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## The transuranium elements: present status

*Nobel Lecture, December 12, 1951*

Mina Damer och Herrar.

Jag är inte van vid kemiska ord på svenska, och det är för att mina föräldrar aldrig talade kemi i hemmet. Jag skulle gärna ända velat hålla hela denna föreläsning på svenska. Men - om jag talade svenska så skulle mina vänner McMillan och Lawrence inte förstå mer än hälften av vad jag säger. Jag ska därför tala engelska, och jag vet att ni alla förstår det språket mycket bra.

As I continue, speaking in English, I want to assure my British and American colleagues here, Sir John Cockcroft and Professors Walton, Lawrence, and McMillan, that they haven't missed anything yet. I want to begin by saying that I am fortunate in being a member of a Chemistry Department which has a long standing tradition of great breadth of research interests, leading to an early program in nuclear chemistry under the active leadership of men like G. N. Lewis and W. M. Latimer. The work on the transuranium elements which I am about to describe was made possible by this circumstance and because of the unusual and excellent spirit of cooperation which exists at the Radiation Laboratory, under the direction of Professor E. O. Lawrence, where the cyclotron bombardments so crucial to the final results were made. I shall try in the course of my lecture to point out the contributions to this work of my many colleagues but unfortunately it will not be possible to do this adequately in the time available.

Beginning at essentially the point where Professor McMillan left off in his lecture, I shall first describe our work on plutonium. The beginning of this can be considered to have taken place in the fall of 1940 when I asked a graduate student, Arthur C. Wahl, to consider the possibility of studying the tracer chemical properties of element 93 as a thesis problem, a suggestion which he was happy to accept. This, and related work on element 94, was carried on in collaboration with Dr. Joseph W. Kennedy who, like myself, was at that time an instructor in the Department of Chemistry at the University of California. After Dr. McMillan's departure from Berkeley in November, 1940, and his gracious assent to our continuation of the search for, and

possible identification of element 94, our group turned its major efforts to this problem.

A bombardment of uranium oxide with the 16-MeV deuterons from the 60-inch cyclotron was performed in December, 1940. Alpha radioactivity was found to grow into the chemically separated element 93 fraction, and this alpha-activity was chemically separated from the neighboring elements, especially elements 90 to 93 inclusive, in experiments performed during the following months. These experiments, which constituted the positive identification<sup>1,2</sup> of element 94, showed that this element has at least two oxidation states, distinguishable by their precipitation chemistry, and that it requires stronger oxidizing agents to oxidize element 94 to the upper state than is the case for element 93. The particular isotope identified has been shown to be of mass number 238 and the reactions for its preparation are shown in the first slide (Fig. 1).

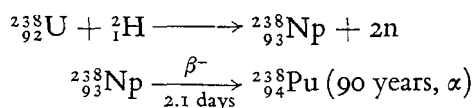


Fig. 1.

The chemical properties of elements 93 and 94 were studied by the tracer method at the University of California for the next year and a half. These first two transuranium elements were referred to by our group simply as "element 93" and "element 94" until the spring of 1942, at which time the first detailed reports concerning these elements were written<sup>3,4,5</sup>. In order to write the report<sup>4</sup> on the chemical properties, it became necessary to have chemical symbols for the two elements. It was remembered that McMillan had suggested the name "neptunium" (symbol Np) for element 93 after Neptune, the planet immediately beyond Uranus, which gives its name to uranium, and, therefore, it was thought proper that element 94 should assume the name "plutonium" (symbol Pu) after the next planet Pluto. These names and symbols have been adopted officially by the International Union of Chemistry and will be used here.

The isotope of plutonium which is of major importance is the one with mass number 239. The search for this isotope, as a decay product of <sup>239</sup>Np, was going on almost simultaneously, and these experiments were being carried on by the same group with the added collaboration of Dr. E. Segrè. The isotope <sup>239</sup>Pu was identified and its possibilities as a nuclear energy

source were established<sup>6</sup> during the spring of 1941 using a sample prepared by the decay of cyclotron-produced <sup>239</sup>Np and later purified by taking advantage of the then known chemistry of plutonium.

Once the value of the isotope <sup>239</sup>Pu was thus established, the paramount problem was that of producing it on a large scale and isolating it after production. The production problem was solved through the development of the chain reacting units, or piles, utilizing the neutron-induced fission reaction on <sup>235</sup>U in natural uranium, in which the extra neutrons beyond those needed to perpetuate the chain reaction are absorbed by <sup>238</sup>U to form the desired isotope <sup>239</sup>Pu. These well-known reactions are summarized in the following slide (Fig. 2).

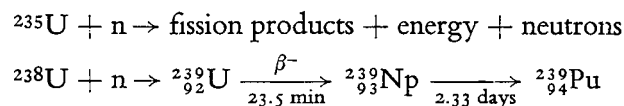


Fig. 2.

The isolation of the plutonium was to be done by chemical means, and in the spring of 1942, I and a number of my colleagues moved to the Metallurgical Laboratory at the University of Chicago to work on this problem. Among the people who made outstanding contributions to this separation program, both at Chicago and at other sites, was Dr. I. Perlman, who, it is interesting to note, before this time had made an outstanding reputation in another field, the application of radioactive tracers to physiology and biochemistry. Investigations continued at the University of California under the direction of W. M. Latimer and A. C. Wahl, leading to further discoveries of importance to the program.

During the first months at the Metallurgical Laboratory, intensive effort was directed toward defining the process which was to be used in the production plants which were then being planned. Although it was felt that the separation process would depend on the use of the two oxidation states of plutonium which had been discovered during the early work at the University of California, the actual details, such as the best carrier compounds and best oxidizing and reducing agents, had not yet been discovered. Dr. S. G. Thompson is largely responsible for the conception and early development of the process which was finally chosen. I cannot, of course, give recognition individually to the large group of scientists who participated so successfully in the diverse phases of this over-all problem. In addition, although this

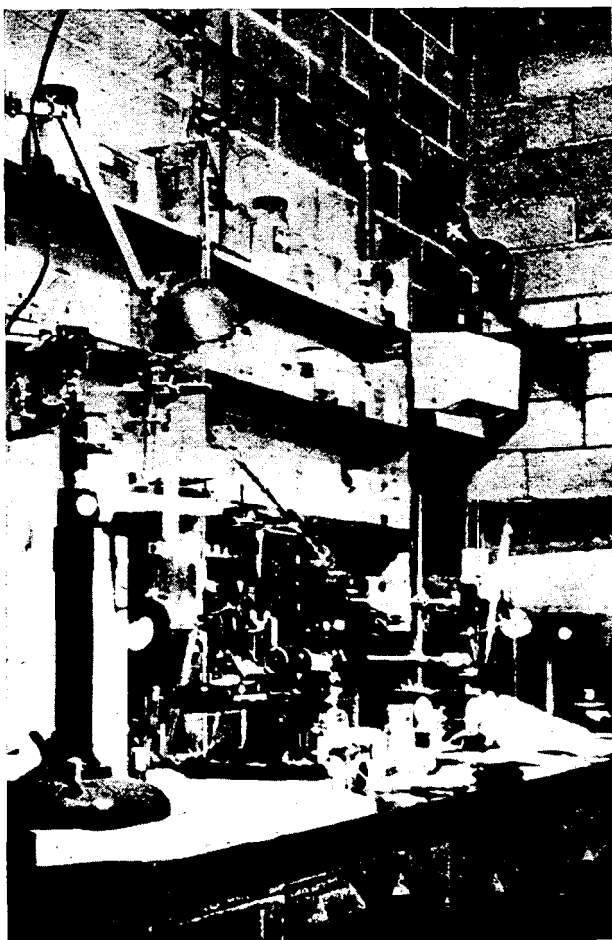


Fig. 3. First laboratory for the study of pure plutonium, Metallurgical Laboratory, Chicago, 1942.

lecture is concerned primarily with the basic chemistry and physics of the transuranium elements, mention should be made of the outstanding contribution of the chemists and engineers of the du Pont Company in the adaptation of the plutonium process for industrial operation and in the plant design, construction and operation.

The laboratory investigations were conducted on the tracer scale, and it soon became apparent that tests would be necessary under conditions where the plutonium concentration would be the same as that anticipated in the production plant. This proved a great difficulty since no one had actually

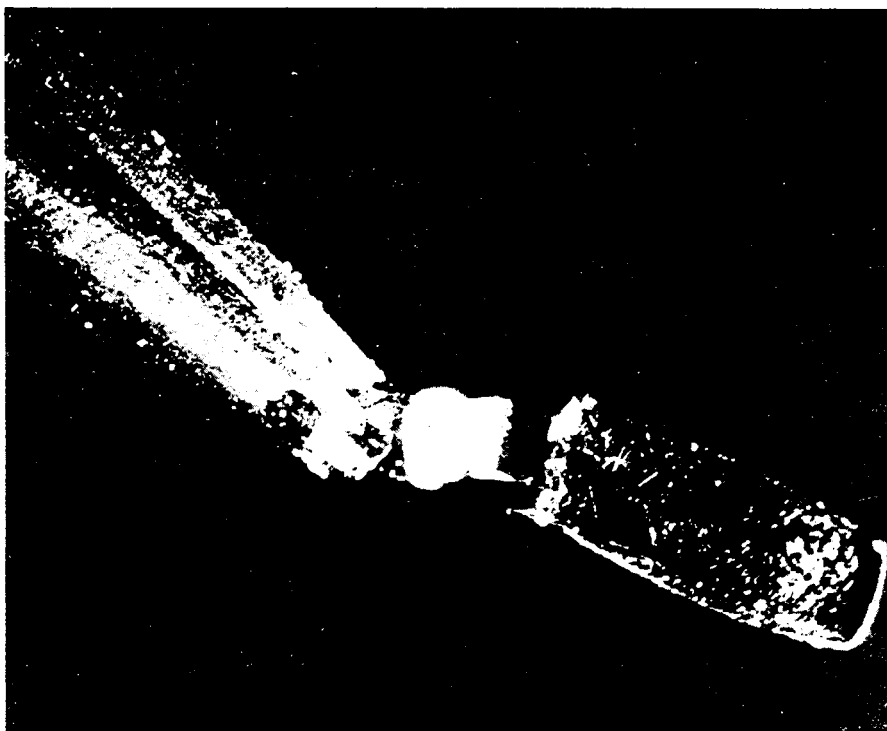


Fig. 4. This highly magnified plutonium compound is the first to be weighed by man and is here shown on a platinum shovel held by forceps. (Magnified approximately 13-fold.) (Courtesy of *Life Magazine*.)

seen any plutonium up to this time, and the design of the separation plants had to begin immediately so that the construction of these plants could take place at the same time as the construction of the chain reacting units. This problem was solved by producing an actually weighable amount of plutonium by bombarding large amounts of uranium with neutrons from the cyclotron, the first time a weighable amount of any transmutation product had been produced with a particle acceleration machine, and by working with this material in such extremely small volumes that ordinary concentrations would prevail. The field which embraces the study of chemical material on this, the microgram scale of operation, has been given the name of "ultra-microchemistry" by P. L. Kirk, a pioneer investigator in the field of quantitative chemistry on the microgram scale.

This work was carried on chiefly by Dr. B.B. Cunningham and L. B. Werner, who had previously been working in the biochemical field, and the



Fig. 5. Twenty micrograms of pure plutonium hydroxide in capillary tube (magnified about 13-fold) isolated in September, 1942. The plutonium is the cloud-like mass at the bottom of the capillary "test tube".

next slide (Fig. 3) shows a photograph of the room at the Metallurgical Laboratory where they worked. The small amount of space in which they worked, apparent from the photograph, is all the more remarkable when one considers that Werner is a man who is more than two meters tall. The first pure chemical compound<sup>7</sup> of plutonium free from carrier material and all other foreign matter was prepared by Cunningham and Werner on August 18, 1942, and the first weighing of such a compound occurred on September 10, 1942 when 2.77 micrograms of the oxide was weighed. A picture of this oxide is shown on the following slide (Fig. 4). Not only was it possible to test the separation processes at the actual concentrations which were going to be used in the plant, tests which were of inestimable importance, but a great number of pure chemical compounds of plutonium were produced and its chemical properties were well studied by a number of investigators working on the ultramicrochemical scale. The next slide shows

an early photograph of a compound of plutonium (Fig. 5). Since plutonium has become available on a production scale from the chain reacting units the chemical properties have been thoroughly investigated until they are as well-known as those of numerous elements that have been studied for a great many years. A contribution of importance was made by W. H. Zachariasen of the University of Chicago, who was able to use his X-ray technique to identify or help identify a number of the compounds which were synthesized, and in many cases, thus to identify their structure.

Before proceeding with a discussion of the other transuranium elements, I should like to say a few more words about neptunium. Another isotope,  $^{237}\text{Np}$ , was discovered early in 1942 in collaboration with Wahl<sup>8</sup>. This isotope is the decay product of the previously<sup>9,10</sup> known approximately 7-day beta particle emitting  $^{237}\text{U}$  which is formed as the result of an n, 2n reaction on  $^{238}\text{U}$ . The reactions for its production are shown in the next slide (Fig. 6).

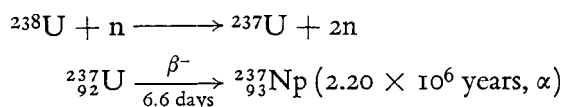


Fig. 6.

This isotope is of particular importance because it has a very long half-life and because it is available in weighable amounts. The first pure neptunium in the form of compounds of the isotope  $^{237}\text{Np}$  was isolated by L. B. Magnusson and T. J. La Chapelle<sup>11</sup> at the wartime Metallurgical Laboratory in October, 1944, and a picture is shown in the following slide (Fig. 7). It is fortunately produced as a by-product in the chain reacting piles which has led to the isolation of gram amounts for research purposes. The chemical properties of neptunium in the macroscopic state have been studied with such material, and this has led to a thorough knowledge of the chemistry of this element.

After the completion of the most essential part of the investigations concerned with the chemical processes involved in the production of plutonium at the wartime Metallurgical Laboratory, our attention turned to the problem of synthesizing and identifying the next transuranium elements. As collaborators in this endeavor, I turned to Albert Ghiorso, trained in electrical engineering, who played a dominant role in the development of the electronic instruments which were used in our radioactivity investigations, and to two young chemists, R. A. James and L. O. Morgan, who had been



Fig. 7. Ten micrograms of pure neptunium oxide at bottom of capillary tube (magnification about 10-fold) isolated in 1944. Above the sample is a U.S. ten-cent piece (dime) and below is a millimeter scale.

especially proficient in the investigations involving the chemistry of the transuranium elements. These investigations, supplemented by later work at the University of California, served as the thesis material for James and Morgan in connection with the graduate work which they undertook at the University a couple of years later.

There followed quite a period during which the attempts to synthesize and identify elements 95 and 96 bore no fruit. These unsuccessful experiments were based on the premise that these elements should be much like plutonium in that it should be possible to oxidize them to the (VI) oxidation state and utilize this in the chemical isolation procedures. It was not until the middle of the summer of 1944, upon the first recognition that these elements were part of an actinide transition series, about which I will say more later, that any advance was made, and then progress came quickly.

As soon as it was recognized that these elements should be oxidized above the (III) state only with extreme difficulty, if at all, the identification of an



isotope of element 96 followed immediately. Thus the isotope  $^{242}\text{Cm}$  was identified<sup>12</sup> in the summer of 1944 as a result of the bombardment of  $^{239}\text{Pu}$  with 32 MeV helium ions in the Berkeley 60-inch cyclotron. The reaction involved was  $^{239}\text{Pu} (\alpha, n)^{242}\text{Cm}$ , and the bombardment took place in the Berkeley 60-inch cyclotron after which the material was shipped to the Metallurgical Laboratory for chemical identification. I should like to digress for a moment here to point out that our research program owes much to the efforts of Dr. J. G. Hamilton, T. M. Putnam, Jr., G. B. Rossi, and their collaborators who have operated the 60-inch cyclotron and made the bombardments which led to the discoveries of elements 96, and elements 97 and 98 to be mentioned later. In fact, I should like to pause further and recall at this time that five of the six presently known transuranium elements were first identified as a result of their initial production through the use of the Berkeley 60-inch cyclotron.

The identification<sup>13,14</sup> of element 95 followed soon thereafter. This came in the very late fall of 1944 as a result of the bombardment of  $^{239}\text{Pu}$  with pile neutrons, the production reactions being as shown in the following slide (Fig. 8).

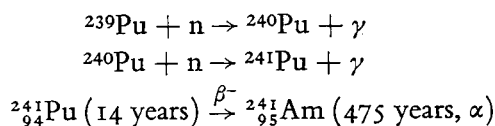


Fig. 8.

At the same time the isotope  $^{242}\text{Cm}$  is formed as shown in the following slide (Fig. 9), and this is presently the best method for its production.

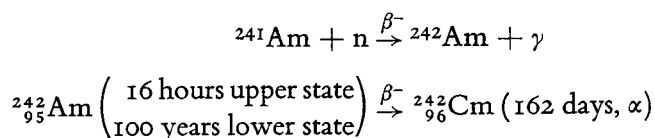


Fig. 9.

There are a couple of comments which should be made here concerning the rare-earthlike properties of these two elements. Our hypothesis that they should have a stable (III) oxidation state and greatly resemble the rare earth elements in their chemical properties proved to be so true that for a time it

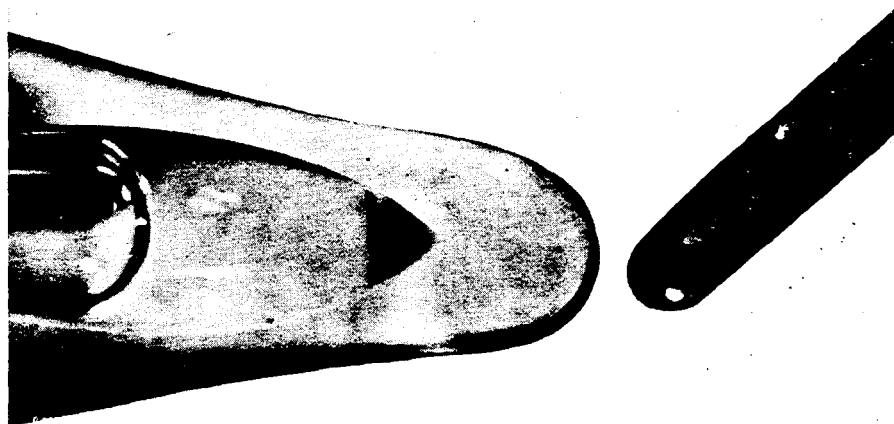


Fig. 10. First americium compound (hydroxide) in bottom of tube (centre). Isolated in the fall of 1945. Eye of sewing needle below indicates magnification of about 10-fold.

appeared to be most unfortunate. The better part of a year was spent in trying to separate chemically the two elements from each other and from the rare earth elements but without success, and although we felt entirely confident, on the basis of their radioactive properties and the methods of production, that isotopes of elements 95 and 96 had been produced, the chemical proof remained to be demonstrated. The elements remained unnamed during this period of futile attempts at separation, although one of our group insisted in referring to them by the names "pandemonium" and "delirium" in recognition of our difficulties. However, they were finally separated and completely identified chemically, and, in fact, their present names were eventually proposed on the basis of their chemical properties but with a more serious basis. The name "americium" (symbol Am) was suggested for element 95, thus naming it after the Americas by analogy with the naming of its rare-earth homologue europium after Europe, and the name "curium" (symbol Cm) was suggested for element 96 after Pierre and Marie Curie

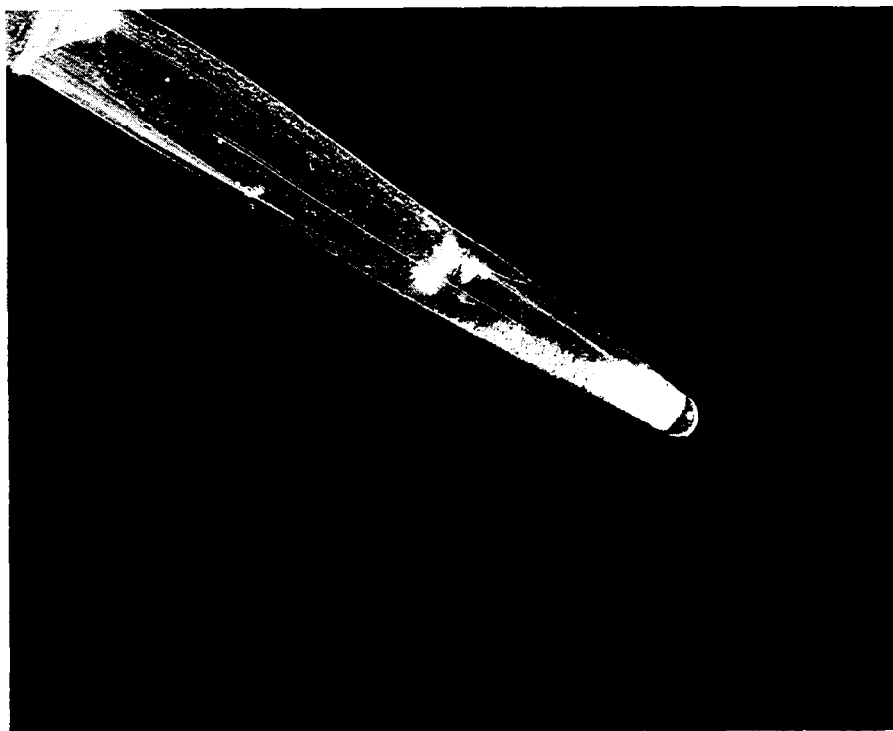


Fig. 11. Photograph of curium hydroxide in bottom of microcentrifuge cone. (Magnified about 2-fold.)

by analogy with the naming of its homologue gadolinium after Gadolin. These names and symbols will be used here and were used in the preceding slides.

Americium was first isolated by Cunningham<sup>15</sup> in the form of a pure compound in the fall of 1945 at the wartime Metallurgical Laboratory, and a photograph is shown on the next slide (Fig. 10). It can be prepared in milligram amounts by the neutron bombardment of plutonium according to reactions shown on a foregoing slide (Fig. 8), and thus it has been possible to investigate its chemical properties extensively through the use of macroscopic quantities.

Curium was first isolated in the form of a pure compound of  $^{242}\text{Cm}$  by L. B. Werner and I. Perlman<sup>16</sup> at the University of California during the fall of 1947. A photograph is shown in the following slide (Fig. 11). The isotope  $^{242}\text{Cm}$  is so highly radioactive, due to its short half-life, that chemical investigations with it in macroscopic concentrations are very difficult. Nevertheless

a large number of such investigations have been carried on and much has been learned about its chemical properties.

More recent work has led to the identification of a number of heavier isotopes of americium, curium, and plutonium which present interesting possibilities for the further nuclear and chemical investigation of these elements. The nuclide  $^{242m}\text{Am}$  formed by the neutron bombardment<sup>12,13,17</sup> of  $^{241}\text{Am}$  decays partially by electron capture<sup>18</sup> to the isotope of plutonium,  $^{242}\text{Pu}$ . The latter nuclide<sup>19</sup> is an alpha emitter with the comparatively long half-life of  $5 \times 10^5$  years and, therefore, may be important in future investigations of the chemical properties of plutonium since it has a specific activity some twenty times lower than that of  $^{239}\text{Pu}$ . This material can be transmuted by neutron bombardment<sup>20,21</sup> to the comparatively long-lived  $^{243}\text{Am}$  (about  $10^4$  years) and, therefore, following chemical separation this latter isotope can be made available comparatively free of other isotopes of americium. Similarly, such  $^{243}\text{Am}$  can be transmuted by neutron bombardment<sup>22,23</sup> to the comparatively long-lived  $^{244}\text{Cm}$  (about 10 years) which can thus be made available in a comparatively pure state following chemical separation. These reactions are summarized on the following slide (Fig. 12).

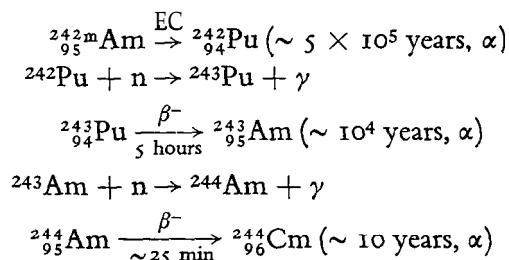


Fig. 12.

Thus the isotope  $^{243}\text{Am}$ , with a specific activity some twenty times lower than that of  $^{241}\text{Am}$ , may supplant  $^{241}\text{Am}$  for use in the chemical studies of the future; it is not yet known whether  $^{243}\text{Am}$  is beta stable, but if it is not, its partial half-life for beta emission appears to be longer than  $10^4$  years so that these considerations would not be altered. Due to the difficulties in studying the chemical properties of curium through the use of the isotope  $^{242}\text{Cm}$ , the isotope  $^{244}\text{Cm}$  with twenty times lower specific activity produced as just indicated, offers great hope for the simplification of future chemical studies of curium.

After the return at the conclusion of the war of a number of us to the University of California late in 1945 and early 1946, a part of the effort was put into the problem of the possible production and identification of further transuranium elements. S. G. Thompson, who had done so much in connection with the development of the separation processes for plutonium during the war, undertook to collaborate on the search for element 97 as the basis for his thesis research problem, and the further collaboration of Albert Ghiorso was also sought. Many problems had to be solved, mostly in connection with the small amounts of material available for irradiation and the intense radioactivity of this material. To help counterbalance the many difficulties were the advances which had been made in the possibility of predicting the radioactive properties of the expected isotopes and especially the exact predictions of the chemical properties made possible on the basis of the actinide concept. According to this view, the elution positions of the transcurium elements should be analogous to those of the transgadolinium elements in the ion-exchange column separation method. This knowledge proved of inestimable benefit in planning the ultimately successful experiments. Two approaches to the problem were undertaken: namely, that of neutron irradiation in the chain reacting piles and that of charged particle bombardment in the 60-inch cyclotron. The difficulties attending the neutron irradiation are illustrated in the following slide (Fig. 13).

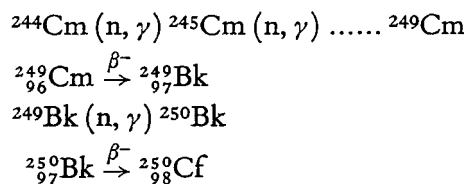


Fig. 13.

The prediction that curium must have a mass number as high as 249 before a negative beta particle emitter is reached is based on considerations involving the nuclear energy surface and the systematics of radioactivity which cannot be described here because of the lack of time. These considerations are, of course, not exact and it is quite possible that negative beta particle emission will be reached as early as  ${}^{247}\text{Cm}$ . The considerations are negated if there should exist a pronounced closed subshell at 148 neutrons in which case the isotopes of curium above  ${}^{244}\text{Cm}$  might be quite short-lived.

Whatever the reason for it may be, the neutron irradiations did not yield

positive results, and, therefore, I will go on to describe the cyclotron irradiations by which it was finally possible in December, 1949 to identify<sup>24</sup> an isotope of the element with atomic number 97 as a result of the irradiation of <sup>241</sup>Am with 35 MeV helium ions. This was followed within a month by the identification<sup>25</sup> of an isotope of element 98 through the irradiation of <sup>242</sup>Cm with 35 MeV helium ions, in a research carried on by the same investigators with the addition of a young colleague, K. Street, Jr., who had already contributed very much to our knowledge of the chemical properties of the transuranium elements. The first identification experiment in the case of element 98 involved the production and separation of only a few thousand atoms. The reactions involved are summarized in the following slide (see Fig. 14).

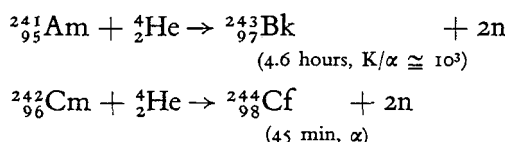


Fig. 14.

It should be mentioned that the successful handling in a safe manner of the huge amounts of radioactivity in the target material was made possible through the use of the excellent protective equipment provided by Nelson Garden and the members of his Health Chemistry Group at our Laboratory.

The name "berkelium" (symbol Bk) was suggested for element 97 after the city where the work was done, in analogy with the naming of its chemical homologue terbium, which was named after the village of Ytterby here in Sweden where the rare earth minerals were first found. The name "californium" (symbol Cf) was suggested for element 98 in honor of the university and state where the work was done; thus the name does not reflect its strong homology to dysprosium. These names are used in the present talk including the various slides.

Soon following this work, it became possible on the basis of the interesting pioneer carbon-ion bombardment experiments of Miller, Hamilton, Putnam, Haymond, and Rossi<sup>26</sup> in the 60-inch cyclotron to produce isotopes of californium in better yield by this method. These experiments, in which uranium is bombarded with carbon ions, led to the production<sup>27</sup> of califor-

niium isotopes according to the reactions given in the following slide (see Fig. 15).

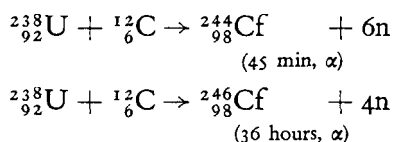


Fig. 15.

There are, of course, many more transuranium nuclides known that I have not been able to describe in the time available. For the sake of completeness these are summarized in the following slide (Fig. 16).

It should be emphasized that these nuclides are the product of the investigations of a number of laboratory groups besides our own. I should like to mention especially the work of W. M. Manning, M. H. Studier and co-workers of the Argonne National Laboratory in Chicago, Illinois, as well as the work of the United States Atomic Energy Commission's Los Alamos Laboratory, and the Chalk River Laboratory of the Canadian National Research Council. I feel that I should especially single out the contributions of my colleague Albert Ghiorso whose name, as you may have noticed, has come up time after time as I have gone through my description here of the work on the transuranium elements. Ghiorso has been a key man throughout and is one of those individuals without whom a laboratory such as ours simply could not run.

I suppose that I should say a few words with respect to the possibility for future production and identification of additional transuranium elements, especially in view of the possibility of their production by heavy-ion bombardment of transuranium elements. As an aid to such a program the radioactive properties can be estimated, as I have already indicated, on the assumption of a smooth nuclear energy surface and the systematics of radioactivity. Again, I must emphasize that such considerations are negated in the event that a stable subshell of 148 neutrons should be found to exist, and this must be regarded as a definite possibility. It is interesting to note that our considerations on the systematics of spontaneous fission<sup>28</sup> indicate that this method of decay will not compete seriously with radioactive decay until the region just beyond element 100. The following slide (Fig. 17) shows a number of predicted half-lives for radioactive decay.

	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	98 Cf
98 Cf																35.7h α	
97 Bk													4.6h EC, α	~4.6h EC	4.95d EC, α		97 Bk
96 Cm								~2.5h α		268d α	35d EC, α	162.5d α	~100y α	~10y α			96 Cm
95 Am								~12h EC	~12h EC, α	~50h EC	475y α	16h-100y EC β <sup>-</sup> IT α β <sup>-</sup>	~10 <sup>4</sup> y α	~25m β <sup>-</sup>			95 Am
94 Pu		36m EC, α		9.0h EC, α	26m EC, α	2.7y α	~40d EC	90y α	2.4x10 <sup>4</sup> y α	~6000y α	14y β <sup>-</sup> , α	~5x10 <sup>5</sup> y α	5.0h β <sup>-</sup>				94 Pu
93 Np	~50m EC, α	13m EC	35m EC, α	4.40d EC	410d EC, α	22h EC, β <sup>-</sup>	220x10 <sup>9</sup> y α	2.10d β <sup>-</sup>	233d β <sup>-</sup>								93 Np
92 U	4.2d EC, α	70y α	162x10 <sup>5</sup> y α	267x10 <sup>5</sup> y α 0.0051%	707x10 <sup>5</sup> y α 0.71%	2x10 <sup>7</sup> y α	663d β <sup>-</sup>	45x10 <sup>9</sup> y α 99.28%	23.5m β <sup>-</sup>								92 U
	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	

Mass number

Fig. 16. Summary of transuranium nuclides.



*Predicted Half-Lives*

$^{249}\text{Bk}$	$\alpha$	years
$^{252}\text{Cf}$	$\alpha$	years
$^{249}\text{Gg}$	EC, $\alpha$	minutes
$^{253}\text{Gg}$	$\alpha$	months
$^{250}\text{I00}$	EC, $\alpha$	minutes
$^{252}\text{I00}$	$\alpha$	hours
$^{254}\text{I00}$	$\alpha$	days
$^{257}\text{I01}$	EC, $\alpha$	minutes
$^{258}\text{I02}$	$\alpha$	minutes

Fig. 17.

These considerations illustrate clearly that one of the problems is that of conceiving means for producing nuclides of sufficiently high mass numbers with half-lives long enough for chemical identification. Thus, the serious problem is again the paucity of starting materials.

A hopeful aspect to the problem of the production and the identification of transcalifornium elements is the feeling that the chemical properties can be predicted with confidence. Thus it is expected that the (III) oxidation state will predominate for the next few elements. Of especial importance in planning experiments is the confidence that the elution sequence will continue to follow that of the analogous rare earths as will be described in a few minutes.

Unfortunately, there is not sufficient time to say as much as I would like about the interesting chemical properties of the transuranium group of elements. As I have already mentioned, the chemical evidence indicates that it is the tripositive oxidation state which is important here and points to a beginning with actinium of an "actinide" transition series in the same sense that the rare earth "lanthanide" series begins with lanthanum<sup>29,30</sup>. There is, however, the important difference that the first elements in the heavy series exhibit the property of oxidation to higher states with much greater ease than is the case for the corresponding elements in the rare earth series. The most important criterion for this classification is the probable presence of seven 5f electrons (analogous to the stable gadolinium structure) in tripositive curium (element 96) rather than the presence of the first 5f electron in thorium. In fact, there might not be any such electrons in thorium with, for example, their first appearance in protactinium (two 5f electrons) or in uranium (three 5f electrons). An important aspect of these considerations is the fact that the 5f and 6d shells of the elements in this heaviest region lie so close

together that the energy necessary for the shift from one shell to the other is in some cases within the range of chemical binding energies.

The earliest element in this series which clearly exhibits the characteristic oxidation state of (III) is uranium, the third element in the series. In going up the series from uranium, each of the successive elements exhibits a more stable (III) oxidation state than the preceding element. When the elements americium (atomic number 95) and curium (atomic number 96) are reached, the (III) state is the predominant one, and, in fact, seems to be the only state of these latter elements which is thermodynamically stable in acidic aqueous solution. In the cases of berkelium (atomic number 97) and californium (atomic number 98) only tracer experiments have been done and, therefore, the information is less certain. These experiments show that berkelium exhibits stable (III) and (IV) oxidation states<sup>31</sup> and indicate that californium exists solely in the (III) state<sup>32</sup>, which behavior is in entire conformity with their expected analogy with their rare earth homologues, terbium and dysprosium, respectively.

Perhaps the most striking chemical evidence as to the course taken in the filling of the 5f electron shell in this region is that offered by the work on the separation of the tripositive actinides and lanthanides by the ion-exchange column method. The use of a cation exchange resin with an eluting agent such as ammonium citrate solution, as developed on the Plutonium Project<sup>33</sup>, has led to a satisfactory solution of the difficult problem of separating in pure form the rare earth elements from each other. The tripositive actinide elements are equally difficult to separate from each other and from the rare earths because of their great similarity to the latter. However, the analogy in behavior of the actinide and lanthanide elements here is much greater than results from a similarity in the difficulty of separation, as can be seen from the following slide (Fig. 18). The simplicity of the apparatus used is illustrated in the next slide (Fig. 19).

A remarkable analogy in the spacing can be seen between the group californium-berkelium-curium-americium and their rare earth homologues dysprosium-terbium-gadolinium-europium. The spacings here reflect the relative changes in ionic radii which determine the relative separations in the ion-exchange adsorption method. It can be seen that the same sequence of changes in the ionic radius is encountered on filling in the 5f electrons as occurs on filling the 4f shell, and, therefore, it seems quite clear that curium represents the midway point in the actinide transition series of elements in view of its position analogous to gadolinium.

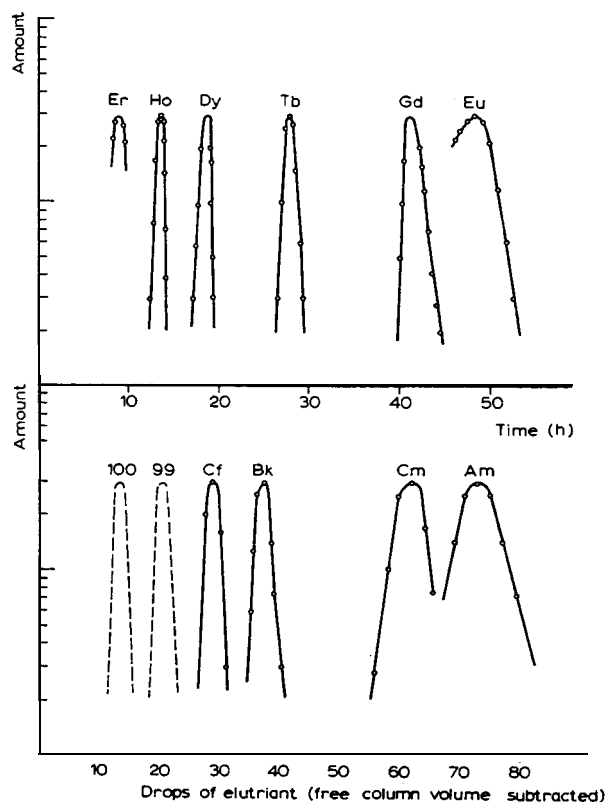


Fig. 18. Relative elution of homologous actinides and lanthanides. The data for the actinides shown here are those of K. Street, Jr., S. G. Thompson, and G. T. Seaborg<sup>32</sup> in which the cation exchange resin Dowex-50 was used and the elution performed at 87° C with ammonium citrate buffered with citric acid to a pH of 3.5 (total citrate concentration 0.2 M). The data on the lanthanide elements are those of B. H. Kettle and G. E. Boyd<sup>34</sup> in which the same resin was used in a somewhat longer column and the elution performed at 100°C using a similar citrate buffer solution (pH 3.28). (The *dotted* lines show the predicted elution positions for elements 99 and 100.)

Magnetic susceptibility measurements on compounds of the heaviest elements ideally should lead to the resultant magnetic moments in fundamental units and in this way give information on the quantum states of the responsible electrons. Actually, as encountered with the rare earth elements, the situation is rather complex and the exact behavior expected for the heaviest elements, on the basis of the presence of either 5f or 6d electrons, cannot be, or at least has not been, predicted. Nevertheless, such measurements should give, and have given, some information on this point.

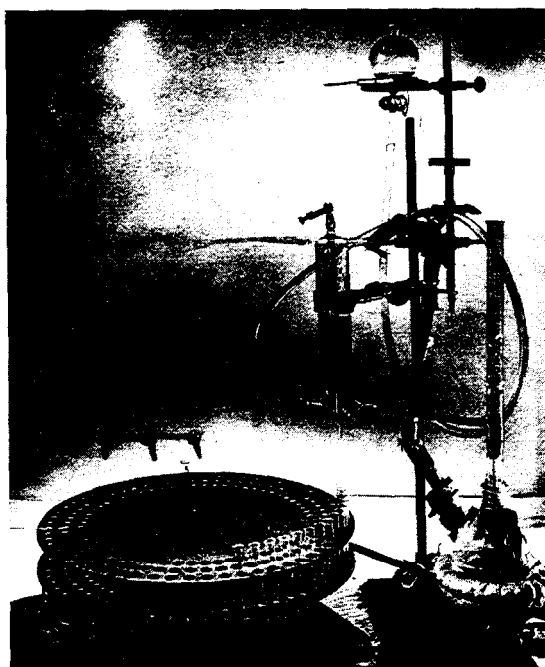


Fig. 19. Ion-exchange column with elution apparatus and automatic sample collection mechanism for separation of actinide and lanthanide elements.

The following slide (Fig. 20) shows a plot comparing the room temperature experimental magnetic susceptibilities of the lanthanide and actinide cations in such a way as to show their remarkable analogy in this property. This plot is admittedly rough because data are used from both aqueous solutions and solid compounds; these are not strictly comparable and even data from different solid compounds of the same oxidation state of an element differ somewhat due to the effects of the crystal fields and exchange effects. Nevertheless, the comparison is sufficiently reliable to show that the magnetic measurements point toward the filling of the 5f shell in the manner expected.

The next slide (Fig. 21) shows in an extremely rough and qualitative way a pictorial representation of the binding energy of the most easily removable 5f and 6d electron (of those present) for each of the heaviest elements.

The best method of presenting the actinide elements in the Periodic Table seems to be in a manner similar to that illustrated in the following slide (Fig. 22). Here are shown the fourteen elements of atomic numbers 90 to 103

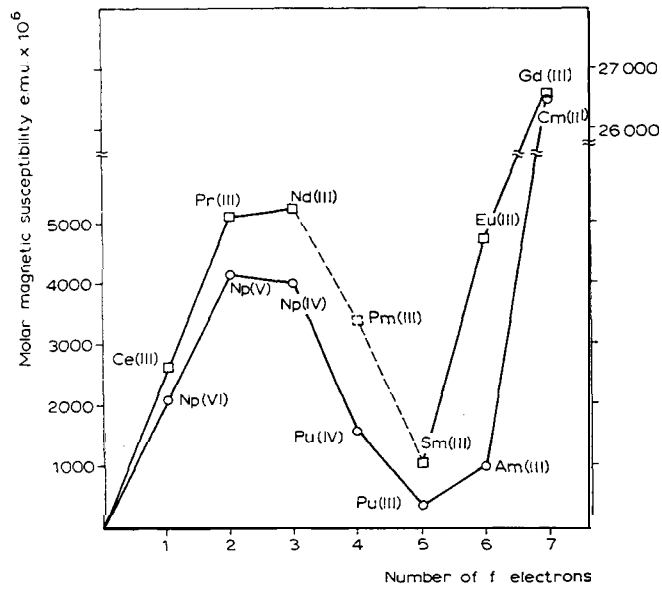


Fig. 20. Plot of molar magnetic susceptibilities of some actinide and lanthanide ions.

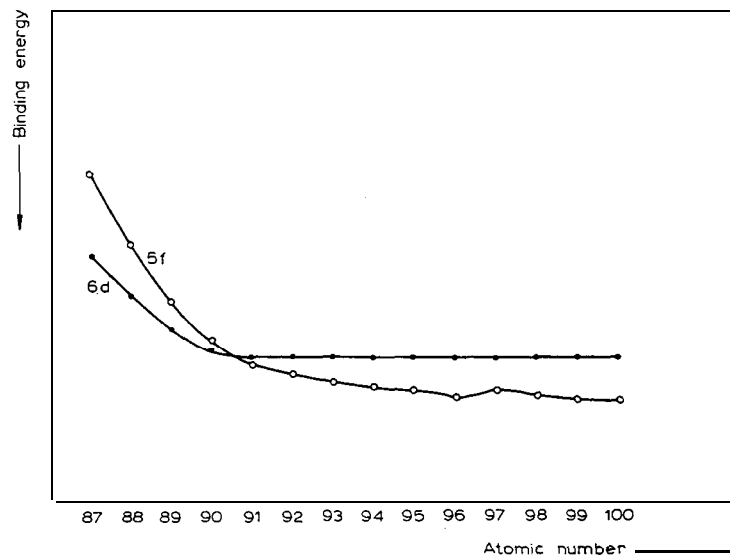


Fig. 21. Qualitative representation of electronic binding energies in the heaviest elements.

1 H 1008	2 He 4003																				
3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183														
11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457	18 Ar 39.944														
19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7				
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc 101.7	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.868	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 Xe 131.3				
55 Cs 132.91	56 Ba 137.36	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm 146.91	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.967					
87 Fr	88 Ra	89 Ac	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 244.06	95 Am 243.06	96 Cm 247.07	97 Bk 247.07	98 Cf 251.08										

Fig. 22. Periodic Table showing heavy elements as members of an actinide series.

inclusive, with actinium (element 89) as the prototype, listed as a series below, and in a manner similar to, the common listing of the fourteen rare earth elements of atomic numbers 58 to 71 inclusive, for which lanthanum (element 57) is the prototype. It is not proposed that this particular form of the Periodic Table has any more merit than any of a number of others which place these elements in positions homologous to the rare earth elements, since it is obvious that they can be analogously placed in a number of other types of tables or charts.

The elements 90 to 96 inclusive or the first few of them could, in addition, be listed separately below the 5d transition elements in recognition of the resemblance of the first few of these to 5d elements. This appears to be undesirable, however, since the last members of this group bear no such resemblance and it is probably impossible to draw a line as to just where the resemblance ends. It should be noted that cerium, terbium, europium, etc., could be put in two places in the Periodic Table in recognition of their two oxidation states, but this practice is not usually followed.

The group probably could have been just as well described by some other term rather than "actinide", which is derived from straight analogy with the term "lanthanide". Irrespective of the name which usage will finally assign to this group of elements, however, it seems that the outstanding characteristics of the group, namely the "eka-gadolinium" character of curium (and the presumed "eka-lutetium" character of element 103), together with the regularly increasing trend toward actinium-like character in going from thorium to curium, are best represented by listing these elements in corresponding positions under the rare earth elements if it is desirable to give each element only one place in the Periodic Table.

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