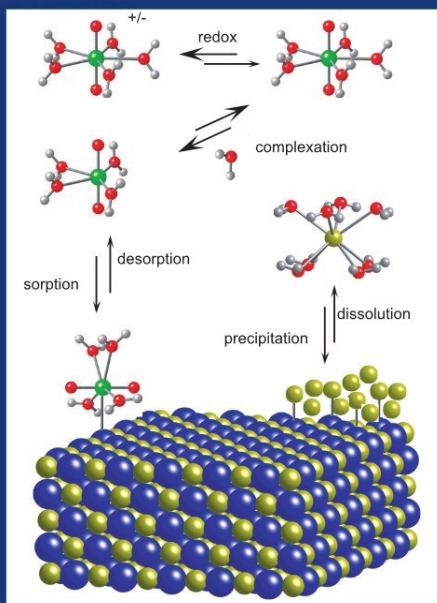


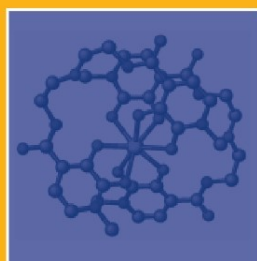
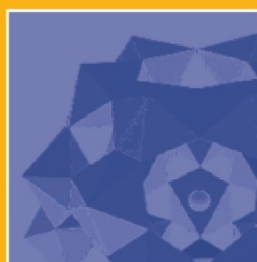
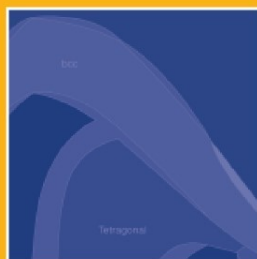
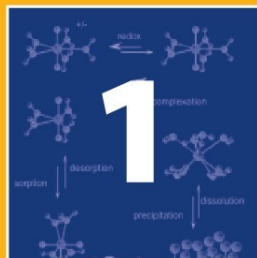
The Chemistry of the Actinide and Transactinide Elements

Fourth Edition



Edited by
Lester R. Morss,
Norman M. Edelstein &
Jean Fuger

 Springer



THE CHEMISTRY OF THE
ACTINIDE AND
TRANSACTINIDE ELEMENTS



Joseph J. Katz



Glenn T. Seaborg

**This work is dedicated to
Joseph J. Katz and Glenn T. Seaborg,
authors of the first and second editions of
The Chemistry of the Actinide Elements
and leaders in the field of actinide chemistry.**

THE CHEMISTRY OF THE
ACTINIDE AND
TRANSACTINIDE ELEMENTS

FOURTH EDITION

Volumes 1–6

EDITED BY

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PREFACE

THE CHEMISTRY OF THE ACTINIDE AND TRANSACTINIDE ELEMENTS FOURTH EDITION

The fourth edition of *The Chemistry of the Actinide and Transactinide Elements* comprises the chapters in volumes 1 through 5 of the third edition (published in 2006) plus the newly published volume 6, with the exception that the subject and author indices and list of contributors now encompass all volumes. Volume 6 (Chapters 32 through 39) consists of new chapters that focus on specialized topics related to actinide species in the environment, actinide waste forms, nuclear fuels, analytical chemistry of plutonium, actinide chalcogenide and hydrothermal synthesis of actinide compounds. Each chapter in volume 6 has been written to provide sufficient background for the substantial parts of the readership that are not specialists in these areas of actinide science.

The editors are deeply indebted to the contributors of each chapter of volume 6, all of whom agreed enthusiastically to write their chapters and all of whom did so as a labor of love as well as a long-term professional responsibility. We thank Sonia Ojo and Claudia Culierat of Springer who provided helpful advice during the production of volume 6.

We note with sadness that Joseph J. Katz, the first author and editor of the first and second editions, passed away in January 2008. We dedicate this edition to the memory of Joseph J. Katz and Glenn T. Seaborg.

All of us who participated in writing, editing, and publishing *The Chemistry of the Actinide and Transactinide Elements* express our sincere hope that these volumes will make a substantive contribution to research in actinide science, and that they will be an appropriate source of factual information for teachers, researchers, and students and for those who have the responsibility for utilizing the actinide elements to serve humankind and to control and mitigate their environmental hazards.

*Lester R. Morss
Norman M. Edelstein
Jean Fuger*

INTRODUCTION

Joseph J. Katz, Lester R. Morss,
Norman M. Edelstein, and Jean Fuger

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The actinide elements are the 15 chemical elements with atomic numbers 89 through 103, the first member of which is actinium and the last member is lawrencium (Fig. 1.1). The transactinide elements (those beyond the actinides) are the heaviest known chemical elements. Both the actinide and the transactinide elements have chemical properties that are governed by their outermost electronic subshells. Each of these groups of elements is a unique transition series (a group of elements in which d or f electronic subshells are being filled).

The actinides are the transition elements that fill the 5f subshell. The actinide series is unique in several respects:

- Most of the elements (those heavier than uranium) were first discovered by synthetic methods: bombardment of heavy atoms with neutrons in nuclear reactors, bombardment with other particles in accelerators, or as the result of nuclear detonations.
- All actinide isotopes are radioactive, with a wide range of nuclear properties, especially that of spontaneous and induced nuclear fission.
- They are all metals with very large radii, and exist in chemical compounds and in solution as cations with very large ionic radii.
- The metals exhibit an unusual range of physical properties. Plutonium, with six allotropes, is the most unusual of all metals.
- Many of the actinide elements have a large number of oxidation states. In this respect plutonium is unique, being able to exist in aqueous solution simultaneously in four oxidation states.
- In metallic materials and in some other compounds with elements lighter than plutonium, the 5f orbitals are sufficiently diffuse that the electrons in these orbitals are “itinerant” (delocalized, chemically bonding, often with unique magnetic moments and electrical conductivity). In metallic materials and in most compounds with elements heavier than plutonium the 5f electrons are “localized” (not contributing significantly to electrical conductivity or to chemical bonds). Materials with plutonium and adjacent

elements can exhibit both itinerant and localized behavior, depending on conditions such as temperature and applied pressure.

- Actinium (which has no 5f electrons in the metal, free atom, or in any of its ions) and the elements americium through lawrencium are similar in many respects to the lanthanide elements (the elements that fill the 4f electron subshell). The elements thorium through neptunium have some properties similar to those of the d transition elements.
- Relativistic contributions to electronic properties and spin–orbit effects are important in the chemical properties of actinides.

The transactinide elements are at the frontier of both the periodic table (Fig. 1.1) and the chart of the nuclides. Transactinide chemistry has been in existence since 1970. Although these elements have unique properties, they are very difficult to study because their synthesis and identification require unique nuclear reactions and rapid separations. The heaviest transactinide element for which chemical properties have been identified (at the time of writing of this work) is hassium (atomic number 108). Experimental evidence and theoretical studies to date indicate that the elements through 112 are part of a 6d transition series of elements.

1																	18
1 H	2 He											13 B	14 C	15 N	16 O	17 F	18 Ne
3 Li	4 Be											5 Al	6 Si	7 P	8 S	9 Cl	10 Ar
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db (Ha)	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	113	114	115	116	(117)	(118)
(119)	(120)	(121)	(154)														
LANTHANIDES		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
ACTINIDES		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		
SUPERACTINIDES		(122)	(123)	(124)	(125)	(126)											(153)

Fig. 1.1 The periodic table of the elements, showing placement of transactinides and superactinides through element 154 (see Chapter 14). (Italics indicate elements reported but not yet confirmed as of 2005. Undiscovered elements are shown in parentheses.)

The transactinides are also unique in several respects:

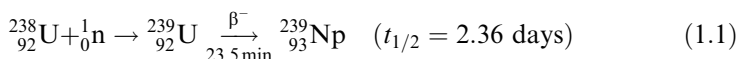
- One-atom-at-a-time chemistry is required to compensate for low nuclear yields and short isotopic half-lives. Ingenious techniques have been developed to study their chemical properties in both gas phase and solution.
- Relativistic effects cause substantial contraction of the 7s (occupied), 7p (empty), and 6d (partially filled) orbitals. (Many electronic configurations have been calculated; see Chapter 14.) The contraction of the 7s orbitals stabilizes the $7s^2$ electron pair. The contraction of the 7p orbitals makes 7p terms accessible, e.g., the first excited multiplet of rutherfordium (element 104) outside the $[\text{Xe } 5f^{14}]$ core is calculated to be $6d7s^27p$.
- The first part of the transactinides constitutes a 6d transition series, with the calculated ionic radii intermediate between those of the 5d ions and actinide ions of the same charge. Relativistic effects decrease the polarizability of transactinide ions.
- Fundamental properties – electronic configurations, ionization energies of atoms and ions, oxidation–reduction potentials in solution – remain to be calculated theoretically and measured experimentally.

In the six decades that have elapsed since the “actinide concept” was enunciated by G. T. Seaborg, great advances have taken place in actinide and transactinide chemistry. As in many other important areas of science, new information and new concepts have accumulated to an extraordinary extent. This, in itself, would be ample justification for a comprehensive examination of the scientific aspects of the actinide elements. Of equal, or perhaps even greater, importance in the preparation of this third edition are the contributions that its many authors have made to provide the foundations for the solution of some of the most urgent technological and environmental problems that face humanity worldwide. We refer, of course, to the problems created by nuclear reactors used for electricity production; nuclear weapons production and dismantlement; the treatment and storage of nuclear wastes; and the cleanup of Cold War nuclear material sites. These are sources of acute global concern, in all of which the actinide elements are intimately involved.

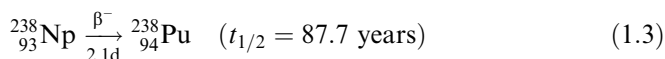
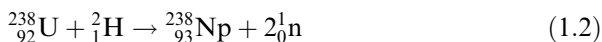
In 1957, when the first edition of this work was published, the chemistry of the actinide elements was remarkably well developed, considering that the actinide concept itself had first been publicly described in 1945. (See Chapter 15, section 1.2, of this book) The elements thorium and uranium had already been studied by chemists for more than 100 years. Uranium enjoyed some small distinction as the heaviest element in nature, and as the terminus of the classical periodic table. In 1895 Becquerel had discovered that uranium undergoes radioactive decay, a discovery that permanently divested uranium of its obscurity, and that inaugurated the era of the Curies, Rutherford, Soddy, Hahn and Meitner, Fajans, and others who mapped the very complex radioactive transformations of the naturally occurring elements. The crucial importance of uranium, however, became fully apparent only after Fermi and his colleagues irradiated many of the

elements, including uranium, with neutrons in the 1930s. They produced new radioactive species with chemical properties that were not identical with any of the known heavy elements. The Fermi group believed that they had created new elements heavier than uranium. In 1938 Hahn, Meitner, and Strassmann conducted definitive chemical experiments showing that the radioactive species produced by neutron irradiation of uranium were in fact fission fragments resulting from the cleavage of the uranium nucleus into smaller nuclei. Their experiments constituted the discovery of nuclear fission. The earlier formation of transuranium elements had been disproved, but the way to their synthesis was now open.

The first transuranium element, neptunium, was nevertheless the by-product of an investigation by McMillan and Abelson into the details of the fission process. While fission fragments recoil with enormous energy from a uranium nucleus undergoing fission, a radioactive species with a half-life of 2.3 days was observed to be formed with insufficient energy to escape from a thin film of irradiated uranium. Chemical investigation confirmed that a new element, neptunium, unknown in nature, with atomic number 93 and mass number 239, had been formed by neutron capture in ^{238}U .



The new prospects opened up by the discovery of the first transuranium element were rapidly explored, and soon the trickle became a flood. Table 1.1 lists the transuranium elements, the discoverers and the date of discovery, and the date of first isolation in weighable amount. The first of the transuranium elements to be synthesized on purpose, so to speak, was element 94 as the isotope of mass number 238. In 1940, Seaborg, McMillan, Kennedy, and Wahl at the University of California in Berkeley bombarded uranium oxide with 16 MeV deuterons produced in the 60 in. cyclotron and succeeded in isolating a long-lived alpha-particle emitter, chemically separable from both uranium and neptunium, which was identified as an isotope of element 94 and later given the name plutonium:



Twenty isotopes of plutonium are now known. The plutonium isotope of major importance has always been the isotope of mass number 239. Research with ^{239}Pu has been strongly motivated by the fact that it was shown to be fissile by slow neutrons in the same way as ^{235}U , and would thus be able to sustain a neutron chain reaction. The isotope ^{239}Pu can thus be used for both military and nuclear energy purposes. To separate ^{235}U from ^{238}U requires an isotope separation of

Table 1.1 *The transuranium elements.*

<i>Atomic number</i>	<i>Element</i>	<i>Symbol</i>	<i>Discoverers and date of discovery</i>	<i>First isolation in weighable amount</i>
93	Neptunium	Np	E. M. McMillan and P. H. Abelson, 1940	L. B. Magnusson and T. J. LaChapelle, 1944
94	Plutonium	Pu	G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl, 1940–41	B. B. Cunningham and L. B. Werner, 1942
95	Plutonium-239		E. Segrè, and A. C. Wahl, 1941	B. B. Cunningham, 1945
95	Americium	Am	G. T. Seaborg, R. A. James, L. O. Morgan, and A. Ghiorso, 1944–45	
96	Curium	Cm	G. T. Seaborg, R. A. James, and A. Ghiorso, 1944	L. B. Werner and I. Perlman, 1947
97	Berkelium	Bk	S. G. Thompson, A. Ghiorso, and G. T. Seaborg, 1949	S. G. Thompson and B. B. Cunningham, 1958
98	Californium	Cf	S. G. Thompson, K. Street, Jr., A. Ghiorso, and G. T. Seaborg, 1950	B. B. Cunningham and S. G. Thompson, 1958
99	Einsteinium	Es	A. Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, M. H. Studier, P. R. Fields, S. M. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizenga, A. Hirsch, W. M. Manning, C. I. Browne, H. L. Smith, and R. W. Spence, 1952	B. B. Cunningham, J. C. Wallmann, L. Phillips, and R. C. Gatti, 1961
100	Fermium	Fm	A. Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, M. H. Studier, P. R. Fields, S. M. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizenga, A. Hirsch, W. M. Manning, C. I. Browne, H. L. Smith, and R. W. Spence, 1953	
101	Mendelevium	Md	A. Ghiorso, B. G. Harvey, G. R. Choppin, S. G. Thompson, and G. T. Seaborg, 1955	
102	Nobelium	No	A. Ghiorso, T. Sikkeland, J. R. Walton, and G. T. Seaborg, 1958	

Table 1.1 (Contd.)

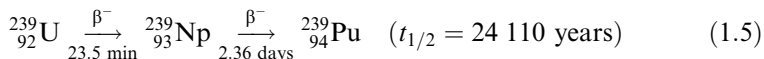
<i>Atomic number</i>	<i>Element</i>	<i>Symbol</i>	<i>Discoverers and date of discovery</i>	<i>First isolation in weighable amount</i>
103	Lawrencium	Lr	A. Ghiorso, T. Sikkeland, A. E. Larsh, and R. M. Latimer, 1961	
104	Rutherfordium	Rf	A. Ghiorso, M. Nurmia, J. Harris, K. Eskola, and P. Eskola, 1969; Y. T. Oganessian, Y. V. Lobanov, S. P. Tretyakova, Y. A. Lasarev, I. V. Kolesov, K. A. Gavrilov, V. M. Plotko, and Y. V. Poluboyarinov, 1974	
105	Dubnium	Db	A. Ghiorso, M. Nurmia, K. Eskola, J. Harris, and P. Eskola, 1970; G. N. Flerov, Y. T. Oganessian, Y. V. Lobanov, Y. A. Lasarev, and S. P. Tretyakova, 1970	
106	Seaborgium	Sg	A. Ghiorso, J. M. Nitschke, J. R. Alonso, C. T. Alonso, M. Nurmia, G. T. Seaborg, E. K. Hulet, and R. W. Loughheed, 1974	
107	Bohrium	Bh	G. Münzenberg, S. Hofmann, F. P. Hessberger, W. Reisdorf, K. H. Schmidt, J. H. R. Schneider, P. Armbruster, C. C. Sahn, and B. Thuma, 1981	
108	Hassium	Hs	G. Münzenberg, P. Armbruster, H. Folger, F. P. Hessberger, S. Hofmann, J. Keller, K. Poppensieker, W. Reisdorf, K. H. Schmidt, H. J. Schott, M. E. Leino, and R. Hingmann, 1984	
109	Meitnerium	Mt	G. Münzenberg, P. Armbruster, F. P. Hessberger, S. Hofmann, K. Poppensieker, W. Reisdorf, J. R. H. Schneider, W. F. W. Schneider, K. H. Schmidt, C. C. Sahn, and D. Vermeulen, 1982	
110	Darmstadtium	Ds	S. Hofmann, V. Ninov, F. P. Hessberger, P. Armbruster, H. Folger, G. Münzenberg, H. J. Schött, A. G. Popeko, A. V. Yereimin, A. N. Andreyev, S. Saro, R. Janik, and M. Leino, 1995	

111	Roentgenium	Rg	S. Hofmann, V. Ninov, F. P. Hessberger, P. Armbruster, H. Folger, G. Münzenberg, H. J. Schött, A. G. Popeko, A. V. Yeremin, A. N. Andreyev, S. Saro, R. Janik, and M. Leino, 1995
112			S. Hofmann, F. P. Hessberger, D. Ackermann, G. Münzenberg, S. Antalic, P. Cagarda, B. Kindler, J. Kojouharova, M. Leino, B. Lonnel, R. Mann, A. G. Popeko, S. Reshitko, S. Saro, J. Uusitalo, and V. Yeremin, 2002 ^a
113			Same as element 115 ^a
114			Yu. Ts. Oganessian, V. K. Utyonkov, Yu. V. Lobanov, F. Sh. Abdullin, A. N. Polyakov, I. V. Shirokovsky, Yu. Ts. Tsyganov, G. G. Gulbekian, S. L. Bogomolov, B. N. Gikal, A. N. Metsentsev, S. Iliev, V. G. Subbotin, A. M. Sukhov, O. V. Ivanov, G. V. Buklanov, K. Subotic, M. G. Itkis, K. J. Moody, J. F. Wild, N. J. Stoyer, M. A. Stoyer, and R. W. Loughheed, 2000 ^a
115			Yu. Ts. Oganessian, V. K. Utyonkov, Yu. V. Lobanov, F. Sh. Abdullin, A. N. Polyakov, I. V. Shirokovsky, Yu. Ts. Tsyganov, G. G. Gulbekian, S. L. Bogomolov, A. N. Metsentsev, S. Iliev, V. G. Subbotin, A. M. Sukhov, A. V. Voinov, G. V. Buklanov, K. Subotic, V. I. Zagrebaev, M. G. Itkis, J. J. Patin, K. J. Moody, J. F. Wild, M. A. Stoyer, N. J. Stoyer, D. A. Shaughnessy, J. M. Kenneally, and R. W. Loughheed, 2004 ^a
116			Yu. Ts. Oganessian, V. K. Utyonkov, Yu. V. Lobanov, F. Sh. Abdullin, A. N. Polyakov, I. V. Shirokovsky, Yu. Ts. Tsyganov, G. G. Gulbekian, S. L. Bogomolov, B. N. Gikal, A. N. Metsentsev, S. Iliev, V. G. Subbotin, A. M. Sukhov, O. V. Ivanov, G. V. Buklanov, K. Subotic, M. G. Itkis, K. J. Moody, J. F. Wild, N. J. Stoyer, M. A. Stoyer, R. W. Loughheed, C. A. Laue, Ye. A. Karelin, and A. N. Tatarinov, 2000 ^a

^a Discovery claimed and published but not confirmed by IUPAC/IUPAP.

formidable proportions, but separating ^{239}Pu in pure form requires only a chemical separation from other elements, likewise an intimidating problem, but one that is in principle a considerably simpler undertaking.

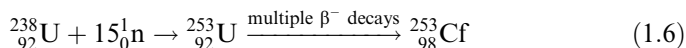
In 1941, Kennedy, Seaborg, Segré, and Wahl successfully obtained ^{239}Pu by radioactive decay from ^{239}Np , which was first produced by irradiating natural ^{238}U with cyclotron-generated neutrons:



The isotope plutonium-239 indeed turned out to be fissionable, with a slow neutron cross section 1.7 times that of uranium-235. Later work at the wartime Los Alamos Laboratory established conclusively that sufficient neutrons were emitted in the act of fission to sustain a nuclear chain reaction. The exigencies of World War II soon made available the massive resources necessary to convert the scientific possibilities of the transuranium elements into actuality, and the nuclear age was truly upon us. Seaborg (1982, 1992) has given a vivid eyewitness account of the discovery and early experiments with plutonium. This chronicle describes in unusual detail the problems that confronted the investigators in this strange and intimidating new field of research, and how they were solved.

Twelve transplutonium elements were added to the periodic table in the 30 years between 1944 and 1974. The syntheses of the elements with atomic number 95 through 106 required the development of new and ingenious experimental techniques as well as new conceptual frameworks, and these were elaborated with remarkable speed. Elements 95 and 96, named americium and curium, respectively, were first prepared in 1944 by bombardment of ^{239}Pu ; curium was synthesized by irradiation of plutonium with helium ions (alpha particles), and soon thereafter americium was synthesized by multiple neutron capture in plutonium in a nuclear reactor. As was the case for neptunium and plutonium, chemical identification was essential; it was not until these elements were predicted to be part of an actinide (5f) transition series with +3 oxidation states that they were isolated and identified. By 1946 the chemical properties of americium and curium were already well defined, and by 1949 sufficient amounts of americium-241 and curium-242 had been accumulated to make it possible to undertake a search for the next members of the actinide series. Bombardment of elements 95 and 96 by helium ions accelerated in the 60 in. Berkeley cyclotron produced alpha-particle-emitting species that could be identified as isotopes of elements 97 and 98. These in turn were named berkelium and californium after their place of discovery. Again, prediction of their behavior as +3 ions in aqueous solution was essential. During this same period of time, magnetic and spectroscopic evidence confirmed that the transuranium elements were indeed members of a 5f series of elements; see the review by Gruen (1992).

The detonation of a thermonuclear device is capable of producing enormously high fluxes of neutrons. The first test thermonuclear explosion was set off at Eniwetok Atoll by the United States at the end of 1952. The huge numbers of neutrons produced by the explosion resulted in multineutron captures in the uranium-238 that was a part of the device. The capture of no fewer than 15 neutrons by a ^{238}U nucleus yielded an isotope of element 98:



Capture of the 15 neutrons must have been accomplished in a fraction of a microsecond, and the subsequent radioactive decay of uranium-253 via a series of beta-particle emissions to form californium-253 must have been completed in a short time. Californium-253 then undergoes decay by beta-particle emission (with a half-life of 17.8 days) to form einsteinium-253. Close examination of the debris from the nuclear explosion revealed another alpha-particle-emitting radioactive species that was identified as an isotope of element 100 with the mass number 255. The new elements were named einsteinium and fermium in honor of two of the most important progenitors of the nuclear age. The unexpected consequences of the vast numbers of neutrons released by the nuclear chain reaction thus led to the synthesis of two new elements and revealed the potential utility of high-flux nuclear reactors in the production of transplutonium elements. Following the earlier use of other reactors in the 1950s, the High-Flux Isotope Reactor (HFIR) and the transuranium processing facility, currently named Radiochemical Engineering Development Center (REDC) were built at Oak Ridge National Laboratory in the 1960s for the production of transcurium elements. The HFIR starting material is highly irradiated plutonium-239 already containing substantial amounts of heavier isotopes of plutonium. Prolonged exposure to the intense neutron flux of HFIR produces considerable amounts of plutonium-242, americium-243, and curium-244, which have been isolated and refabricated into new targets for irradiation in the HFIR. Work-up of these targets, a task of no mean proportions because of the intense radioactivity from fission products and the newly formed transcurium elements, yields heavy isotopes of curium, berkelium, and californium plus smaller quantities of einsteinium and fermium.

The discovery of elements 99 and 100 in a sense was a watershed in the search for elements of ever higher atomic number. The experimental methods developed to isolate and identify neptunium and plutonium, refined and elaborated, were adequate for the task of isolation and characterization of the transplutonium elements up to element 100. With the transfermium elements, matters became much more difficult. Among the isotopes of the elements uranium, neptunium, plutonium, and curium, there is at least one that has a half-life of 10^6 years or more. For americium and berkelium, the longest-lived isotopes, produced by neutron irradiation, have half-lives of the order of 10^4 years and 1 year, respectively. The most stable californium isotope has a half-life less than

1000 years, einsteinium a half-life less than a year, and fermium a half-life of about 3 months. The elements of atomic number greater than 100 have isotopes with lifetimes measured in days, hours, minutes, seconds, and fractions of a second. The short half-lives severely limit the amount of a heavier isotope that can be made. Whereas the elements up to atomic number 100 could be characterized with amazingly small amounts of material, these, nevertheless, still contained large numbers of atoms. All of the actinides with atomic numbers up to 99 have been studied with weighable amounts (Table 1.1) but there is no prospect for producing weighable amounts of heavier elements. The elements of higher atomic number had to be identified with as little as one atom of a new element. That this feat was achievable was a result of the rapid developments in nuclear systematics, which made it possible to predict the nuclear properties of new isotopes; the actinide concept, which predicted the chemical properties of transuranium elements; and the development of new experimental techniques, which made it possible to isolate a single atom of a new isotope almost simultaneously with its formation in a nuclear reaction, and to measure half-lives in the millisecond range.

On the complex subject of nuclear systematics, it will be sufficient here to mention that the great progress made in the theoretical understanding of the behavior of atomic nuclei allowed predictions about lifetimes and the nature of radioactive emissions and their energetics to be made with considerable confidence, and this played a major role in the search for new elements. The actinide concept similarly played a crucial part. When the first transuranium elements were studied in the laboratory, it soon became apparent that the new members of the periodic table did not have the chemical properties that might be expected of them if they were placed in traditional sequence after uranium. Neptunium did not behave like rhenium, and in no way did plutonium resemble osmium, which would have been positioned directly above plutonium had the first two transuranium elements merely been inserted in the next vacant positions in the periodic table directly after uranium. Because similarities in chemical behavior arise in the periodic table from similarities in electronic configuration of the ions of homologous elements, simple insertion of the transuranium elements into the periodic table would have precluded its use as a reliable guide to the chemistry of the new elements.

The actinide hypothesis advanced by Seaborg systematized the chemistry of the transuranium elements, and thus greatly facilitated the search for new elements. From the vantage point of the actinide concept, the transuranium elements are considered to constitute a second inner transition series of elements similar to the rare-earth elements. In the rare-earth series, successive electrons are added to the inner 4f shell beginning with cerium and ending with lutetium. In the actinide series, fourteen 5f electrons are added beginning, formally, with thorium (atomic number 90) and ending with lawrencium (atomic number 103). Although the regularities are not as pronounced in the actinide as in the lanthanide series, the concept of the actinide elements as members of a 5f

transition series is now accepted and has served as a unifying principle in the evolution of the chemistry of the actinide elements. A more detailed discussion of the actinide hypothesis can be found in Chapter 15.

The first chemical studies on neptunium and plutonium were made using classical radiochemical techniques in the 1940s. Amounts far too small to be weighed were studied by tracer methods, where solutions are handled in ordinary-sized laboratory vessels. Concentrations of the order of 10^{-12} mol L⁻¹ or less are not unusual in tracer work, and valuable information could be acquired on solutions containing only a few million atoms. The radioactive element is detected by its radioactivity, and the chemistry is inferred from its behavior relative to that of an element of known chemistry present in macro amounts. When weighable amounts were available, ultramicrochemical methods were used. These manipulations were and still are carried out with microgram or even lesser amounts of material in volumes of solution too small to be seen by the naked eye at concentrations normally encountered in the laboratory. Ultramicro methods make possible the isolation of small samples of pure chemical compounds, which can then be identified by X-ray crystallography or electron diffraction in a transmission electron microscope. All of the actinide elements are radioactive, and, except for thorium and uranium, special containment and shielded facilities are mandatory for safe handling of these substances. Gloved boxes are required (Fig. 1.2)



Fig. 1.2 A modern laboratory with a bank of gloved boxes for carrying out experimental chemistry of transuranium elements. (Reproduced by permission of Los Alamos National Laboratory.)

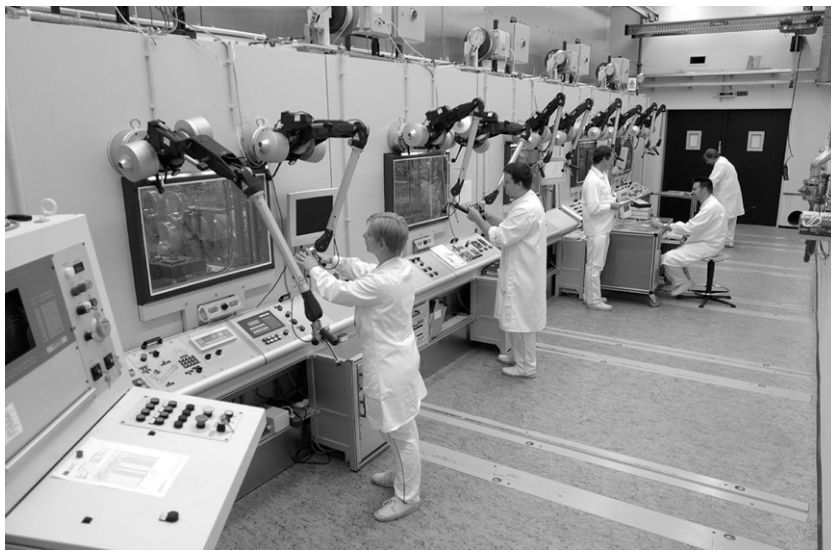


Fig. 1.3 *A hot-cell facility for remote synthesis and characterization of gram-scale transuranium materials. (Reproduced by permission of Institute for Transuranium Elements, Karlsruhe, part of the Joint Research Centre, European Commission.)*

and, where high levels of penetrating radiation (gamma rays or neutrons) are encountered, which is not infrequent, all manipulations may need to be performed by remote control (Figs. 1.3 and 1.4). Even when radiation can easily be shielded, as is the case with alpha-particle emitters, containment to prevent inhalation is still essential because of the toxicity of the transuranium elements. Inhaled transuranium isotopes may be deposited in the lungs and ingested isotopes may be translocated to the bone, where the intense alpha radioactivity over a period of time can give rise to neoplasms. The shorter the half-life, i.e., the higher the specific activity of the radioactive isotope, the more serious are the difficulties of experiments with macro amounts of material. Consequently, every effort has been made to produce long-lived isotopes. There are available isotopes of neptunium, plutonium, and curium with half-lives longer than 10^5 years, and isotopes of americium and californium that have half-lives of the order of 1000 years can be used in chemical studies. These long-lived isotopes greatly reduce the extent of radiolysis of water or other solvents for experiments in the liquid phase, they minimize radiation damage in the solid phase, and they also considerably reduce the health hazards in the experiment. Even with the longest-lived isotopes, most laboratory research with transuranium elements is carried out on the milligram or smaller scale.

The syntheses of the transfermium elements presented an even more challenging set of problems. Because of the short lifetimes of these isotopes, production by successive neutron capture in a high-flux reactor was not possible. Methods



Fig. 1.4 Example of an experimental setup within a hot-cell facility. (Reproduced by permission of Institute for Transuranium Elements, Karlsruhe, part of the Joint Research Centre, European Commission.)

for the rapid collection of the newly formed isotopes had to be developed and very rapid separation procedures were required to isolate a pure product for identification. Ghiorso (1982) described in fascinating detail how these problems were surmounted. A newly formed nucleus contains sufficient energy to eject it from a target undergoing bombardment; the atom that recoils can be caught on a clean foil placed in close proximity to the target. The catcher foil can then be dissolved and the solution examined. For identification, ion-exchange chromatography proved to be ideal. Elution from an ion-exchange column can be carried out very rapidly. The order of elution is very specific and provides an unmistakable fingerprint for identification. In this way, it was possible to synthesize and identify element 101, subsequently named mendelevium, in experiments in which it was made one atom at a time. Even more highly refined collection procedures were evolved to complete the actinide series of elements by the discovery of nobelium (atomic number 102) and lawrencium (atomic number 103).

The transactinide elements 104 through 112 have been discovered at Berkeley and Darmstadt (see Table 1.1). Scientists at the Dubna Laboratory in Russia also made claims for the discovery of a number of these elements, but their evidence did not meet the accepted criteria for the discovery of new elements (Wilkinson *et al.*, 1991, 1993). No names have been suggested for elements