THE CHEMISTRY OF THE ACTINIDE ELEMENTS

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PREFACE

THE actinide elements play important roles both in nuclear technology and in modern inorganic chemistry. The chemistry of the actinide elements, particularly that of thorium, uranium and plutonium, is vital in the realization of nuclear power, and the chemical properties of the entire group are intimately involved in the developing nuclear technology. Similarly, the addition of the large number of synthetic transuranium elements to the Periodic Table has had great significance for modern inorganic chemistry. This book is intended to provide a comprehensive and unified treatment of the chemistry of the actinide elements for both the nuclear technologist and the inorganic and physical chemist. For the nuclear technologist considerable emphasis has been placed on nuclear process chemistry. For the inorganic and physical chemist, the quantitative aspects of the subject have been stressed. A particular effort has been made to summarize the extensive descriptive material as well as to describe in detail the present situation regarding the electronic configuration of the actinide elements. It is thus hoped that the present volume will serve both as an introduction to the subject and as a convenient reference work for the specialist.

The literature has been treated critically and quite exhaustively, although no attempt has been made to supply a complete key to the older literature. We have, however, made an effort to include important literature citations through 1956. It is hoped to keep this volume abreast of future development by way of future editions, and to this end we solicit reprints on all phases of the subject.

The task of the authors has been immeasurably lightened by the co-operation of their colleagues. Unpublished data relating to the spectroscopy of the actinide elements were given us by Dr. J. R. McNally, Jr. and Dr. Mark Fred. Dr. Fred prepared several of the spectroscopic level diagrams, and he and Mr. J. G. Conway gave us valuable aid in the preparation of the manuscript. Dr. S. G. Thompson supplied us with unpublished material on the transcurium elements. Dr. Dieter M. Gruen contributed material for the sections on the magnetic properties of the actinide elements, and read all of Chapter11 with a critical and perspicacious eye. Dr. Henry R. Hoekstra contributed material on the salts of uranium; we also received the benefit of his expert advice on other matters dealing with uranium chemistry. Mr. John Axe compiled Table 11.11 dealing with the thermochemistry of the actinide elements and their compounds. This table was critically reviewed by Dr. E. F. Westrum, Jr., who also supplied some data for it. Dr. Frank Stephens, Jr., compiled Appendix II, and Dr. D. Strominger carefully reviewed all of the material dealing with the nuclear properties of the actinide elements. We have also consulted Dr. John R. Huizenga frequently on nuclear matters.

We owe our very sincere thanks to several of our colleagues who have reviewed portions of the manuscript and who have given us expert advice. Dr. James C. Hindman gave frequent advice on many aspects of the solution chemistry of the actinide elements. We have greatly benefited from his kindness and patience in unravelling for us the complexities of plutonium and neptunium solution chemistry. Dr. Robert E. Connick gave the chapter on plutonium a very thorough reading, resulting in undoubted improvement of the treatment. Dr. R. A. Penneman, Dr. L. B. Asprey, and Dr. J. S. Coleman read the chapters on americium and curium very carefully, and portions of both chapters were rewritten by them. Dr. James Cobble reviewed both the neptunium and plutonium chapters. We are also indebted to Drs. L. Brewer, G. R. Choppin, B. B. Cunningham, R. E. Elson, S. Fried, B. G. Harvey, H. H. Hyman, C. D. Jeffries, L. I. Katzin, Amos S. Newton, G. C. Pimentel, Frank H. Spedding, D. H. Templeton, and R. Edward Wood for reading various portions of the manuscript.

To Dr. James C. Wallmann we owe a particularly heavy debt of gratitude. Dr. Wallmann read all of the manuscript, the galley and the page proofs. His penetrating and frequently disconcerting observations have contributed much to this book.

Mrs. Beth Hines was responsible for the typing of the manuscript, for securing the illustrations, and furnished much help in many other ways. We wish to express our very sincere thanks to her for her very valuable contributions. Miss Doral Buchholz also participated in a most helpful way in making it possible to prepare the manuscript for the publishers.

Miss Eileen Carson served as a technical assistant in the preparation of the manuscript, and Mrs. Elinor Potter numbered and checked all of the references in the book. Miss Carson and Mrs. Potter read and checked all of the galleys and proofs. The author and subject indices were also compiled by Mrs. Potter. We take sincere pleasure in acknowledging the very considerable help they rendered us.

Dr. Winston M. Manning has helped us in many ways in the preparation of the book, and we are happy to express our thanks for his many kindnesses.

To all of the aforementioned, we again express our deep appreciation.

J. J. K.
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I

INTRODUCTION

The last fifteen years have witnessed a revolution in the physical sciences. The discovery of nuclear fission by Hahn and Strassmann⁽¹⁾ in 1939 led very shortly afterward to the successful utilization of the energy of the nucleus. The development of nuclear reactors and other nuclear devices has, to be sure, been largely at the hands of the physicist. But the impact of nuclear fission has had scarcely less far-reaching implications for the chemist. At this writing, ten new transuranium elements have been successfully synthesized, some on a large industrial scale. The preparation and isolation of these new elements and the characterization of their compounds have added a considerable volume of new descriptive material to inorganic chemistry. Included among these newcomers are elements with a rich and varied chemical behaviour, manifested by the formation of unusual compounds and in some cases by an extraordinary complexity in solution. Because of the radioactivity of the new elements, new and unconventional experimental procedures have of necessity been developed to permit the study of these new substances in safety. Of even greater significance to the chemist, however, are the problems which arise from attempts to interpret the relationship of the new elements to each other and to the remainder of the Periodic Table. The electronic configuration of these heaviest elements is being studied by the physical chemist by all appropriate methods. In many instances, it has been necessary to re-examine and re-evaluate older regions of the Periodic Table, resulting, for example, in a large volume of new researches, on the rare-earth elements and on such long-known elements as thorium and uranium. The inorganic chemist, then, has ample reason for familiarizing himself with new developments in the theory and practice of the heaviest elements. The object of this book is to present in concise fashion the experimental and theoretical aspects of the chemistry of the heaviest elements, to point out gaps in our present knowledge in this general field, and to provide a background for the future developments in inorganic chemistry which must inevitably proceed from the incorporation of such a substantial number of new elements into the Periodic System.

While much of the chemistry of the elements under consideration here resembles closely that of the elements of the older portions of the Periodic Table, there are also significant differences. Thus, the preparation of the

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(1) O. Hahn and F. Strassmann, *Naturwissenschaften* **27,** 11 (1939).

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elements and their compounds is for the most part accomplished by well-known chemical reactions. The radioactivity of many of these heaviest elements, however, necessitates special laboratory procedures both for preparations and subsequent characterization. Although X-ray crystallographic methods have played an important role in inorganic chemistry, it is in the study of the compounds of the heaviest elements that these methods have probably received their most intensive application. In the hands of Zachariasen⁽²⁾ and others, it has been found feasible to identify and characterize microgram amounts of new compounds, providing results of the greatest value during the early stages of investigation of a new element when only minute amounts of material may be available. For the study of the new elements in solution, two general procedures have been followed. Investigations may be carried out on the *tracer* level, where solutions are handled in ordinary-sized laboratory beakers and flasks, but where the substance studied is present at very low concentrations. Concentrations of the order of $10^{-12} M$ or lower are not unusual, and the radioactivity of the substance under investigation provides the means for detecting its presence. Alternatively, studies may be carried out with microgram (or even somewhat smaller) amounts of material at ordinary concentrations, say $10^{-1} M$ to $10^{-3} M$, but in very small volumes. These so-called 'drop-scale' or ultramicrochemical manipulations are carried out on amounts and volumes of material too small to be seen with the unassisted eye, but in concentrations normally encountered in the laboratory. Such procedures have been described by Kirk⁽³⁾ and by Cunningham,⁽⁴⁾ pioneers in the development and application of these methods. Tracer procedures have been applied to solutions containing only a few score atoms (see Chapter 10); tracer studies are usually not definitive, but do serve to give very useful and quite reliable information on oxidation states, complexing, solubility of various compounds, and similar information. Much experience is required to assess properly results of tracer experiments. Ultramicrochemical investigations yield results of normal validity, but much skill is necessary to carry out such experimentation. It is not surprising, therefore, that most of the chemical results described in this book were obtained as the result of work on the milligram scale. With milligram amounts, manipulations can be readily carried out in a conventional manner, and the results are usually quite unambiguous. It is interesting to note that working on the milligram scale (or somewhat less) may be from choice rather than from limitations on supply. With intensely radioactive substances such as actinium or curium, work on the microgram scale is preferred even when more material is available; with

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(2) An excellent description of the application of X-ray crystallographic methods is given by S. Fried and W. H. Zachariasen, 'The Chemistry and Crystal Chemistry of Heavy Element Compounds,' *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955*, **7**, 235 (1956).

(3) P. L. Kirk, *Quantitative Ultramicroanalysis.* (John Wiley and Sons, Inc., New York, 1950.)

(4) B. B. Cunningham, *Nucleonics* **5**, 62–85 (1949).

actinium, for example, useable X-ray patterns cannot be obtained on larger amounts because of the gamma radiation associated with milligram amounts of actinium and its daughter decay products. Health considerations may likewise limit the amount of material used in a given experiment, since many of these elements are exceedingly toxic because of their radioactivity. From the experimental point of view, then, most of the chemical results described herein were obtained on about the milligram scale, using semi-micro procedures.

In order to facilitate the manipulation of the frequently highly toxic and intensely radioactive actinide elements, special equipment and facilities have been devised. Fig. 1.1 shows the type of enclosed containers (gloved boxes) which are used to confine the spreading of radioactive materials. A more intimate view of the interior of such a box can be obtained from Fig. 1.2; the variety of chemical manipulations which can be carried out may be judged from the equipment present in the box. Fig. 1.3 shows a typical laboratory devoted to the study of the actinide elements; in addition to gloved boxes, shielded facilities for working with beta and gamma radioactive substances are also present. Fig. 1.4 depicts a shielded facility for handling intensely radioactive samples such as are frequently involved in the isolation of the actinide elements from neutron bombarded sources. Here all operations are effected by remote control. Some of the complexities inherent in the study of the actinide elements can be gauged from these figures.

The experimental results, which are described systematically for the individual elements in the earlier chapters of this book, provide the basis for an evaluation of the relationship of the new synthetic elements to each other and to the remainder of the Periodic Table. The thesis advanced in this book is that the chemistry of the heaviest elements can best be understood if these elements are regarded as a rare-earth-like family, with actinium as the first member of the series in the same sense that lanthanum inaugurates the 'lanthanide' series. This concept, that a new rare-earth-like group of elements begins with actinium, endows these conveniently entitled 'actinide elements,' with special interest for the inorganic chemist. Previously, the rare-earth or 'lanthanide' elements were the only example of a series of elements which were related to each other in the unique fashion in which inner electronic orbitals were completed. Now, in the actinide elements, a quite comparable situation exists with respect to the completion of the electronic configurations. Studies of both the similarity and differences between the actinide elements and the lanthanide elements (and other transition elements) may with some confidence be expected to shed light ultimately on the thorny question of the general relationship between electronic configuration and chemical properties.

In one important respect, some of the actinide elements differ in a pronounced way from most of the other elements in the Periodic Table, and that is with respect to *atomic weight*. The elements which occur in nature have atomic weights which are, for all practical purposes, invariant. Each of the actinide elements, even those of natural occurrence, have a multitude of isotopes, many of which can be obtained in isotopically pure form. Some of these isotopes have such short half-lives that they are of no interest for conventional chemical studies, although they may be useful for tracer studies. The relatively longer-lived isotopes can be used for conventional studies, but it is necessary to specify precisely the isotope being used, for although the chemical behaviour of various isotopes will be very nearly identical, differences in atomic weight can lead to serious analytical errors. Thus, although uranium chemistry is usually studied using the natural mixture of U^{234}, U^{235}, and U^{238} (atomic weight 238·04), it can also be studied using pure U^{238} or U^{233} which have sensibly different atomic weights. By analysis of the radioactive decay data, it has been possible to calculate the isotopic masses of the trans-mercury isotopes, making a direct calculation of the atomic weights on the chemical scale practical.(5) The chemical atomic weights of the actinide elements and their isotopes are given in Appendix I.

Much of the early work on the actinide elements was carried out in secrecy during World War II. The scientifically important results of the war-time and subsequent research carried out in the United States of America have been published as part of the National Nuclear Energy Series;(6, 7) these volumes give a comprehensive description of the chemistry and nuclear properties of the actinide elements, and may be consulted for details.

The International Conference on the Peaceful Uses of Atomic Energy held in Geneva in 1955 provided an enormous amount of technical information relating to all phases of nuclear energy. The United Nations, under whose auspices this important conference was held, has published the material contributed to the conference in a monumental series of sixteen volumes.(8) Volumes 7, 8, and 9 are of particular interest to the chemistry of the actinide elements.

(5) R. A. Glass, S. G. Thompson, and G. T. Seaborg, *J. Inorg. Nucl. Chem.* **1,** 3 (1955).

(6) G. T. Seaborg, J. J. Katz, and W. M. Manning, editors. *The Transuranium Elements: Research Papers, Natl. Nuclear Energy Ser.* Div. IV, **14B,** 1733 pp. (McGraw-Hill, New York, 1949).

(7) G. T. Seaborg and J. J. Katz, editors. *The Actinide Elements, Natl. Nuclear Energy Ser.* Div. IV, **14A,** 870 pp. (McGraw-Hill, New York, 1954).

(8) *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva 1955* (United Nations, New York, 1956).

II

ACTINIUM

1.0. Historical

In 1899, Debierne,⁽¹⁾ working in the Curie laboratory, discovered a new radioactive element. Geisel,⁽²⁾ in 1902, independently observed the existence of this same radioactive substance. In both cases, the new radioactive species appeared in that fraction of uranium ore in which rare-earth elements concentrate during processing, and the rare-earth-like nature of the new element was soon recognized. It is now known that this isotope of element 89 was that of mass 227; the name actinium (*aktis*, ray) is now applied to all of the isotopes of element 89.

Until 1950 the element was not known in pure form, being heavily admixtured with rare earths from which it was almost impossible to effect separation by the techniques then available. In 1950 the isolation of pure Ac^{227} produced by the transmutation of Ra^{226} was announced. Actinium chemistry may now be studied in the customary ways, instead of by the tracer techniques required previously. Present interest in actinium chemistry stems largely from its role as the prototype element of the actinide series, corresponding to lanthanum in the rare-earth series.

2.0. Isotopes

A considerable number of isotopes, both natural and artificial, of actinium are now known, and these are listed in Table 2.1. Actinium 227 is the only isotope of element 89 with a half-life sufficiently long to permit of normal chemical manipulations. The Ac^{227} exists in nature in very small amounts in all uranium ores as a decay product of U^{235}, but is more conveniently obtained by synthetic procedures. The isotope Ac^{228} ($MsTh_2$) is useful as a tracer for actinium in radiochemical studies.

The isotope Ac^{227} decays primarily by emission of a very weak beta particle which appears to have a maximum energy of 45·5 kev. This is radiation which has so little penetration as to make it difficult indeed to detect, so that at one time Ac^{227} was considered 'rayless.' Analysis by radioactivity thus is somewhat more difficult than usual. Perey and Hettler⁽³⁾ have described a

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(1) A. Debierne, *Compt. rend.* **129,** 593 (1899).
(2) F. O. Geisel, *Ber.* **35,** 3608 (1902).
(3) M. Perey and A. Hettler, *Compt. rend.* **242,** 2551 (1956).