

interaction, which together make informative reading and a very useful addition to any biochemical library. These articles include a general introduction by the late E. J. Cohn; a discussion of "Special Problems in the Formation of Metal Complexes" by C. D. Coryell, which includes recent physicochemical information on the specificity in complex formation of hemoglobin and ferrihemoglobin; thorough and valuable reviews by J. Schubert on "Interactions of Metals with Small Molecules and Ions"; and a paper by G. Schwarzenbach giving a theoretical foundation and pertinent experimental data for "The Specificity of Metal Complex Formation" with special reference to proteins. Other papers deal with radiation injury (by S. Warren), physicochemical properties of steroids (by R. B. Turner), clinical studies of steroid hormones (by T. F. Gallagher), purification and analysis of hormones of the posterior pituitary gland (by V. du Vigneaud), and are related to varying extents to the general theme of the symposium.

The book is well indexed both for subject and author, and is in other respects as well a technically handsome publication.

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Cellulose and Cellulose Derivatives. Part I. High Polymers, Volume V. Second completely revised and augmented edition. By EMIL OTT, HAROLD M. SPURLIN and MILDRED W. GRAFFLIN, Research Department, Hercules Powder Co., Wilmington, Delaware. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1954. xvi + 509 pp. 16 X 24 cm. Price, \$12.00.

Subsequent to the appearance of the first edition in 1943, "Cellulose and Cellulose Derivatives" has become the standard reference work in its field. The first of the three parts planned for the second edition appeared in 1954. The high quality of Part I indicates that the standards of the first edition will be maintained in the revision.

The new first part covers essentially the material of Chapters I-V of the first edition, and the emphasis is placed on the basic chemistry and properties of cellulose. The space devoted to this phase of the subject is slightly greater than in the first edition. Evidently the principal expansion of 500 pages planned for the entire work will be devoted subsequently to the more practical and technological aspects of cellulose.

Although not expanded significantly, the presentation of the basic aspects has been reorganized and definitely improved. The coverage of related subjects such as the hemicelluloses and lignin is brief but is adequately handled by competent specialists. Although sixteen specialists contributed to Part 1, the necessary integration has been successfully accomplished by the editors.

The individual contributions vary somewhat in the quality and extent of revision. The important section on End Groups was changed only in minor details from that of the first edition. The coverage of cellulases is inadequate, and a special section should have been included. A more adequate coverage of biochemical aspects might be expected of a book with such a general title. More references to the old work might have been given in some sections. This problem is difficult but cannot be solved simply by the elimination of old work.

The editors and publishers are to be commended for this revision and for maintaining the standards of the first edition. The format is good, the illustrations excellent (particularly the frontispiece in color), and the editorial work superb. Librarians and catalogers may be confused, however, by the listing of three editors on the title page and two on the cover. Confusion also might be avoided by the elimination of this work from its artificial classification as Volume V of the High Polymer Series.

The revised book is one that will be needed personally by all chemists and technologists in the field, even those with copies of the first edition, and is a required addition for all chemical and technological libraries with any coverage of the field.

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WARD PIGMAN

New Instrumental Methods in Electrochemistry. Theory Instrumentation and Applications to Analytical and Physical Chemistry. By PAUL DELAHAY, Louisiana State University. Interscience Publishers, Inc., 250 Fifth Avenue, New York, N. Y. 1954. xvii + 437 pp. 16 X 23.5 cm. Price, \$11.50.

Dr. Delahay deserves the gratitude of electrochemists and of chemists in general for his having been willing and able to provide them with such a clear and detailed survey of the new instrumental methods of electrochemistry in a period during which he has been so thoroughly busy making his own important contributions to the subject.

This is not just another book on electrochemical instrumental analysis but a complete theoretical and practical treatise on the various methods which have been developed since the pioneering electroanalytical contributions of Cruikshank, in 1801, and with particular intensity and richness during the years which have followed Heyrovsky's discovery of polarography in 1922.

After a flattering Foreword by I. M. Kolthoff, a brief Preface by the author and a very detailed Table of Contents occupying nine pages, the text begins with a historical sketch and a general review of electrochemical methods, 27 pages which clearly settle the confusing jargon which the subject requires (coulometry, potentiometry, voltammetry, polarography, amperometry, etc.). This constitutes Chapter 1 of Part One ("Voltammetric and Related Methods") and includes six sections divided themselves into a total of eighteen sub-sections. This four-stage systematization of the subject holds throughout most of the book, the numerous mathematical formulas being numbered in a separate sequence in each chapter. Chapter 2 gives a brief sketch of the theory of electrode potentials and a fairly detailed treatment of electrode kinetics (27 pages again, but a more fundamental approach to the still very fluid theory of electrode kinetics would have been desirable). The so-called European signs of electrode potentials are adopted, as is natural in a presentation of electrochemical phenomena, but Dr. Delahay has chosen the unusual convention of giving a negative sign to anodic currents and a positive sign to cathodic currents. If overvoltages are taken (as is done in this book) equal to the differences between European electrode potentials under current and at zero current, anodic overvoltages are positive and cathodic overvoltages negative. Currents and overvoltages should have the same signs, making their products positive in accordance with the requirement that these irreversible electrode processes must create entropy. Chapters 3, 4 and 5 (of, respectively, 25, 14 and 27 pages) have a common main title, "Voltammetry and Polarography at Constant Voltage" ("potential" replaces "voltage" in the title of Chapter 5), the sub-titles being "Reversible Processes," "Irreversible Processes" and "Kinetic and Catalytic Processes." On pages 52-55 the author gives a particularly satisfying derivation of the classical formula of polarography relating the potential to the logarithm of the $i_a - i/i$ ratio in place of the intuitive approximate proof of other books. Chapter 4 presents the very interesting advances of the last few years in the interpretation of irreversible waves. Here and elsewhere in the book one is struck by the continued vitality and high-level productivity of the Prague school founded by Heyrovsky. It also is remarkable to notice how frequently different groups of workers have made the same or similar contributions simultaneously, an obvious indication of the great activity which electrochemistry displays at present throughout the world. Dr. Delahay is to be congratulated for the care with which he has assembled his bibliography and for his complete fairness in giving full credit to his competitors in these pioneering investigations. Chapter 6 of 30 pages treats "Voltammetry and Polarography with Continuously Changing Potential," while Chapter 7 of 32 pages treats the same techniques with "Periodically Changing Potential" and contains a detailed presentation of recent developments on the faradaic impedance (a term coined by Grahame) of an electrochemical process and on the component parts of this impedance, the polarization resistance and the pseudocapacity. Here again the numerous contributions originating in different countries amount to an impressive total. Chapter 8 of 37 pages treats "Voltammetry at Controlled Current," a method whose theoretical literature dates back to 1879, and includes numerous contributions from the turn of the century. The use of its main feature, the transition

time, in analytical and physical chemical applications is, however, very recent. Chapter 9 of 42 pages on "Current Potential Curves Obtained in Stirred Solutions or with Moving Electrodes" contains authoritative treatments of the diffusion layer and of mass transfer in electrode processes. Chapter 10 of 15 pages deals with voltammetric titrations of the potentiometric and amperometric type.

We now arrive at Part Two on "Coulometry, Electrolytic Separations and Related Methods." Chapter 11 of 14 pages treats "Current Efficiency and Degree of Completion of Electrode Processes," Chapter 12 of 16 pages treats "Electrolysis at Controlled Potential and Related Methods," Chapter 13 of 2 pages briefly mentions the literature of "Electrolytic Separations and Related Methods," Chapter 14 of 15 pages discusses "Coulometry at Controlled Current."

Part Three with its unique Chapter 15 of 27 pages is concerned with "High Frequency Methods" and is contributed by Dr. C. N. Reilly of the University of North Carolina. It contains its own section on instrumentation, while Dr. Delahay presents his discussion of instrumentation for the other methods in Part Four. Here we find a most lucid presentation with clear block diagrams and in a language which does not necessitate any special training in electronics. The material is divided into four chapters, 16 to 19: 33 pages for "Voltammetry and Related Methods," 9 pages for "Voltammetric Titrations," 11 pages for "Electrolysis at Controlled Potential," 6 pages for "Coulometry at Controlled Current." A 3-page appendix on "Special Forms of the Nernst Equation" and a 5-page one on "Solutions of Some of the Boundary Value Problems" outlining the important mathematical methods based upon the Laplace transformation which have become essential adjuncts of electrochemistry will both be found most useful. The 8-page author index testifies to Dr. Delahay's thoroughness in covering the literature of his subject, while the 9-page subject index is one which really will enable the reader to locate any particular specific point.

It is seldom in our busy times that an authoritative, well digested treatment of very recent scientific developments becomes available as early as this one. It is to be hoped that Dr. Delahay will keep us equally well informed about further progress in this field, possible reinterpretations and refinements, etc., through successive editions of this fine work. Few electrochemists and physical chemists will find it possible not to own this book or to have ready access to it.

The Interscience Publishers have produced another book which, from the point of view of physical presentation, is fully up to their customary high standards.

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PIERRE VAN RYSSELBERGHE

The Strengths of Chemical Bonds By T. L. COTTRELL.
Academic Press, Inc., Publishers, 125 East 23rd Street,
New York 10, N. Y. 1954. viii + 310 pp. 15 X 22
cm. Price, \$5.50.

This book is a monograph that deals with the present status of our knowledge of energetic data from which bond dissociation energies ($D(D_1 - R_2)$) and bond energies ($E(A - B)$) of molecules may be computed. The author's primary concern has been to describe and to evaluate the reliability of the methods that are available for obtaining the raw data from which the quantities of interest are computed and then to supply a systematic and critical review of what is known of $D(R_1 - R_2)$ and $E(A - B)$ for polyatomic molecules. A particularly interesting feature of the monograph is the fact that the author has carefully refrained from attempts to interpret the values of D 's and E 's that appear in his summary tables. To the best of the reviewer's knowledge, discussions such as appear in Cottrell's monograph have usually been incidental chapters in volumes on valence theory (Sidgwick or Pauling) or reaction kinetics (Steacie). This separation of the critical evaluation of quantities from their interpretation tends to give the reader confidence in the conclusions reached, since there is no suspicion lurking in the reader's mind that in choosing a particu-

lar value as best for a much debated quantity the author does so because he has an "axe to grind."

With regard to the structure of the monograph, Chapter I is of an introductory and philosophical nature. Chapters II and VI discuss the definition and determination of dissociation energies and bond energies, respectively. Chapters III through V describe the various experimental methods that have been used to determine dissociation energies, segregated according to thermal equilibrium methods (III) kinetic methods (IV), and photon or electron excitation methods (V). Chapters VII and VIII deal with the precision of modern calorimetry as applied to the determination of heats of combustion and formation of organic compounds (VII), and inorganic compounds (VIII).

In Chapter IX bond dissociation energies are dealt with bond by bond. Here Cottrell follows the procedure of simply listing the bond and its dissociation energy if he agrees with the conclusion of a previous reviewer (Herzberg, Gaydon or Swarc) adding remarks only in those cases where his conclusion differs by virtue of either logic or new data from those of the previous reviewers. In the discussion the author treats each bond as an independent problem and discusses the direct evidence pertaining to it. It is the reviewer's opinion that the usefulness of this chapter would have been greatly enhanced if it had concluded with a summary table giving Cottrell's listing of the "best values" of the heats of formation of radicals and atoms that have been considered.

Chapter X considers the numerical values of thermochemical bond energy terms derived from heats of atomization of molecules. Particular attention is devoted to the reliability of the experimental data that enter into the calculation. Thus the author finds himself fencing with those perennial windmills, the heat of sublimation of carbon and the dissociation energy of nitrogen. Despite the recent work of Ingraham and co-workers, and the reputed conversion of Goldfinger, the reviewer believes Cottrell has chosen rightly in taking the low value, 138 kcal./mole for L_0 . However, the evidence now available suggests the 7.38 e.v./molecule value for $D(N_2)$ not to be tenable. Certain of Cottrell's bond energy calculations will require revision to make them consistent with $D(N_2) = 9.76$ e.v./molecule. Those who prefer $L_0 \cong 170$ kcal./mole will find pleasure in recalculating bond energy terms involving carbon to this latter basis.

There appears to be a slight lapse in logic in Chapter X. In the introduction to this chapter the author states, "Only molecules for which an unambiguous valence bond structure can be written are discussed so that the question of empirical resonance energies is not treated." The author rigidly follows the latter part of this prescription but there are many who will doubt that the first part of the quotation is consistent with the discussion (or tabulation) of bond energies for the halides of such diverse elements as boron, silicon, germanium, etc., or the statement that B-trichloroborazole has 6 B-N bonds (page 244). All would be well if the sentence quoted above had read, "Bond energy terms will be derived as they exist for bonds in molecules without regard to valence bond structure or structures that may be written for the molecule."

The volume concludes with a terse account of those properties of bonds other than dissociation energies or energies that may be considered as measures of the strengths of the bonds. In the first chapter Cottrell has given his reasons for considering such quantities as force constants and interatomic distances of secondary interest. A long table summarizes the D 's, E 's, k 's and r_e 's that Cottrell believes are known for the bonds considered in the volume.

Although he was not always in agreement with the author's credo, the reviewer found much pleasure and stimulation in reading this volume. Both valence chemists and reaction kineticists should find the discussions, tabulations and the bibliography very useful. Those who have occasion to consult such tabulations of thermal data as now exist in Circular No. 500 of the National Bureau of Standards, will find chapters VII and VIII particularly worthwhile reading.

The printing, paper and binding are quite satisfactory, and the price is probably not out of line with those that currently prevail.

SHELL DEVELOPMENT COMPANY
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D. P. STEVENSON