energy ($\delta_s\Delta G°_{int} \approx \delta_s\Delta H°_{int} \approx \delta_s\Delta E_{int}$) in conformity with a vast array of free energy–structure correlations in highly aqueous media,[6-8] even for acids[6] and amines[9] in water where the ΔH_{ext} and ΔS_{ext} terms are large and erratic.[9,10]

A number of other workers have measured the heats of interaction for several series of amine bases with various strong acids of both the protonic (*e.g.*, methanesulfonic acid in nitrobenzene,[11] trichloroacetic acid in benzene[12]) or Lewis-type[11,13,14] (both in the gas phase and inert media). In the absence of steric hindrance, they have usually found, as we do, a good correlation between the free energy of ionization in water and the heat of acid–base interaction in their chosen medium. Furthermore, each class of amine generates its own correlation line as we find for the pyridines (upper line).

Since their results have all dealt with strong amine bases of well-established pK_a values, they do not anticipate the results presented here (testing the H_0 overlap method over a wide basicity range).

Preliminary results of F. Jones in this laboratory indicate that the heat of ionization of di- and triarylcarbinols to carbonium ions in sulfuric acid will correlate with their pK_R values[15] in water.

In recent years, there has been much discussion of extrathermodynamic ΔH–ΔS correlations.[6,7] We wish to emphasize that whenever a true relationship (not due merely to correlated errors) of this kind is found, it automatically requires that there be correlation of ΔG and ΔH. These latter two properties can be determined independently and one is often much harder to measure than the other, so that an extensive knowledge of *bona fide* ΔG–ΔH correlations should be of considerable use in estimating unknown values of either of these properties.

The heats of solution in sulfuric acid and tetrachloroethane were measured conveniently in a simple solution calorimeter[16] on carefully purified and protected amines. It is mandatory that exactly the same strength of acid be used for all bases to be compared, since ΔH_a is very sensitive to the concentration of sulfuric acid.

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Book Reviews

Advanced Quantum Chemistry. Theory of Interactions between Molecules and Electromagnetic Fields. By HENDRIK F. HAMEKA, Department of Chemistry, University of Pennsylvania. Addison-Wesley Publishing Co., Inc., Reading, Mass. 1965. x + 277 pp. 16 × 23.5 cm. $13.75.

The title of Hameka's book is "Advanced Quantum Chemistry." The stated purpose of the book is to bridge a communications gap between physicists and chemists in the area of the theoretical description of interactions between molecules and electromagnetic fields.

In his preface Hameka interprets and attempts to extend Coulson's 1959 classification of quantum chemists into *ab initio* ists and *a posteriori* ists. His interpretation of Coulson's categorization is that both groups have as their primary objective determination of more or less approximate molecular wave functions and corresponding energies. The extension of Coulson's classification is described by a passage from Dante which, somewhat loosely translated, means, "I thought how many worthy souls there were suspended in that Limbo." Somewhat earlier in Canto IV occurs a perhaps more appropriate passage, "Death-pale, the Poet spoke: 'Now let us go into the blind world waiting here below us. I will lead the way and you shall follow'." If one were to accept both Coulson's polarization of the field and Hameka's further resolution into higher order moments, then at least one other emerging overlap area can be identified where exchange may prove to be even more fruitful, namely, scattering theory and chemical reactivity, and this brings us to the first of several minor criticisms.

The title of the book, "Advanced Quantum Chemistry," is misleading. The qualifying statement following the title, "Theory of Interactions between Molecules and Electromagnetic Fields," would have been more appropriate as a title. Anyone stimulated by the title into picking up the book may reasonably expect to find a presentation of closed-shell, open-shell, and extended Hartree–Fock theory, Brillouin's theorem, natural orbitals, nonbonding interactions, scattering theory, and a host of other subjects.

Chapter 4 is entitled "Approximate Methods in Quantum Theory" while Chapter 5 is entitled "Time-Dependent Perturbation Theories." The author index is incomplete.

The book is somewhat uneven in level. On one hand a derivation is given for the Thomas factor of $\frac{1}{2}$ in the expression for the energy of a spinning electron in an electromagnetic field, while on the other hand neither the Breit equation nor the problem of retardation is discussed.

Hameka's remarks on page 67 relating to perturbation theory and direct analytical solution of the equations for certain cases are well illustrated in the book by H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-Electron Atoms," Academic Press Inc., 1957, on pages 27 and 229. In fact, those stimulated to apply some of the theories discussed by Hameka will find much helpful material in Bethe and Salpeter's book where the stated second aim is to be of some use to graduate students who wish to learn "applied quantum mechanics."

Although English is not Hameka's native tongue, about the only trace apparent is his use of "Apparently . . . ." instead of "It is apparent that . . . ." as on page 61.

The chemist wishing to apply quantum mechanics has had his share of problems just dealing with an electrostatic hamiltonian. Magnetic phenomena involve vector potentials, and life has become even more complicated for the chemist. Hameka's treatment of the gauge is a welcome sight and should go a long way toward helping the chemist identify and cope with the problem.

Hameka's book provides an overview of the "Theory of Interactions between Molecules and Electromagnetic Fields." This overview is somewhat polarized by his own research interests. Where the theory is shaky and ill defined, he has not hesitated to so label it. Furthermore, he has not hesitated to speculate. The book should help bridge the communications gap as stated in its purpose. Perhaps an even more important effect of the book will be to suggest ways in which chemists can probe even more deeply into nature's molecular secrets.

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Introduction to Quantitative Ultramicroanalysis. By I. M. KORENMAN, Professor of Analytical Chemistry, Gorkiy State University, U. S. S. R. Academic Press Inc.,111 Fifth Ave., New York, N. Y. 1965. ix + 234 pp. 16 × 23.5 cm. $9.50.

This book is most welcome because it brings to the attention of the American research scientist a considerable portion of the work done in Russia in the field of ultramicroanalysis, in which there is growing interest. The author is a foremost Russian scientist in his field, and it is of equal importance that the translation editor (Dr. Ronald Belcher) is one of the pioneers on the subject.

The book is divided into seven chapters. Chapter 1 devotes eight pages to a general discussion of the subject matter defining terms. The author uses a number of mathematical calculations to illustrate the points of his discussion.

Chapter 2 devotes 53 pages to the principal techniques of operation and includes a number of subjects such as sampling techniques, isolation of precipitates, electrolysis, extraction, chromatography, determination of sample size, etc. Sixty illustrations are used to clarify the text.

Chapter 3 devotes 30 pages to the subject of gravimetric analysis. A good portion of this chapter deals with a discussion of various ultramicrobalances and includes a number of schematic drawings to illustrate various points of the subject.

Chapter 4 (64 pages) deals with volumetric analysis. Considerable space is devoted to various types of burets and pipets and the errors involved through their use. The latter portion of the chapter covers a number of specific cases such as the determination of acids, bases, calcium, copper, chromate, chloride, and silver.

The fifth chapter presents a number of physical–chemical methods of analysis. A number of schematic drawings are used in helping to describe what can be done with potentiometric, colorimetric, spectrophotometric, etc. methods.

The sixth chapter, which is quite short, is termed "Other Analytical Techniques" and provides information on determinations on paper and gelatin films, kinetic methods, and determinations based on the volume of the precipitate.

The final chapter, which occupies 11 pages, gives information on gas analysis when dealing with minute volumes.

In general, this book will be of interest to both the experienced microanalyst, who wishes to extend his work to the ultramicroanalytical field, and to the beginner, who wishes to work in the ultramicroanalytical range.

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Treatise on Electrochemistry. By G. KORTÜM, Professor of Physical Chemistry, Tübingen University. Translated from the third German Edition of 1962. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1965. xxii + 637 pp. 17.5 × 25 cm. $30.00.

The first English edition of this well-known work appeared in two volumes in 1951 with J. O'M. Bockris as collaborator and translator. The present version returns to a single-volume format and single authorship.

Early in the book there is a substantial chapter on chemical thermodynamics in general; one wonders whether this space might not have been better used in a specialized text, but the author's philosophy appears to be to make the book as self-contained as possible. In the same way, one finds fairly detailed treatments of dipole, induction, and dispersion forces in the chapter on the solvation of ions. The treatment of activities and conductances of strong electrolytes follows conventional lines. The discussion of experimental techniques is too brief to be of value; the reviewer considers that a fuller treatment of these could advantageously have replaced some of the general thermodynamic background material in earlier chapters. There is a good chapter on the uses and interpretation of conductance measurements, including those on molten salts. The various practical applications of emf measurements are also well treated. A chapter on acids and bases follows, with some discussion of substituent effects.

The long Chapters XI and XII deal with potential differences at phase boundaries, including discussions of the double layer, polarized electrodes, membrane potentials, and electrokinetic phenomena, and with electrode kinetics. The final chapter on applications of electrochemical processes deals with electrochemical energy sources (including fuel cells), polarography, and other analytical techniques, electrometallurgy, and corrosion. The tabular material in the appendix is greatly reduced in comparison with the earlier two-volume edition, but there is a considerable number of useful tables throughout the text.

If one admits the desirability of having a single book to cover a subject as large and important as electrochemistry, there is probably no better one available today. For the advanced student seeking an over-all picture of the subject, Professor Kortüm has done a great service. For the research worker, the book is also very useful but will naturally require supplementation. The author has provided extensive references, frequent general bibliographies, and a very detailed index.

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