tetrachloride, and water. It is diamagnetic and relatively stable in the absence of light and under nitrogen. *Anal.* Calcd for $Mn(CO)_5SCN$: C, 28.47; N, 5.53; S, 12.67; Mn, 21.70; mol. wt., 253. Found: C, 28.04; N, 5.50; S, 12.55; Mn, 21.60; mol. wt. (cryoscopic in nitrobenzene), 247, 259.

Infrared spectroscopic evidence serves to indicate the manner of attachment of SCN to the manganese. In addition to the stretching absorptions at 2135 cm.$^{-1}$ (m) (CN), 2110 cm.$^{-1}$ (w), 2060 cm.$^{-1}$ (s), and 1960 cm.$^{-1}$ (s) (CO) (chloroform solution), the compound shows a band at 676 cm.$^{-1}$ (Nujol), which is assigned to the CS stretching mode. Since the known S-bonded thiocyanates absorb between 690 and 720 cm.$^{-1}$ and N-bonded thiocyanates between 780 and 860 cm.$^{-1}$,[1] the band at 676 cm.$^{-1}$ indicates the presence of a Mn–SCN linkage in the compound.

Reactions of $Mn(CO)_5SCN$ with a variety of neutral ligands yield complexes which are analogous to those prepared from $Mn(CO)_5Br$.[2,3] The derivatives[4] *cis*-$Mn(CO)_3(py)_2NCS$ (py = pyridine), *cis*-$Mn(CO)_3$-bipyNCS (bipy = 2,2′-bipyridine), *cis*-$Mn(CO)_3(p\text{-}CH_3C_6H_4NH_2)_2NCS$, and *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2$-NCS exhibit a band in the 780–860 cm.$^{-1}$ region and are therefore assigned thiocyanato–N structures. The same complexes may be obtained from the reaction of the corresponding chlorocarbonyl derivatives and potassium thiocyanate. Unlike the above compounds, *cis*-$Mn(CO)_3[Sb(C_6H_5)_3]_2SCN$ appears to contain S-bonded thiocyanate.

Turco and Pecile[1] made an interesting observation that, for Pt(II) and Pd(II) complexes, the nature of metal–thiocyanate attachment depends on the other ligands present. Good π-bonding ligands favor M–NCS linkage, whereas non-π-bonding ligands prefer a M–SCN bond. This approach has been successfully employed in the synthesis of thiocyanato-N and -S isomers.[5]

The preliminary experiments on manganese carbonyl systems prompt us to suggest that, in the presence of strongly π-bonding ligands (*e.g.*, CO), the effective charge on the metal may play an important role in determining the nature of the linkage isomer obtained. Thus, complexes containing bases weaker than $P(C_6H_5)_3$ (CO, $Sb(C_6H_5)_3$) are S-bonded, whereas complexes containing $P(C_6H_5)_3$ and stronger bases such as amines (py, bipy, $p\text{-}CH_3C_6H_4NH_2$) are N-bonded. The generality of this statement and a possible explanation must await further experiments, which are now in progress.

Acknowledgment.—The financial support of the National Science Foundation is gratefully acknowledged.

Department of Chemistry
The Ohio State University
Columbus 10, Ohio

Andrew Wojcicki
Michael F. Farona

Received August 22, 1963

---

[1] A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

[2] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

[3] R. J. Angelici, F. Basolo, and A. J. Poë, *Nature*, **195**, 993 (1962).

[4] *cis* and *trans* refer to mutual positions of the two neutral ligands, *e.g.*, py. These are *cis* to SCN in both forms.

[5] F. Basolo, J. L. Burmeister, and A. J. Poë, *J. Am. Chem. Soc.*, **85**, 1700 (1963).

Book Reviews

Advances in Fluorine Chemistry. Volume 3. Edited by M. Stacey, University of Birmingham, J. C. Tatlow, University of Birmingham, and A. G. Sharpe, Cambridge University. Butterworth, Inc., 7235 Wisconsin Avenue, Washington 14, D. C., 1963. 287 pp. 15.5 × 25 cm. Price, $9.95.

Volume 3 of this series, well known to "fluorine chemists," continues the high standards of the two earlier works. The chapters are written by experts who speak with authority about their topics. They have reviewed various areas of current interest with thorough coverage of the literature so that the reader can get an up-to-date understanding of each topic. The book is intended primarily for persons engaged in research on compounds of fluorine.

The specific topics covered are indicated by the titles of the chapters: (1) Effects of Adjacent Perfluoroalkyl Groups on Carbonyl Reactivity, by H. P. Braendlin and E. T. McBee, Purdue University; (2) Perfluoroalkyl Derivatives of the Elements, by H. C. Clark, University of British Columbia; (3) Mechanisms of Fluorine Displacement, by R. E. Parker, University of Southampton; (4) Nitrogen Fluorides and Their Inorganic Derivatives, by C. B. Colburn, Rohm and Haas Company; (5) The Organic Fluorochemicals Industry, by J. M. Hamilton, Jr., E. I. du Pont de Nemours and Company; (6) The Preparation of Organic Fluorine Compounds by Halogen Exchange, by A. K. Barbour, L. J. Belf, and M. W. Buxton, Imperial Smelting Corp., Ltd.

The fifth chapter is written in a way which helps the research chemists to understand something about the organic fluorochemicals industry. The reviewer found it to be both interesting and informative.

In recent years it has become increasingly apparent that the words "fluorine chemistry" do not mean the same thing to all chemists working in the field. Since most of the research on fluorides deals with organic compounds, there is a tendency for some people to think only of such substances when the words are used. An illustration of this point of view may be found on p. 122 in the statement, "This then was the general state of fluorochemistry in 1928, when it was suddenly swept into its industrial phase by the rapidly expanding field of mechanical refrigeration." Obviously this statement does not apply to the fluorochemicals industries which were in operation before 1928. The confusion of meanings could be relieved by a more extensive use of words such as "organofluorine chemistry" or "organic fluorine chemistry." Editors can be helpful by encouraging such a practice.

This book is highly recommended reading matter for "fluorine research chemists."

Department of Chemistry
University of Washington
Seattle 5, Washington

George H. Cady

Les Réactions Chimiques dans les Solvants et les Sels Fondus. By G. CHARLOT and B. TRÉMILLION. Gauthier-Villars Editeur, Paris, 1963. xii + 602 pp. 16 × 25 cm. Price, $20.00.

If there exists a life-bearing planet with oceans of liquid ammonia, the chemists of such a planet probably have not been able to resist the temptation of developing a solution chemistry in this solvent. Earth-bound chemists have devoted a great deal of attention to aqueous solutions partly due to the ubiquitous presence of water. The point of view which developed as a result of aqueous solution studies has influenced all of the concepts important for solution chemistry: ionic species, complexity constants, acid–base behavior, kinetics, reaction mechanisms, oxidation–reduction potentials, solubilities, and electrical conductivities.

In the past few decades, however, the area of solution chemistry has expanded tremendously thanks to the persistent efforts of chemists who felt that one of the frontiers lies in the exploration of the chemistry of nonaqueous media. The range and type of solvents in which "inorganic" solution chemistry is studied today includes a large number of organic solvents in addition to the intensively studied inorganic solvents like liquid ammonia. Within the past decade, the list has grown to encompass the varied class of fused salt solvents for which an interesting solution chemistry is in the process of being established. It is not unreasonable to expect that still other classes of liquids such as the liquid metals will be investigated from the point of view of nonaqueous solution chemistry in the future.

As a result of all of this activity, a re-examination of many of our conceptual notions concerning solution chemistry has occurred. The present-day situation is characterized by the existence of data on large numbers of solvent systems requiring extensions and modifications of classical theories for a unified understanding of all the experimental facts. The task of correlating the available information so as to make it accessible to theoretical treatment is an important one.

The book "Les Réactions Chimiques dans les Solvants et les Sels Fondus" by G. Charlot and B. Trémillion is a welcome addition to the literature of nonaqueous solution chemistry at this time because it offers a compendium of experimental results for many solvent systems treated from a self-consistent point of view. Results for more than 150 organic, 60 inorganic, and 100 fused salt solvents are discussed and references are given to more than 5000 publications.

The book is divided into two principal parts: General Properties and Chemical Properties. Under General Properties there are five chapters entitled, respectively, (1) Acid–Base Reactions in Nondissociated Solvents, (2) Acid–Base Reactions in Dissociated Solvents, (3) Complexes, (4) Oxidation–Reduction Reactions, (5) Solubilities. Under Chemical Properties there are ten chapters entitled (6) Hydrocarbons and Halogen Derivatives, (7) Acids, (8) Bases, (9) Alcohols, Phenols, (10) Amides, (11) Nitrogen Derivatives, Nitriles, Ketones, (12) Anhydrides, Ethers, Esters, (13) Miscellaneous Solvents, (14) Inorganic Halogen Compounds, (15) Fused Salts.

It is gratifying that the basic ideas set out in the first part of the book are consistently applied to the experimental data in the second part. A very large amount of data is correlated in this way on the basis of a few concepts: relative acid–base strengths, ionic dissociation equilibria, oxidation–reduction potentials, and solubility relations. The data are summarized in numerous tables and displayed graphically (qualitative) in the form of acid–base and oxidation–reduction potential scales.

The tabular presentations are frequently followed by long lists of references. However, it is not possible to tell from which piece of work a particular datum was taken. This constitutes a serious limitation on the usefulness of the tables. A similar criticism can be leveled at the references to the textual discussion. Thus, the section on liquid ammonia which is less than 10 pages in length is appended by 308 references.

A more judicious and critical selection of the literature would have been an aid to the reader in directing his attention to those key papers which formed the basis for the author's discussion.

Used properly, this book becomes not only a literature compendium but also a starting point for the development of more adequate theories of solution chemistry.

ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS
DIETER M. GRUEN

Inorganic Chemistry. Revised Edition. By R. B. HESLOP and P. L. ROBINSON. Elsevier Publishing Co., 52 Vanderbilt Ave., New York 17, N. Y., 1963. vii + 591 pp. 16 × 23 cm. Price, $9.00.

This second edition of a well-known textbook on inorganic chemistry is very similar to the first edition. In fact, the authors state that "the only major additions are a description of phosphonitrilic compounds, a section on complexes in aqueous solution, and a short chapter on inorganic polymers." In a few places small changes have been made to clarify the meaning or to include the results of recent research. The book is 36 pages longer than the first edition.

This reviewer has found errors (some minor and some serious) and omissions in the discussions of topics with which he is familiar. On p. 200, the self-ionization constant of liquid ammonia at $-33°$ is given as $\sim 10^{-22}$, whereas the actual value is close to 10^{-32}. Potassium amide is referred to by the quaint term potassamide. The subject of metal–ammonia solutions is confined to a mere one-third of p. 201, and no mention is made of modern ideas regarding the nature of these solutions. The boron hydrides and borohydrides are discussed on pp. 218–223 without any mention of the very fascinating species $B_3H_8^-$, $B_{10}H_{13}^-$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$, $B_{12}H_{12}^{2-}$, $B_{10}H_{16}$, and $B_{18}H_{22}$. Five methods are given for preparing B_2H_6; however the very convenient method involving the reaction between $NaBH_4$ or KBH_4 and H_2SO_4 is not given. On p. 227, it is stated that germanes from di- to penta- have been made by circulating germane through a discharge tube, whereas it has been reported that germanes as high as Ge_9H_{20} have been made in this way. On p. 312 it is stated that the solid germanium dihalides possibly have bridged structures, although it is known that GeI_2 has the CdI_2 structure. On p. 338 it is stated that N_4S_4 (written elsewhere as S_4N_4) can be chlorinated to a tetrachloride $S_4N_4Cl_4$, whereas only the trimer has been identified. On the same page it is stated that the polymeric $(SN)_n$ is yellow, whereas it has a metallic blue-black color. On p. 397, the aqueous reduction potential for O_2 at pH 7 is given as that at $a_{H^+} = 1$, and as a consequence all the calculated potentials and free energies on that page are wrong. Throughout the entire book, the authors are inconsistent in their writing of equations for reactions in aqueous solutions. Thus in some cases net reactions are written, while in others species such as HNO_3, NaCl, and NaOH are written as if they were weak electrolytes. In Chapter 13 (The Inert Gases) the compound $XePtF_6$ is not mentioned even though the preface was dated as late as September, 1962.

It is clear that the book is not completely reliable as a reference book. However, it can be used very satisfactorily as a textbook if the instructor warns his students of its errors and omissions. In spite of this rather cool recommendation, the book is probably one of the top three or four textbooks on inorganic chemistry today. It is lamentable that no inorganic textbook has been published since 1944 in which a reasonable balance has been struck in the systematization of *reactions* and *structures*. Modern books overemphasize the correlation and rationalization of molecular structures. Not enough space is devoted to the use of thermodynamics and kinetics, including mechanistic concepts, in correlating reactions, and reactions, after all, are the primary interest of inorganic chemists.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA
WILLIAM L. JOLLY

Lectures in Materials Science. Edited by PAUL LEURGANS, Cornell University, Ithaca, N. Y. W. A. Benjamin, Inc., New York 25, N. Y., 1963. viii + 109 pp. 16 × 23.5 cm. Price, $7.00 clothbound, $3.95 paperbound.

This little volume consists of four lectures given at the Cornell University Materials Science Center by P. J. W. Debye, P. J. Flory, N. Bloembergen, and F. Bitter. Each lecturer is eminently qualified to discuss his topic. The first two lectures (Debye and Flory) constitute reviews of certain recent advances in the physical chemistry of high polymers. Bloembergen's lecture is an excellent survey of the many ways in which magnetic resonance measurements have given valuable information, while Bitter's lecture is a much more detailed discussion of certain plasma phenomena.

While each lecture is excellent in its own way and their oral presentation was doubtless valuable to the program at Cornell, it is not clear to this reviewer why these lectures were published in their present form. There are now an abundance of "recent advances" or "annual reviews" type of publications which serve the reviewing purpose far better than the present arbitrary collection of four lectures in three different fields.

Financial gain for the publisher and advertising for the Cornell Materials Science Center would appear to be the motives for this publication. The high price of seven dollars (hard cover) for 109 pages indicates that the publisher hopes to make a profit on even a very small edition. This pattern of publication is unduly expensive and is not subject to satisfactory indexing.

In spite of the fact that each individual lecture is excellent in its own particular way, the present volume does not appear to be attractive for purchase generally by either individuals or libraries.

RICE UNIVERSITY K. S. PITZER
HOUSTON, TEXAS

Quantum Theory of Molecular Electronic Structure. By ROBERT G. PARR. W. A. Benjamin, Inc., New York, N. Y., 1963. xiv + 510 pp. 18.4 × 23.5 cm. Price, $10.00 clothbound, $6.95 paperbound.

The book "Quantum Theory of Molecular Electronic Structure" by Professor Robert G. Parr is one of a new series, "Frontiers in Chemistry," in which an active worker in a field indicates his opinion of the current status and future direction of that area of research as well as providing a critical guide to the voluminous series of original articles. Professor Parr's book consists of a set of lecture notes and a group of 32 reprints of the most important original papers in the field of molecular quantum mechanics.

The lecture notes describe the theoretical research done since World War II on the development of methods for precisely determining the electronic wave functions for molecules. These lecture notes are written in an easy, informal style, which, while still preserving physical and mathematical rigor, makes their perusal pleasurable as well as informative. Throughout the notes there is extensive reference to the original literature (about 500 references) with, most important of all, Professor Parr's own critical evaluation of the research reported in these references. It is this feature of the book which makes it particularly valuable to persons not familiar with the field who wish to appreciate the significance of current investigation or who wish to learn to use quantum chemistry as a tool in their own research.

The lectures discuss both the purely theoretical, rigorous calculational methods used for small molecules and the semiempirical methods currently used for large conjugated organic molecules. It is this latter section which I believe will, perhaps, be of the greatest interest to the majority of inorganic chemists. These semiempirical methods have already been applied successfully to such planar inorganic molecules as the borazine family. The basic concepts discussed in this section should have considerable applicability to such questions of current interest to inorganic chemists as π-bonding and back-bonding in inorganic compounds.

A knowledge of elementary quantum mechanics is presupposed for understanding of the lecture notes. Part I of the notes delineates the electronic structure of the helium atom and introduces the types of orbitals commonly used in quantum chemistry and the concepts of electron correlation and configuration interaction. Part II discusses the hydrogen molecule, which is the prototype for the normal covalent bond, describes valence bond and molecular orbital descriptions of wave functions and the theory of antisymmetrized wave functions, and presents a survey of purely theoretical calculations on small molecules. Part III discusses the π-electron system of planar unsaturated molecules in considerable detail. Part IV describes three approaches to the many-electron problem: the method of atoms in molecules, the theory of separated electron pairs, and the sophisticated many-electron theory of Sinanoglu. Part V summarizes Professor Parr's views on the current situation in quantum chemistry and the extensive past and potential applications of molecular quantum mechanics in the field of chemistry.

The 32 reprints in the last half of the book were thoughtfully chosen to supplement the topics discussed in the lecture notes. The majority of these papers discuss the chemically interesting π-electron problem.

This book should prove valuable both as a textbook for a course based on the lectures it contains and as a reference book by virtue of its extensive and careful documentation of the topics discussed.

QUANTUM CHEMISTRY GROUP, RIAS JOYCE J. KAUFMAN
RESEARCH INSTITUTE FOR ADVANCED STUDIES
BALTIMORE 12, MARYLAND

BOOKS RECEIVED

October 1, 1963–November 30, 1963

H. ZEISS. "Organometallic Chemistry." ACS Monograph No. 147. Reinhold Publishing Corporation, Dept. J, 430 Park Avenue, New York 22, N. Y. 1960. xiv + 549 pp. $14.31.

R. STOCK and C. B. F. RICE. "Chromatographic Methods." Chapman and Hall, Ltd., 37 Essex Street, London, W. C. 2, England. 1963. viii + 206 pp. 40 s.

JOHN P. HUNT. "Metal Ions in Aqueous Solution." Series: Physical Inorganic Chemistry. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1963. xi + 124 pp. $5.50.

WILLIAM N. LIPSCOMB. "Boron Hydrides." W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1963. ix + 275 pp. $14.00.

G. F. LOTHIAN. "Electrons in Atoms." Butterworth, Inc., 7235 Wisconsin Avenue, Washington 14, D. C. 1963. x + 196 pp. $6.95.

GEORGE T. RADO and HARRY SUHL. "Magnetism, A Treatise on Modern Theory and Materials." Vol. III. Academic Press, Inc., 111 Fifth Avenue, New York 3, N. Y. 1963. xv + 623 pp. $18.00.

H. EYRING, Editor. "Annual Review of Physical Chemistry." Vol. 14. Annual Reviews, Inc., Palo Alto, Calif. 1963. vii + 433 pp. $8.50.

W. FEITKNECHT and P. SCHINDLER, Editors. "Solubility Constants of Metal Oxides, Metal Hydroxides and Metal Hydroxide Salts in Aqueous Solution." International Union of Pure and Applied Chemistry, Butterworths, London, England. 1963. v + 69 pp.

ALBERT ROSE. "Concepts in Photoconductivity and Allied Problems." John Wiley and Sons, Inc., 605 Third Avenue, New York 16, N. Y. 1963. x + 168 pp. $5.95.