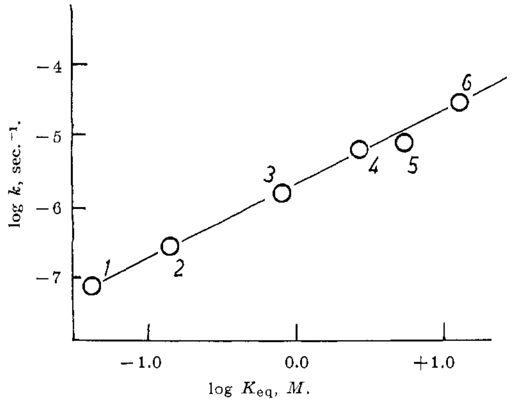

Figure 1.—Plot of log rate constant *vs.* log of equilibrium constant for the acid hydrolysis reaction of $[Co(NH_3)_5X]^{+2}$ ions. Measurements made at 25.0°. Points are designated: 1, $X^- = F^-$; 2, $X^- = H_2PO_4^-$; 3, $X^- = Cl^-$; 4, $X^- = Br^-$; 5, $X^- = I^-$; and 6, $X^- = NO_3^-$. (Data for all X except I^- and F^- appear in ref. 2. Data for I^- are in ref. 4 and F^- in ref. 3.)

expect the transition state to lie at an intermediate point along the reaction coordinate if the molecule derives significant stabilization from a forming bond. The reactions shown in Figure 1 lie in the neighborhood of $\Delta F^\circ = 0$. We may conclude that water is at best weakly bound in the transition state of reaction 1.

The linear free energy relationship suggests a transition state with at most weak bonds to both the entering and the leaving group. The possibility that the entering group is not present at all has been considered by Haim and Taube,[2] and competition factors for a five-coordinate intermediate which are consistent with the equilibria, rates, and water exchange rates have been calculated. Pearson and Moore's[1] experiments failed to verify some of these competition factors. They cited several lines of evidence indicating that there is no five-coordinate intermediate and that both the entering group and the leaving group are stoichiometric components of the transition state. Pearson and Moore discussed a "solvent assisted dissociation" which considers the activation process as primarily bond breaking but with a requirement for a little assistance from some nucleophile in the transition state. This seems a quite reasonable proposal, but it may be useful to compare it to a slightly different formulation.

The "linear free energy relationship" argument places the transition state at a point with weak bonds. Let us consider these *no bonds* for a moment to give the "five-coordinate intermediate." If the activation energy for reaction of this "intermediate" with an entering nucleophile is so low that the reaction rate is higher than the rate of reorganization of solvent molecules around the complex, the "intermediate" must react with a nucleophile already in position in the second coordination sphere. On such a reaction path, the only possible reaction is an interchange between the first and second coordination spheres of the complex. The entering group must be present in advance. But, it is possible for the interchange to take place *without* nucleophilic assistance. This process may have an intermediate in the sense of *transition state theory* (a minimum in the potential surface) but still not have an intermediate in the *phenomenological kinetic* sense of that intermediate being detectable by any sort of competition experiment. Highly charged complex ions interact strongly with their second coordination spheres (contact solvation shells). As Eigen has shown,[8] the reorganization rates are not always close to diffusion control. The above interchange process is most probable in just this circumstance.

In this letter, we suggest that it is possible to formulate a mechanism equivalent in explanatory power to the "solvent assisted dissociation" which does not invoke nucleophilic assistance by the solvent. It is not suggested that a simple experiment will distinguish between the two. Contrarily, the intention is to call attention to the need for *operationally* satisfactory mechanistic categories. Perhaps the best course is to insist on success in competition experiments as the defining criterion for an intermediate (dissociative mechanism) and to use the neutral term "unassisted interchange" for all reactions *failing* to satisfy two opposite operational criteria: (1) presence of an intermediate and (2) well-defined nucleophile order for entering groups.

(8) M. Eigen, *Discussions Faraday Soc.*, **24**, 25 (1957).

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Book Reviews

Reaction Heats and Bond Strengths. By C. T. Mortimer. Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962. xii + 230 pp. 14.5 × 22 cm. Price, $5.00

This small volume consists of the treatment and use of thermochemical data to generate bond energies for a number of largely organic molecules. Based upon a series of lectures given by the author at the University of Keele (Staffordshire, England) the subject matter seems to be accurately and well explained, and summarizes a wealth of experimental data. In this respect the effort is of significant value, because bond energies are not normally calculated or compiled in the more standard sources of thermochemical data. Although a number of metallo-organic bonds are discussed, most of the text is oriented toward organic-like species, with a corresponding loss of general interest among inorganic chemists. A notable exception is the chapter on silicon, phosphorus, and sulfur compounds; however, the short chapter on ionization energies in aqueous solution is totally inadequate.

Further, there is not even a summary on the well-known dissociation energies of simple inorganic gaseous molecules, such as N_2, F_2, OH, CaO, etc. The discussion of experimental calorimetry in Chapter I is so brief and incomplete that it might well have been omitted entirely.

In spite of these shortcomings, the author is to be commended for having made a valuable contribution in organizing and summarizing new bond energy data.

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Technique of Inorganic Chemistry. Volume III. HANS B. JONASSEN and ARNOLD WEISSBERGER, Editors. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. vii + 345 pp. 16 × 23.5 cm. Price, $11.50.

The present volume is number three in a series designed to be a companion to the series "Technique of Organic Chemistry," also edited by A. Weissberger. The announced purpose of the new series is to be a comprehensive presentation of synthetic and instrumental techniques used in inorganic and radiochemistry. Each article tries to offer "a theoretical treatment of specific techniques" and to evaluate critically "their limitations and merits. . .In all cases, the authors stress recent developments." The quotations were taken from the jacket of the book.

This volume contains four articles, each about 80 pages in length, on the following subjects: gas chromatography, by W. W. Brandt; electron microscopy, by J. F. Hamilton; technique of handling highly active β- and γ-emitting material, by D. C. Stewart; and glove box techniques, by C. J. Barton. At the end of each article there is an extensive list of references.

The first two articles are of a different type from the last two, in that they deal with subjects that are major research fields in themselves. The last two articles pertain to specialized topics and are more in keeping with the kind of articles found in volume I of this series. It strikes this reviewer as a very difficult task to write a pertinent article on gas chromatography or electron microscopy which serves the purposes of this series. The latest references are only for 1961, and so the article cannot be of the "annual reviews of. . ." type, which bring current information to people in a specific field. The basic question is: why would someone wish to read a relatively short exposition on electron microscopy, say, when there are a number of good books on the subject—particularly when the exposition cannot be considered up to date. In this reviewer's opinion, the purpose of such a chapter should be to interest the reader in the subject as a possible tool. The chapter should have a sufficient theoretical introduction so that the reader can appreciate the advantages and disadvantages of the method, and become versed in the terminology. Then the chapter should discuss applications of the method and the kinds of information that can be obtained. Finally, an effort should be made to discuss what present limitations there are, and perhaps where future breakthroughs in techniques may occur. A reasonable, although not necessarily exhaustive, set of references should be included. What are not needed are detailed discussions of the hardware or experimental techniques, or great lists of out-of-date references. To these ends, the chapter on electron microscopy succeeds to a greater extent than the chapter on gas chromatography.

The chapter on gas chromatography is concerned almost entirely with gas–liquid systems. Justifiably, consideration is given only to the elution approach, as opposed to displacement and frontal approaches. Only 6 out of the 79 pages are on applications, while the body of the chapter is concerned with the carrier gas, sample introduction, columns, detectors, and special techniques such as high speed, high temperature, and programmed temperature operations. The applications discussed include separations of materials that are gaseous under normal conditions, such as the elemental gases, nitrogen oxides, etc., as well as materials that have relatively high vapor pressures at elevated temperatures. The latter group includes metal halides, metal chelates, phosphorus compounds, water, and hydrides. Compared to organic compounds, of course, the applications are few in number. However, the importance of high temperature chromatography, using, for example, molten salts as the liquid phase, is brought out. Also mentioned is the occasional use of gas chromatography in the determination of such physical constants as the ΔH of vaporization and activity coefficients. Besides the severely limited discussion of applications and the preponderance of details on the hardware and operational techniques, there are a number of minor distractions. There is occasional use of terminology and jargon that are not defined, and, in this way, the treatment is somewhat uneven in depth. Figure 13 is incorrectly referred to on p. 21. The few pages devoted to theory at the beginning of the article are inadequate, and the one page at the end of the article on the evaluation of chromatograms seems to be an afterthought. There are 34 figures and 7 tables included by the author—most of which are of little value to a person interested in what benefit chromatography can be to him as a tool. On the other hand, the author performs a valuable service in pointing out areas in need of research, such as inorganic spray-dried matrices as solid column packing, and the arrangement and availability of pore surfaces inside column particles.

The second chapter deals with electron microscopy and was written to stand alone, and not to serve merely as a supplement to F. A. Hamm's article in "Technique of Organic Chemistry." An effort is made to stress inorganic applications, in particular, new applications, new ways to obtain information not available before, and to point out such topics as coherence of scattering from crystals where the treatment differs from the organic case.

This article presents a good theoretical section, basic to the appreciation of the uses to which this technique may be put. Twenty pages are devoted to a clear exposition of applications. It is emphasized that an extension of electron microscopy to new areas is usually due to new specimen techniques. An example is the study of internal crystalline features by direct examination of transmission-type specimens (rather than using replicas). Volume features, such as the direct resolution of lattice planes, are now being studied in favorable cases. Limitations of the method, such as certain optical effects that produce contrast caused by the microscope and not the sample, are discussed. Most of the figures are not only pertinent but also interesting. In this reviewer's opinion, the author has succeeded in producing a useful introduction to electron microscopy of interest to inorganic chemists in general.

The two remaining articles, on techniques with β- and γ-emitting material and glove box techniques, both represent excellent summaries of a vast amount of material, often originally in hard-to-get report form. In these two articles the references (over 200 in each case) will be of particular value to the reader—much more so than the references of the first two articles. In the first of these two articles, by D. C. Stewart, there is a particularly fine discussion of γ-ray shielding. Other interesting features include discussion of the design of laboratories having shielding facilities and brief summaries on decontamination and waste disposal, which supplement the principal discussion of remote manipulation of radioactive materials. However, some discussion of the effect of radiation fields on the electronic components of remotely controlled systems, in particular the sensitivity of transistorized equipment relative to tube type equipment, would have been of interest, and the definition of the roentgen on p. 170 is incomplete. In the second article, C. J. Barton concerns himself with glove boxes for both toxic and nontoxic materials. The first half of the article deals primarily with the various types of glove boxes, design aspects, and suitable construction materials. Here the author points out the lack of attention often given to the possibility of fires and explosions, and how this has affected the choice of construction materials. The last half of the article is devoted to techniques of glove-box operation and the many types of measurements that can be carried out in glove boxes.