Elsevier Publishing Co., London. 1972. xi + 272 pp. \$27.75.

As the author states, the volume consists of a "... broad survey in some depth..." rather than a detailed account of the field of actinide chemistry. It contains twelve chapters, beginning with a short historical account of the discovery or synthesis of these elements. Following this is a general discussion of the stabilities of various oxidation states, separation and purification of the elements, properties and preparation of the metals, and seven chapters arranged by ligands. The final chapter is a short discussion of magnetic properties and absorption spectra of the series and properties of *f* orbitals.

The book is very readable and presents the material in an interesting manner. Sufficient detail, references, and critical evaluation are present to make the volume a valuable reference for a graduate level inorganic chemistry course. For graduate students or researchers interested in entering the field, it should provide a good overview of the structural nature of actinide compounds and the basic means of their synthesis. A major shortcoming, however, is that the rather extensive kinetic studies of actinide ion reactions are essentially ignored.

Very recent work has extended the information available on organometallic compounds of the actinides (Chapter 11) well beyond the coverage in the book. Compounds with uranium-carbon sigma bonds, for example, are now known. Better crystal structures of actinide organometallics have been obtained, providing more insight into possible bonding geometries and, hence, the nature of bonding.

The limited depth would not make this book an inclusive reference. The price will probably limit acquisition to libraries.

D. K. Lavallee, *Colorado State University*

**Mathematical Methods for Chemists.** By R. K. MACKIE, T. M. SHEPHERD, and C. A. VINCENT (University of St. Andrews). Halsted Press (John Wiley & Sons), New York, N. Y. 1972. v + 154 pp. \$8.95.

The major part of this relatively short book consists of the following eleven chapters: Functions and Operators, Differential Calculus, Integral Calculus, Differential Equations, Coordinate Systems, Complex Numbers, Vector Analysis, Determinants and Matrices, Expansion of Functions, Statistical Methods, and Graphical Methods. In addition, there are five appendices on Basic Equations (trigonometric, logarithmic, etc.), Derivatives, Standard Integrals, Laplace Transforms, and Solution of Polynomial Equations, plus a number of miscellaneous tables of logarithms, trigonometric functions, atomic weights, physical constants, etc.

According to the Preface, "The object of the book is... to provide a background knowledge of the mathematics relevant to the

chemist, together with an introduction to concepts which may not have been encountered previously." In the opinion of this reviewer, the authors have met this goal as well as could probably be expected given the amount of space they have to treat the wide range of topics covered. The book is, in general, clearly written and there are some very good discussions of the mathematics, using problems of direct interest to chemists, e.g., solutions of differential equations using Laplace transforms, detailed discussion of work in terms of line integrals, and the use of geometric transformations to illustrate matrix multiplication. Many readers, however, will find the treatments much too short to be useful, and, in fact, several sections of the book will be seen to be little more than presentations of definitions and listings of mathematical equations. In general, chemists desiring more than a simple nodding acquaintance with these mathematical topics will probably bypass this book for one of the more nearly complete texts in this area, of which there are now quite a variety.

J. E. Mark, *The University of Michigan*

**Surface Active Chemicals.** By H. E. GARRETT. Pergamon Press, New York, N. Y. 1973. x + 167 pp. \$9.00.

This book is one of a series of monographs on the chemical industry designed as teaching manuals for senior students. Although aimed at the United Kingdom, the scope and contents of this volume are applicable on a world-wide basis. The student is frequently unaware of the relationship between fundamental theory in such a field as interface science and the industrial (practical) utilization of this technology. The author bridges this gap by a brief survey of fundamental principles in interface science followed by applied chapters on soap and detergents, ancillary surface active chemicals (i.e., lather promoters and solubilizers), adhesives, flocculating agents, dispersing agents, and, finally, an overview of the market for surface active chemicals.

The monograph is not intended as a reference text, as illustrated by the fact that cited references are mainly previously published comprehensive reference texts. Instead, the intent is to give a brief overview of industrial research in the hopes that his descriptive material will encourage the student into studying a particular facet of surface chemistry in greater detail elsewhere.

This monograph is an excellent primer for students who have had some physical chemistry and wish to study industrial applications of surface chemistry. It also will be of interest to any person who wishes a good overview of the subject material in the applied chapters.

J. Wade Van Valkenburg, *3M Company*

**Compounds Containing Phosphorus-Phosphorus Bonds.** Edited by A. H. COWLEY (University of Texas at Austin). Dowden, Hutchinson, and Ross, Inc., Stroudsburg, Pa. 1973. xiii + 322 pp. \$18.00.

This handsome volume in the "Benchmark Papers in Inorganic Chemistry" series contains reprints of 27 papers originally published in English, plus one Russian and five German papers both in the original and in English translation. There are three groupings: synthetic methods, structure, and reactions of P-P compounds. The classical 1877 paper of Michaelis initiates the field; the other papers are from the last 25 years. The selection is not intended to be comprehensive, but "to identify articles which have opened up new synthetic avenues, elucidated important molecular and electronic structures, or led to important general reactions."

Considering all the papers which have been published in this field, the editor has done a very good job in selecting fundamental contributions, although it was a surprise not to find any papers of K. Issleib or of L. Maier included. The editor has provided an interesting introduction covering the past, present, and future of P-P compounds. In addition, "Editor's Comments" are given on 24 occasions throughout the book. These are valuable in identifying the significance of each paper and in placing it in the context of a rapidly developing field.

While anyone interested in phosphorus chemistry would find it a pleasure to have this book available, it should be classified as a luxury in an age of tight budgets. The original papers are in journals readily available in most well-stocked libraries.

John T. Yoke, *Oregon State University*