Chemical Co., St. Louis, Mo., for a supply of the starting ketone IV.

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THE OUTER SPHERE ACTIVATED COMPLEX IN THE REDUCTION OF Co(III) SPECIES[1]

Sir:

In much of the work done on oxidation-reduction reactions of Cr(II), the role of the bridged activated complex has been emphasized.[2,3,4,5] In particular, when Co(III) or Cr(III) complexes are oxidizing agents, proof has been adduced that the reactions proceed through activated complexes in which there is interpenetration of coördination spheres. We now report the results of experiments using a complex of Cr(II) which reacts by means of activated complexes in which there is no interpenetration in the same sense.

The reaction of Cr^{++}aq. with $Co(NH_3)_6^{+++}$ is slow[2] and the specific rate at 25° at $\mu = 0.41$ (Cl^- as the anion) has now been measured as 0.16 m.$^{-1}$ min.$^{-1}$. However, when Cr^{++}aq. is converted to $Cr(dip)_3^{++}$ (dip = 2,2′ bipyridine), the rate of the reaction is much increased. Thus at $\mu = 0.20$ (NaCl) and 25°, the specific rate of the reaction between $Cr(dip)_3^{++}$ and $Co(NH_3)_6^{+++}$ is 1.5×10^4 m.$^{-1}$ min.$^{-1}$. The rate is independent of the concentration of 2,2′ pyridine as long as a sufficient excess is present, and it is independent of *p*H over a considerable range, 5.5 to 3.5. It has been shown that 3 bipyridine groups are associated with each Cr^{++} under these conditions, and that the chromium product is $Cr(dip)_3^{+++}$. At low *p*H, the rate of the reaction increases, presumably because $Cr(dip)^{++}$ or $Cr(dip)_2^{++}$ reacts with $Co(NH_3)_6^{+++}$ even more rapidly than does $Cr(dip)_3^{++}$.

The interest in the observation we report is not so much that 2,2′-bipyridine so markedly increases the reactivity of Cr^{++} for $Co(NH_3)_6^{+++}$, but rather that it opens up the possibility of studying the reduction of the large class of Co(III) complexes by a reagent which acts retaining an intact coördination sphere. Considerable work with Cr^{++}aq., which with all Co(III) complexes studied except $Co(NH_3)_6^{+++}$ and perhaps $Co(NH_3)_5OH_2^{+++}$ makes use of a bridged activated complex, has already been done. Thus a systematic study can be made of the influence on the rate by each of the distinct mechanisms of changing the composition of the oxidizing agents; furthermore the chemical and isotopic effects characteristic of each type of mechanism can now be assessed. It perhaps needs to be emphasized that Co(III) complexes qualify especially for these studies because they undergo substitution slowly.

It is interesting to note that even when a bridged activated complex is not involved, $Co(NH_3)_5OH_2^{+++}$ reacts with a reducing agent much more rapidly than does $Co(NH_3)_6^{+++}$, and the rate ratio using $Cr(dip)_3^{++}$ is *ca.* 90. On changing the solvent from H_2O to D_2O, the rate at which $Co(NH_3)_6^{+++}$ reacts with $Cr(dip)_3^{++}$ is reduced by less than 10%, but a slight decrease, *ca.* 30%, is noted when $Co(NH_3)_6^{+++}$ is used as oxidant. However, when $Co(NH_3)_5OD_2^{+++}$ reacts in D_2O the rate is decreased by a factor of *ca.* 2.5 from the rate for $Co(NH_3)_5OH_2^{+++}$ in H_2O (this rate ratio can be compared to the decrease of 3.9 observed[6] in making a similar comparison with Cr^{++}aq. as reductant). A striking difference between the two kinds of mechanisms is in the sensitivity to the change from $Co(NH_3)_5OH_2^{+++}$ to $Co(NH_3)_5OH^{++}$. This change occasions an increase in specific rate by a factor of *ca.* 10^7 when Cr^{++}aq. is the reductant,[6] but by less than 100, and perhaps by as little as 10, when $Cr(dip)_3^{++}$ reacts.

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[1] This work is supported by the Atomic Energy Commission under Contract #AT(11-1)-378.

[2] H. Taube and H. Myers, THIS JOURNAL, **76**, 2103 (1954).

[3] H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954).

[4] D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

[5] A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

[6] A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959).

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BOOK REVIEWS

Nouveau Traité de Chimie Minerále. Tome IV. Group II: Glucinium – Magnesium – Calcium – Strontium – Baryum – Radium. PAUL PASCAL, Membre de l'Institut, Professeur honoráire à la Sorbonne. Masson et Cie., 120 Boulevard Saint-Germain, Paris 6, France. 1958. xxxix + 973 pp. 17 × 26 cm. Price: Broché, 7.500 fr., cartonné toilé, 8.500 fr.

The preparation of a systematic and encyclopaedic treatise on inorganic chemistry was no trifling job, seventy-five years ago; every decade that has passed since then has made it a progressively more daunting enterprise. The Arcadian simplicity of Roscoe and Schorlemmer and the earliest editions of Gmelin have given place to multi-volume productions of size and price so formidable as to restrict them almost automatically to the institutional market. The reviewer is inclined to regard the 1908–1937 edition of Abegg-Auerbach as the last comprehensive account of inorganic chemistry that had some claim to readability; those skeptical of the validity of such a claim are reminded of Donnan on copper. Mellor's treatise, staggering as the single-handled labor of a sexagenarian with little more than secretarial assistance, is known to all of us as a mine of information and references on early experimental observations but it is only intermittently readable. The gallant attempt of Yost and Russell to use a portion of the Periodic Table to illustrate how a modern systematic treatise on inorganic chemistry might be written has been much and justly admired; but their effort has, alas, provoked no "envious fever of emulation."

The encyclopaedic treatise is here to stay unless it is doomed to ultimate displacement by the punch-card. Since no such work is likely to complete a cycle of revision in less than twenty-five years, it is highly desirable that more than one such "magnum opus" should be available, preferably with publication schedules appropriately out of phase. The work under review is accordingly a welcome addition to chemical libraries. Out of twenty contemplated volumes this is the fourth to be published; it hoped to complete the series by 1960 though this is perhaps unwarranted optimism. As with Gmelin the obituary crosses in the list of collaborators are silent testimony to the truth of the ancient saying "Ars longa vita brevis." Comparisons with Gmelin are inevitable. "Pascal" will be a good deal shorter than "Gmelin"; if Volume IV is typical, the individual elements will be covered at lengths ranging from three quarters down to one fifth of that of the corresponding treatment in the eighth edition of Gmelin. The format is satisfactory and the typography more pleasing than that of Gmelin; on the other hand the French work seems less richly provided with tables and diagrams.

The distant contemplation of such a formidable accumulation of experimental fact tends to be a trifle depressing but it is impossible to come to close quarters with any section of the book without encountering intriguing observations and many challenges to further investigation. It is probable as a source of references that such works are most useful to the investigator. Here Pascal will be of great value; the deadline for references in each bibliographical section is clearly indicated and for some elements brings the literature survey forward some twenty-five years later than the corresponding Gmelin volume. In such cases the value of Pascal as a complementary guide to the more recent literature is self-evident.

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Phosphorus and its Compounds. Volume I: Chemistry. By JOHN R. VAN WAZER, Assistant Research Director and Senior Scientist, Inorganic Chemicals Division, Monsanto Chemical Company, St. Louis, Missouri. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1958. xiii + 954 pp. 15.5 × 23.5 cm. Price, $27.50.

In his Preface, the author says "the purpose of this book is to lay the foundation for a new, separate discipline of chemistry—phosphorus chemistry." However laudable such a purpose may be, the creation of a new discipline that can occupy a position of equality among the classical disciplines of inorganic, organic, analytical and physical chemistry is complicated by the twin problems of ample systematization of fact and principle and of acceptance of the body of information as sufficiently comprehensive and varied to permit continued fruitful study. By presenting phosphorus chemistry as an approach embodying many of the principles of structure and homology that distinguish an orderly organic chemistry from an often much less orderly inorganic chemistry, the author has done much to overcome the first complication. By presenting a massive, but not encyclopedic, array of coördinated information and suggesting innumerable areas for expanding research, he has done even more to overcome the second. Whether he has succeeded in devising a new discipline must be determined by the test of time. However, it cannot be denied that he has produced a volume that will be both an outstanding reference for all workers in phosphorus chemistry and a stimulus to continuing research in this fascinating area.

This volume is concerned primarily with the development of a set of underlying principles for phosphorus chemistry and the implementation of these principles by a thoroughly and carefully documented body of factual information. The emphasis throughout is upon modern interpretation of fundamental chemistry. Technology and related aspects of the chemistry of phosphorus are to be considered in a subsequent companion volume. No attempt has been made to cover every subject with absolute completeness. Rather, the author has attempted to examine available information critically and to include only that which has survived his scrutiny. Although some may question his judgment on specific points, none can disagree that his over-all selection is consistently good and that his coverage is excellent.

Phraseology, clarity of expression and style are considerably above average and render the text both readable and understandable. The author's boundless enthusiasm for his subject is evident throughout. In large measure, this compensates for certain interpretations with which others may take issue and for occasional overly generous statements such as the "millions of known structures with sp^3 bonding" (p. 71). Quite understandably, the author's not inconsiderable contributions to phosphorus chemistry provide the central themes for many of his discussions.

The text is remarkably free from mechanical errors. This and the over-all excellence of printing, binding and presentation attest the carefulness with which the manuscript was handled. Both author and publisher are to be complimented on a job well done.

The book is strongly recommended both to those specifically interested in phosphorus chemistry and to those interested in a significant contribution to the "renaissance in inorganic chemistry." It is unfortunate that the price is so high that many individuals will find it impossible to acquire personal copies.

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Some Problems in Chemical Kinetics and Reactivity. Volume I. By N. N. SEMENOV. Translated by MICHEL BOUDART. Princeton University Press, Princeton, New Jersey. 1958. xii + 239 pp. 15 × 23 cm. Price, $4.50.

This is the second edition of a book which was published first in 1954 in a limited edition of the Academy of Sciences of the U.S.S.R. and was written in preparation for a national symposium on Chemical Kinetics and Reactivity. After the discussions of the symposium, the author was asked to prepare a new edition. This was expanded to include new data from the literature and certain major additions were made to the text of the original. Two English translations, the present one by Boudart and one by Bradley for the Pergamon Press (see review below), have been authorized as well as a German edition.

The present volume is the first of two to be issued by the Princeton Press and comprises the first two of a total of four parts of this work. These two parts cover Radical Reactions (reactions of chain propagation and branching) and Chain Initiation and Termination. The third and fourth parts, on "Kinetics of Chain Reactions" are scheduled to appear in Volume II.

The book was not written as a textbook or treatise, but is a survey, by an outstanding scientist in the field, of developments in the twenty years or more since his first book on "Chain Reactions" was published. It emphasizes radical and radical-chain reactions and there is a frankly personal flavor in the discussion of these. As such, readers interested in chemical kinetics will find it both interesting and rewarding.

The first part of this volume includes an extensive discussion of monoradicals and their reactivity in competitive reactions of addition, decomposition, isomerization, or substitution; the role of polar factors; etc. There is also a much briefer discussion of diradicals. Reactions such as oxidation of hydrocarbons and polymerization are discussed in some detail. In the second part, reactions of chain initiation and termination are discussed on the basis of homogeneous molecular reagents, initiation by ions, and wall effects.

This volume has the minor technical disadvantages which are to be expected in such an edition. It is a paperback edition. There are a fair number of typographical errors, and several instances in which limitations of type have resulted in rather odd notations or in the use of a letter or symbol with more than one meaning in a single equation or paragraph. In a number of instances new materials have simply been appended as footnotes rather than actually incorporated into the text.

The author expresses a note of disappointment that so much of the extensive literature which has appeared is concerned with "disjointed observations on this or that reaction and not with a plan of investigation from all sides." He notes also that it seems to him that the majority of the fundamental problems have not been completely solved as yet. Nonetheless, his book does give a picture which shows much accomplished in building up knowledge of a new group of substances, such as the free radicals represent. The