

- ENCYCLOPEDIA OF

CHEMICAL REACTIONS

COMPILED AND EDITED BY

C. A. JACOBSON

Professor of Chemistry, West Virginia University

VOLUME I

ALUMINUM BERYLLIUM
ANTIMONY BISMUTH
ARSENIC BORON
BARIUM BROMINE

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AN IRREVERSIBLE REACTION

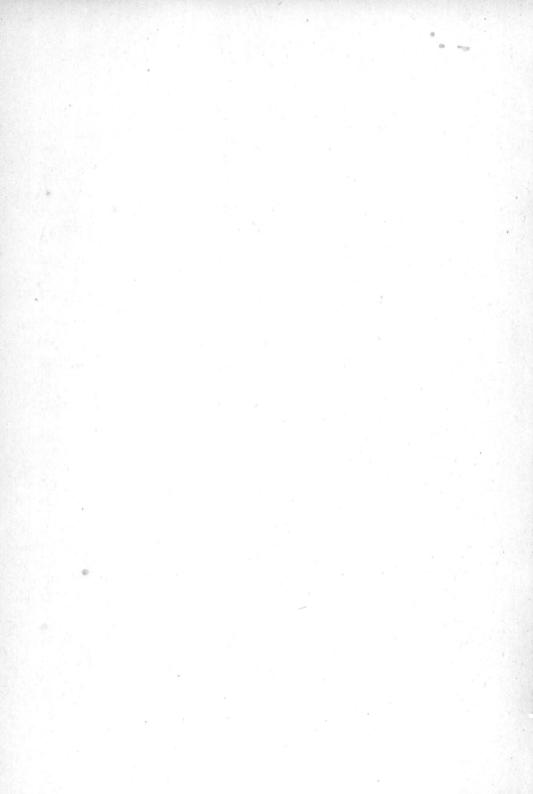
When Solomon had formulated his plans for building a temple at Jerusalem his father, King David, offered him the following encouragement: "Arise therefore and be doing, and the Lord be with thee."

Inspired effort + gold, silver, brass, etc. → Solomon's Temple.

The Bible, 1 Chron. 22: 16 (300 B.C.)

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Introduction

HISTORICAL

Conception of the Plan

In 1925 the Williams & Wilkins Company of Baltimore, Maryland, published a book for me entitled "A Pronouncing Chemical Formula Speller and Contest Guide," which contained about fifteen hundred chemical reactions expressed in equation form. These reactions embraced only elementary chemical tranformations, and were especially designed to meet the needs of freshman students and others who were beginning the study of chemistry. Although the book referred to contained other features, its popularity was essentially due to the section on chemical reactions.

The frequent use to which this book was put led me to envisage a complete reaction book or set of books that would contain all, or practically all, the published chemical reactions, described briefly and expressed in equation form. It has taken twelve years for this air castle to begin to assume material form. I was told by many that it was too great an undertaking.

The plan was discussed with Dr. E. W. Washburn, formerly of the Bureau of Standards, Washington, D. C., who had completed the "International Critical Tables" a short time before. No one was better able to judge the tremendous amount of work involved in producing an encyclopedia of this sort than he, but he told me it was not impossible if sufficient help could be secured to go through the literature.

Funds were not available to employ abstractors for reviewing the chemical journals and consequently the plan would have to be abandoned unless I could secure volunteer abstractors who would think enough of the project to donate their time to get the work under way.

Cooperation from Editors of Scientific Periodicals

A prospectus of the plan was drawn up and submitted to Dr. Otto Reinmuth, then Editor of the *Journal of Chemical Education*, for his evaluation and comments. The idea impressed him sufficiently not only to give a prominent place in his journal (Vol. 10, 1933) for the article, "A Proposed Encyclopedia of Chemical Reactions", but also to head it with the following editorial note:

"Despite the excellent abstracting service available to us and the reference compilations to be found in all well-equipped chemical libraries, the labor of making a reasonably thorough search of the literature pertaining to even a very limited field of chemical subject matter is tremendous. A truly exhaustive search is seldom attempted

and probably represents in reality only an ideal to be approached as closely as possible.

"The usual literature search may be roughly divided into four stages: (1) accumulation from reference works of a summary of facts with corresponding references for subsequent checking and amplification by direct resort to the literature; (2) extension of the original summary by search of abstract indices; (3) examination of abstracts to determine which references are worthy of fuller investigation; (4) verification of facts and references already accepted as useful and supplementation of summaries by direct resort to the literature.

"It is obvious that if any of these processes could be performed more efficiently or if any two of them could be combined, library research would be significantly facilitated. A work of the type proposed by Dr. Jacobson would combine the convenience of an index with a considerable portion of the informational content of abstract and reference works."

Dr. J. McKeen Cattell published in *Science* for June 15, 1934, an article entitled "An Encyclopedia of Chemical Reactions" and has since then released notes about the progress of this work.

To the above editors as well as to the late Dr. Harrison E. Howe, Editor of Industrial and Engineering Chemistry, and to Mr. Watson Davis, Editor of the Science News Letter must be given much credit for letting people know about the proposed undertaking, without whose cooperation it would have been impossible to proceed. Foreign publications, such as the Journal of the Society of Chemical Industry, Journal of Canadian Chemistry and Metallurgy, Journal of the Indian Chemical Society, Chemicky Obzor, etc. have published notices about the Encyclopedia.

Personnel

After explaining the aim of the E.C.R. to some graduate students in the Department of Chemistry of the West Virginia University, the first volunteer to apply the plan to a search of chemical literature as a topic for the Master's thesis was Miss Kathryn Huffman, who started the work of recording, under each element, the conditions governing the chemical reaction between a given compound and another element or compound called a reagent, and then expressing that reaction in the form of an equation. Such literature search proved of considerable didactic value.

Miss Mary B. Larcher and Mr. Carl Armour also abstracted assigned sections of chemical literature, equivalent to the requirements for their Master's theses.

In addition to the above-mentioned work, Miss Huffman was employed on a special University fund to do abstracting for the E.C.R. during an entire summer vacation. Dr. Virgil Lilly was likewise employed to abstract German chemical literature during the summer months.

Other graduate students who accepted assignments to do abstracting work are: P. S. Potesta, Benjamin Tatterson, John Russell, David Posten, and later, Dorothy Franz, Lawrence T. Johnson, Herman A. Reda, Ralph E. Wilmer, and Owen C. Greenwell.

After the publication of the above-mentioned articles many inquiries about the project and promises of support were received, but the most valuable one for the E.C.R. was from Prof. Wilhelm Segerblom of Exeter New Hampshire. He wrote me as follows:

"Your account of a proposed 'Encyclopedia of Chemical Reactions,' as printed in the Journal of Chemical Education for October 1933 has interested me much. When I think of the hours that were spent, the volumes that were consulted, and the leaves that were turned in the preparation of my own little book on 'Properties of Inorganic Substances', I stand aghast at the magnitude of the undertaking you are proposing. But when I think of the time and effort that your encyclopedia will save chemists in future years, then I realize that the results more than warrant the effort. The sooner you get the book compiled and published the better for the progress of Chemistry."

This friend of the E.C.R. took hold of the abstracting of the Scandinavian chemical journals in dead earnest and covered practically all of them found in this country, spending his entire vacations for four years in the libraries of the universities of Harvard, Yale, Columbia and Madison. He also spent some weeks at the Library of Congress, all at his own expense. Unfortunately, Professor Segerblom did not live to see the fruit of his enormous labor, but as a deserved memorial to his devotion I want to inscribe his name at the very top of the list of associate editors of the "Encyclopedia of Chemical Reactions." He contributed freely and without stint to a cause that he considered of lasting importance.

Professor Thomas W. Davis of New York University also wrote me at an early date expressing his convictions about the need and usefulness of a work like the E.C.R. in the following terms:

"There is a continuing need for such a compendium, a need which is not lessened by industrial and economic crises. Its success will depend on the loyal efforts of a corps of abstractors and compilers—each making a small sacrifice of time and energy in the interest of the common undertaking. The general prospectus is sound—we need now the detailed work of following it through. When the 'Encyclopedia' is finally issued, I am sure that it will at once be accepted into the literature as an indispensable reference work. Its place is not filled by descriptive treatises on inorganic chemistry—there can be no adequate

substitute for it. We shall see the truth of this statement more clearly after the 'Encyclopedia' has been used a short time. I am happy to be able to contribute in a small way to its final success."

The roster of abstractors for the E.C.R. numbered only 31 up to December 1940. Shortly after that date notices about the progress of the E.C.R. were published in the News Edition of Industrial and Engineering Chemistry, in the Journal of Chemical Education and in Science, which revived an interest in the work, so that in December of the following year (1941) there were 103 listed abstractors. Although perhaps less than half of them had shown very little or no interest in doing any abstracting, yet the sum total of all reactions submitted up to that time was 12,768.

The interest in the E.C.R. continued to spread until on June 1, 1942, the abstractor personnel numbered 116 and the total reactions submitted to that date was 15,863.

On July 1 of that year we began assembling the reactions under aluminum, antimony, and arsenic with a view of putting these in condition for publication in the first volume. There were found to be 659 under Al, 372 under Sb, and 1021 under As.

TESTIMONIALS

The value of any work or publication is determined by the consensus of opinion of people interested along a similar line. Before chemists in general will take seriously a work like this, it is natural that they should inquire what other chemists think about it. For this reason it was thought advisable to include, in the introduction, a brief section of opinions contributed by chemists in different fields of the profession. The original letters containing these statements are on file, and are reproduced without regard to any order of importance.

Prof. Ralph E. Dunbar, Dean of the School of Chemical Technology,

Fargo, N. Dak. says:

"Busy chemists will recognize the value and importance of having the inorganic chemical literature systematically and conveniently abstracted. This is the first consistent effort to assemble all available inorganic reactions into one complete and comprehensive work. The saving in time and effort on the part of research workers will more than compensate for the combined activities of all faithful abstractors who have cooperated in the compilation of these volumes. The specific references to the original chemical literature of the world will be an important lead to those workers who desire more detailed information regarding any reaction. Even ambitious students may find here the answer to many perplexing problems. Perhaps it is not too ambitious an ideal to hope that the 'Encyclopedia of Chemical Reactions' may

eventually find its place along with the 'International Critical Tables,' Mellor's 'Comprehensive Treatise on Inorganic Chemistry,' Abegg-Auerbach's 'Handbuch der Anorganischen Chemie,' and Beilstein's 'Handbuch der Organischen Chemie,' as an essential addition to all industrial and educational research libraries. At least such is our hope.''

Dr. Paul A. Giguére, Assistant Professor of Chemistry, Laval University,

Quebec, Canada, says:

"While it is obvious that such a work as the E.C.R. will be useful to all chemists in general, it seems that it will prove of exceptional assistance in research work. Indeed, not only will this encyclopedia provide a complete and adequate source of information regarding the numerous inorganic compounds already described in the literature, but it will further contribute to the progress of chemistry by offering a concise picture of what is left to be done, for instance on such topics as the molecular structure and properties of the various compounds, their methods of preparation, the mechanism of the reactions in which they take part, etc. A simple glance through the book should not fail to suggest scores of interesting problems, as yet unsolved."

Dr. Walter Wagner, Assistant Professor of Chemistry, Worcester Poly-

technic Institute, Worcester, Mass., says:

"Many chemists engaged in research, teaching or technical laboratory work will find the need for a work containing all hitherto published chemical reactions in available form. The vast amount of material presented in this comprehensive list is invaluable to them.

"Of particular value, it seems to me, is the perpetuity feature of the work, permitting the scholar to follow the most recent achievements in chemistry. At the same time it enables him to pursue the historic

development of certain reactions in which he is interested.

"After all, I feel certain that this outstanding work will become a reliable and even indispensable companion of everyone engaged in chemistry."

Dr. G. E. F. Lundell, Chief Chemist of the Bureau of Standards, Wash-

ington, D. C. wrote me the following several years ago:

"When you first discussed the matter with me I was somewhat dubious of the plan, chiefly on account of the enormous amount of work that would be necessary if the compilation were to be anywhere near complete. I now believe that it is feasible and that it would be a tremendous help to the chemist, particularly to the analytical chemist."

Mr. James A. Austin, Chairman, Kansas City Section A.C.S., Kansas

City, Mo., says:

"The recorded observations of the reactions of the elements are scattered throughout the vast literature of chemistry and many that may have potential value, either academic or economic, lie buried in this mass.

"It is the purpose of this publication to bring together these observations in one work with the hope that, from it, workers may receive inspiration for further research leading to a better knowledge of the fundamental nature of chemistry and also to the utilization of some of these reactions in present day problems.

"The intense interest in micro or semi-micro technic, especially as applied to qualitative analysis, has developed rapidly in the past few years and the search for methods of producing materials which were formerly imported are just two reasons for supporting this compilation of reactions of the elements.

"If these pages lead to just one single application toward these ends, the contributors will feel amply repaid for their efforts."

Mr. E. J. Crane, Editor of *Chemical Abstracts*, Columbus, Ohio, wrote in 1933:

"I have read your article descriptive of the proposed 'Encyclopedia of Chemical Reactions' and have thought about it a good deal: Such a compilation would serve as a handy tool for chemists and it certainly would be fine if some magician could wave a wand and a completed copy would drop into the hands of each of us."

Dr. Frederick C. Nachod, Research chemist, Permutit Company, res. Mt. Holly, N. J., says:

"Chemists realized very early the need for standard works of reference to coordinate and check on old and new findings. A chemist nowadays would feel lost without Chemical Abstracts, Chemisches Zentralblatt, etc. Such reference works had to be supplemented by others of a different nature like Landolt-Bernstein's 'Tabellen,' Gmelin-Kraut, Mellor's treatise, etc., but up to now we have no complete handbook summarizing the chemical reactions which are encountered in the literature. This gap is now to be filled by the Encyclopedia of Chemical Reactions. There will probably be many criticisms and suggestions before the E.C.R. reaches its final form, but we hope that it may grow quickly and steadily in order to become an essential tool for the chemist of today and tomorrow."

Many other excellent testimonials are at hand equally worthy of inclusion in this section, but lack of space prevents.

NOMENCLATURE

No doubt greater variations in both the spoken and written language of chemistry may be found than in the language of any other science. These variations exist not only in pronunciation but in the spelling and hyphenating of words and in the writing of formulas. The American Chemical

Society have a standing committee whose efforts have been directed, over a long period of years, to the standardization of nomenclature, spelling and pronunciation of chemical words and the writing of formulas, but the impression made upon the body of chemists as a whole leaves much to be desired.

This subject might properly be introduced by saying that there is still confusion in the chemical trade due to the fact that manufacturers of chemicals are slow to follow the advances made in chemical nomenclature. A few illustrations are doubtless apropos: Should we desire to buy some sodium fluosilicate we must ask for sodium silicofluoride; if we need boron trioxide we must specify acid boric. White arsenic or arsenic trioxide is sold under the name "acid arsenious." Suppose we are in need of some sodium dihydrogen orthophosphate; we find listed in the chemical catalogs "sodium phosphate, primary, secondary, and tertiary." The beginner in chemistry would have to consult his dictionary before he could order the right chemical. When we buy periodic acid we receive H₅IO₆ instead of HIO4. In other words, there is no indication in the catalog that the substance offered for sale is the dihydrated acid. Should we wish to purchase some vanadium trichloride, we find listed "vanadium chloride, dry, liquid. or sirupy." Vanadium occurs as either the di-, tri-, or tetrachloride, and we have no direct way of telling if the manufacturer or agent has what is wanted.

Both VOSO₄ and V₂O₂(SO₄)₈ are called vanadium oxysulfate or vanadyl sulfate. We have arbitrarily named the former vanadyl sulfate and the latter divanadyl trisulfate. HgNH₂Cl has been called ammono basic mercuric chloride; mercury amido chloride, amino mercury chloride and mercury II ammonium chloride. We favor mercury amido chloride. HN₃ is known as hydrazoic acid, azoimide or hydrogen azide. We favor triazoic acid, and triazides for its salts.

Enough has been said to show that there is still an enormous amount of work to do for a committee on chemical nomenclature.

In the present volume the editors have tried to follow as closely as possible the recommendations made by the Committee for the Reform of Inorganic Chemical Nomenclature of the International Union of Chemistry, issued in 1940.

Some of the exceptions and the reasons therefore may be listed as follows: "The ous and ic endings for the copper and iron salts are retained because they have been very firmly established, and there is no ambiguity about them, so that we call Fe(CNS)₃ ferric thiocyanate instead of iron III thiocyanate as given in the report.

For the same reason we also retained the common names of the acid salts of carbonic, sulfurous, and sulfuric acids, so that NaHCO₃, NaHSO₄, NaHSO₄, and KHCO₃, KHSO₃, and KHSO₄ have been named sodium

bicarbonate, sodium bisulfite, etc. All other acid salts like Na₂HPO₄, disodium hydrogen orthophosphate, have been named according to the Committee's recommendation.

Whenever an inorganic element in the formula of a salt was separated from the acid radical by oxygen, as for example BiONO₈, the ending yl of the name has been adopted, so that this salt is called bismuthyl nitrate. Whenever this system might cause ambiguity, the term oxy has been used. Consequently, UO₂(NO₈)₂ was called uranium dioxydinitrate. The names recommended by the Committee for K₄Fe(CN)₆ and K₃Fe(CN)₆, potassium hexacyanoferrate II and potassium hexacyanoferrate III, have not been used, since the departure from the common names seemed too revolutionary. However, the Committee's names are very explicit, though long.

Ammonia addition compounds have all been treated alike and called ammoniates, just as water addition compounds have all been called hydrates, using the proper Greek prefix to designate the number of each addition product. Dr. E. C. Franklin, formerly of Leland Stanford Junior University made these compounds his life work, and was very positive in calling them all ammoniates. Conditionally the "Committee" also sanctions this usage. In representing the ammoniates by formulas we have inserted the NH₃ radicals at the end of the formulas exactly as is done with H₂O in hydrates. This is done for the sake of clearness of representation. and not with any regard to linkage of NH₃ radicals in the molecule when the compound is ionized or electrolyzed. For example, if we found the compound Cr(NH₃)₆Cl₃ described in the literature the formula entered in the equation was CrCl₃ 6NH₃ and the name given to it, chromium III chloride hexammoniate. Some writers do not drop the a in hexa and write the name hexaammoniate, but the former is more euphonious and its meaning cannot be misunderstood.

The name "stibine" is used interchangeably in the literature for SbH₃ and for SbH₅. In this work we have applied this name to SbH₃ and its derivatives only, and have called SbH₅ and its derivatives antimony pentahydride. To illustrate, the compound H₃SbO is called trihydrogen antimony oxide, and H₃SbCl₂, trihydrogen antimony dichloride. The same nomenclature has been applied to arsine, AsH₃ and its derivatives.

The editors of the E.C.R. are desirous to cooperate with any committee or body of chemists duly appointed for the purpose of studying and improving the present nomenclature and formula writing in the field of inorganic chemistry.

Rules Adopted for E.C.R. Abstractors

The following revised rules, having been developed over a period of years, are recommended to abstractors for the E.C.R. They represent the best