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THE TRANSCALIFORNIUM ELEMENTS

Glenn T. Seaborg
University of California
Berkeley, California, U.S.A.

During the past sixty years, four elements beyond californium on the atomic number scale (Slide No. 1) have been synthesized by the transmutation of lighter elements. The first preparation of einsteinium (No. 99) and fermium (No. 100) occurred in a thermonuclear explosion. Mendelevium (No. 101) and element 102, however, were prepared by a more conventional method, that of charged particle bombardment of elements of high atomic number.

The transcalifornium elements are members of a group of chemically similar elements, the actinide transition series, which begins with actinium (No. 89) and includes thorium, protactinium, uranium, and the transuranium elements through the undiscovered element 103. The concept that the heaviest known elements are actinides has led to their placement in the periodic table as shown in Slide No. 2. A close chemical resemblance exists between the actinide series and the lanthanide series (which begins with lanthanum (No. 57) and ends with lutetium (No. 71), and the members of each group correspond in chemical behavior. Thus the homologues of einsteinium, fermium, mendelevium, and element 102 are the rare earths holmium, erbium, thulium, and ytterbium, respectively.

The analogy between the ion-exchange behavior of corresponding actinides and lanthanides has provided the basis for the initial identification of most of the transuranium elements which are usually first prepared in exceedingly small amounts and may have very short half lives. An added difficulty in their isolation lies in the fact that the transplutonium

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elements have a very close chemical resemblance. The ion-exchange adsorption and elution technique unlike most conventional chemical separation methods offers the necessary selectivity and rapidity in isolating such elements. Ion exchange resins are organic polymers. Dowex-50 (a copolymer of styrene and divinyl benzene with nuclear sulfonic acid groups) is a commercial resin which is frequently used in such experiments. Separations by ion exchange can be performed as follows. The solid ion exchange resin is stirred into an aqueous solution containing tripositive actinide or lanthanide ions, or tripositive ions of both groups of elements, which replace the exchangeable cations of the resin. The solid resin is then usually placed at the top of a glass column filled with untreated resin. A solution containing anions (the eluant) which form complex ions with the adsorbed elements is poured through the column to effect their removal. The drops of eluant are collected and analyzed by means of their radioactivity. Solutions of chloride, nitrate, lactate, citrate, or alpha hydroxyisobutyrate ions, for example, can be used as eluants. The adsorption and elution reactions can be written, for example, as follows: (Slide No. 3)

$$M^{+3}(aq) + 3NH_4R(s) \rightleftharpoons MR_3(s) + 3NH_4^+(aq) \text{ - adsorption}$$

$$M^{+3}(aq) + 4A^-(aq) \rightleftharpoons MA_4^-(aq) \text{ - elution,}$$

where M represents the actinide or lanthanide ion ion; NH_4R, the ion exchange resin, ammonium ions being the exchangeable cation in this case; and A^-, the eluant; the actual formula for the complex ion or ions may be more complicated and may not be known. These two reactions, of course, occur many times during the passage of the eluant down the column. An experimental arrangement for an ion exchange separation is shown in Slide No. 4.

The column is sometimes maintained at higher than room temperature in order to hasten the establishment of the equilibria.

In certain systems the actinide and lanthanide elements are eluted in the inverse order of their atomic numbers as is illustrated in Slide No. 5. These experiments were performed before the discoveries of elements 99 through 103, the positions predicted for these elements being shown by dotted lines. Similar separations can be made using a polymer with exchangeable anions, in which case the actinide or lanthanide elements must be present in the initial solution as complex ions.

Einsteinium and Fermium

The discoveries of einsteinium and fermium were unexpected results of the first test thermonuclear explosion. A search for transcalifornium elements in the explosion debris began when heavy isotopes such as the previously unknown Pu^{244} and Pu^{246} were found in fall-out substances. The presence of these very heavy isotopes suggested that the capture of many successive neutrons by the uranium in the device had occurred during the microsecond existence of the extremely high neutron flux. Since beta decay will not, in general, proceed with a half life shorter than about 0.1 second, these heavy uranium isotopes had no opportunity to undergo beta decay during synthesis. Their subsequent decay by many successive beta particle emissions formed the nuclides found in the explosion debris. Slide No. 6 shows the reaction paths by which these heavy elements were formed. Thus, for example, the synthesis of Fm^{255} was via the production of U^{255} by neutron capture in U^{238}, followed by a long series of short-lived beta decays, $U^{255} \xrightarrow{\beta^-} Np^{255} \xrightarrow{\beta^-} Pu^{255} \xrightarrow{\beta^-} \ldots\ldots Fm^{255}$, all of which occur after the neutron capture reactions are completed. Slide No. 7 shows the relative yields of heavy

nuclides obtained in this first thermonuclear explosion.

Ion exchange experiments of the type mentioned previously led to the identification of isotopes of elements 99 and 100. The source material for these experiments was first collected on filter papers attached to drone airplanes which flew through the explosion area. Later, in order to obtain larger amounts of material it was necessary to process many hundreds of pounds of coral from one of the nearby atolls. The elution data obtained for einsteinium are shown in Slide No. 8; the elution was found to occur very approximately in the eka-holmium position. In the case of fermium, the first chemical identification was successfully accomplished although only about 200 atoms were available. With such an extremely small amount of material it was not possible to make the usual plot of a complete elution curve. Slide No. 9, therefore, is a plot of the elution data corresponding to the second chemical identification of fermium; as anticipated, its elution occurs approximately in the eka-erbium position. The chemical properties of einsteinium and fermium have been investigated with tracer amounts, and it appears that the tripositive oxidation state may be the only one which exists in aqueous solution for these elements.

Einsteinium and fermium can be prepared in a number of ways. The most important, however, is the intense neutron irradiation of plutonium or other elements of high atomic number for several years in a high flux reactor such as the Materials Testing Reactor at Arco, Idaho. The nuclear reaction sequences for the preparation of heavy nuclides up to fermium are shown in Slide No. 10. This is a slow process in which successive neutron absorptions are followed by beta decays to produce elements of higher atomic number. Slide No. 11 gives an indication of the time required to prepare the nuclides Cm^{248}, Cf^{252}, and E^{254}. It can be seen

that by starting with one kilogram of Pu^{239} it would require approximately five to ten years to produce about one milligram of Cf^{252} using a neutron flux of 3×10^{14} neutrons per square centimeter per second. In the United States we have a program in progress for the production of milligram amounts of berkelium and californium, and microgram amounts of einsteinium. Einsteinium is the only remaining transuranium element capable of being isolated in macroscopic amounts (as the 280-day isotope E^{254} or the 20-day isotope E^{253}) but not yet so isolated by traditional methods. Fermium and higher elements are not expected to have isotopes with sufficiently long half lives to permit their isolation in macroscopic quantity, although new techniques permitting special measurements are possible. Isotopes of einsteinium from E^{246} to E^{256} inclusive and isotopes of fermium from Fm^{248} to Fm^{256} inclusive are known, being prepared by neutron irradiation or charged particle bombardment.

Mendelevium

The first preparation and identification of mendelevium was planned, and successfully accomplished, although calculations indicated that only one atom of the element per bombardment could be expected. In addition, there was the formidable task of separating this one atom from the target material and effecting its chemical identification. The techniques used, however, were adequate, and mendelevium was synthesized and identified in spite of the fact that the initial prediction of its yield was correct.

The amount of mendelevium expected in each bombardment was calculated as follows. (Slide No. 12). The number of atoms of mendelevium, N, prepared in each bombardment should be approximately equal to:

$$N \cong N'\sigma It$$

where N' is the number of einsteinium atoms used as a target; σ, the cross

section or probability for the reaction; I, the intensity of the helium ion beam; and t, the effective time of the bombardment. The cross section for the reaction was predicted to be about 10^{-27} square centimeters on the basis of the known values for previously observed similar reactions. Only about 10^9 atoms of einsteinium, in the form of the isotope E^{253} which had been prepared by the neutron irradiation of plutonium, were available as target material. As the result of some fundamental changes in the 60-inch cyclotron at Berkeley, the intensity of the helium ion beam was increased to 10^{14} particles per second per square centimeter. Predictions indicated a half life of the order of hours for the expected isotopes, so an effective value for t of 10^4 seconds was used. Substituting these numbers in the equation, the calculation was made as follows:

$$N \cong (10^9)\ (10^{-27})\ (10^{14})\ (10^4) \cong \underline{\text{one atom per experiment}}.$$

Thus under optimum conditions, the preparation of only about one atom of mendelevium per experiment could be expected. This was the first time that the detection of transmutation products produced by the charged particle bombardment of an invisible amount of material had been attempted.

Adding to the complexity of the experiment was the separation of the one atom of the new element from the 10^9 atoms of einsteinium in the target and its chemical identification by separation in the eka-thulium position by the ion exchange method. A new technique was used to accomplish a preliminary separation. This was the recoil method which is illustrated in Slide No. 13. The einsteinium was plated on a gold foil as a very thin layer. The helium ion beam was sent through the back of the foil so that the transmuted atoms, recoiling due to the momentum of the helium ions, could be caught on a second thin gold foil. This second foil was dissolved, and the chemical separations performed beginning with this solution.

In early experiments, the actinide chemical fractions were examined for short-lived alpha emitting isotopes, but no alpha activity was detected that could be attributed to element 101. In one of the later experiments, however, we observed a spontaneous fission event. At that time rapid decay by spontaneous fission was known to occur only in a few isotopes, none of which should have been present or produced in the experiment. The result thus appeared to be significant. In addition, the background for this type of decay should be essentially zero in the proper equipment. As the experiments continued, a spontaneous fission or two was detected in the products from some bombardments, while none was observed in others. This variation was not unexpected, owing to the statistical fluctuation inherent in the production of one atom per experiment. Most promising, however, was the fact that the spontaneous fissions when they did occur were detected in the element 101 or element 100 chemical fractions.

Mendelevium was definitely identified in the transmutation products formed in three successive three-hour bombardments. A total of five spontaneous fission counts, and hence, five atoms, was observed in the element 101 elution position and a total of eight spontaneous fission counts was observed in the element 100 elution position. No spontaneous fission events were detected in any other elution position. Slide No. 14 shows the elution data obtained in the discovery experiments. The isotope E^{253}, which was added, and the isotope Cf^{246}, which was formed from the Cm^{244} added to the target, served as tracers to define the element 101 and element 100 elution positions. The spontaneous fission activity in both the element 101 and element 100 fractions decayed with a half life of about 3 hours. This and other evidence has led to the conclusion that the mendelevium isotope thus prepared has the mass number 256 and decays by

electron capture with a half life of about an hour to the isotope Fm^{256} which is responsible for the spontaneous fission decay. The fact that the decay involves the spontaneous fission process was a fortunate circumstance. This mode of decay has a high, almost 100%, detection efficiency and zero background.

Slide No. 15 summarized in graphic form all of these experimental steps and was reproduced from an interesting review of the discovery of mendelevium which was published in the soviet journal "Priroda."

Subsequent experiments using larger amounts of E^{253} in the target have led to the preparation of hundreds of atoms of mendelevium. The indications are that mendelevium exists in solution as a tripositive ion and resembles its homologue thulium.

A second isotope of mendelevium with mass number 255 has recently been synthesized by the helium ion bombardment of E^{253}; this decays by electron capture with a half life of about one half hour. The new isotope was separated and identified using techniques similar to those used in the discovery of the isotope Mv^{256}. This research was also performed by a group at the University of California Radiation Laboratory.

It seems especially fitting that an element be named in honor of Dmitri Mendeleev as was done in the case of element 101, which was given the name mendelevium. The methods of identification of most of the transuranium elements have been based on the chemical properties predicted for their position in the periodic table and are thus applications of his great generalization. As will be mentioned later, we expect to continue to rely on this principle in the investigation of future elements if isotopes with sufficiently long half lives to allow chemical studies exist.

Element 102

The most recent research on the transuranium elements includes the synthesis and identification of an isotope of element 102.

In 1957, a team of scientists from Argonne National Laboratory in the United States, the Atomic Energy Research Establishment in England, and the Nobel Institute for Physics in Sweden announced the discovery of an isotope of element 102 as a result of research performed at the Nobel Institute. The isotope was reportedly produced by bombarding Cm^{244} with cyclotron-produced $C^{13(+4)}$ ions and reported as decaying by the emission of 8.5-Mev alpha particles with a half life of about 10 minutes. The name nobelium was suggested by this group for element 102. Unfortunately it has not been possible to confirm this discovery in repeated experiments with the facilities at the University of California Radiation Laboratory and related experiments performed in the U.S.S.R. have also failed to confirm this Stockholm work.

In 1958, a group at the Radiation Laboratory reported the positive identification of isotope 102^{254} as a product of the bombardment of Cm^{246} with C^{12} ions accelerated in the heavy ion linear accelerator (Hilac) at Berkeley. The new element was detected by the chemical identification of its known daughter Fm^{250}. The separation of the element 102 isotope from the target material and the separation of the daughter element from the parent element 102 were performed by the use of a new method in which two physical separations were performed.

Slide No. 16 shows the experimental arrangement used in the California experiments. The target consisted of curium deposited on a thin nickel foil and was enclosed in a container filled with helium gas. The curium was bombarded with the C^{12} ions and the transmuted atoms were knocked

into the helium gas to absorb their recoil energy. With a sufficient electric field strength it was found that practically all of these positively-charged atoms could be attracted to a moving, negatively-charged metallic belt placed directly beneath the target. The belt was then passed under a foil (the catcher foil) which was charged negatively relative to the belt. Approximately half of the element 102 atoms undergoing radioactive decay by alpha particle emission would cause their daughter atoms to recoil from the surface of the belt to the catcher foil. The catcher foil was cut transversely to the direction of the belt motion into five equal length sections after a time of bombardment suited to the half life of the daughter atom to be examined, and each section was analyzed simultaneously in counters. All of the desired measurements could be made for identifying the daughter atoms caught on the catcher foils and thus the half life of the parent of the recoiling atoms could be determined. It was found that Fm^{250} could be collected on the catcher foils in accordance with a parent half life (i.e., half life for 102^{254}) of 3 seconds. Changing the belt speed was found to change the distribution of the Fm^{250} on the catcher foil in a manner conforming to a three-second parent.

The isotope Fm^{250} was identified chemically by dissolving the radioactive material from the catcher foil and separating it from the other actinide elements by the ion exchange method. Slide No. 17 shows the elution curve obtained in an experiment where nine atoms of Fm^{250} were observed in the element 100 position.

In experiments starting in 1957 and continuing in 1958, a group at the Atomic Energy Institute in Moscow has produced an isotope, emitting 8.8±0.5 Mev alpha particles, in the bombardment of Pu^{241} (and Pu^{242}) with high energy O^{16} ions accelerated in their cyclotron. This product was separated from the target by the recoil technique and the energy of the alpha particles was

measured by use of a photographic emulsion technique. No chemical identification was made. It is quite possible that this alpha activity is due to the isotope 102^{254} identified by the California group. It appears that the Moscow work complements the Berkeley work nicely, and it is hoped that we can proceed from here on in this field of investigation with close cooperation between the two laboratories.

Although the name nobelium for element 102 will undoubtedly have to be changed, no suggestion for a new name has been made as yet.

Future Elements

From our present knowledge of the nuclear and chemical properties of the transuranium elements it seems probable that elements with atomic numbers greater than 102 will be discovered. About seven dozen isotopes in the transuranium region are known and it has been possible to determine very precisely many of their nuclear properties. This has led to a systematization of radioactive decay data so that the decay properties of undiscovered nuclides can generally be successfully predicted. The predominant mode of decay is by alpha particle emission, but decay by the spontaneous fission process becomes more and more important as the elements of highest atomic number are approached. In fact, this latter mode of decay begins to proceed at a rate comparable to decay by alpha particle emission for some isotopes by the time element 100 is reached. Data for spontaneous fission have also been correlated in a manner which makes predictions for undiscovered isotopes feasible. In both the alpha and the spontaneous fission modes of decay, the regularities have been found to be greatest for nuclei which contain an even number of neutrons and an even number of protons, thus making predictions of the properties for undiscovered isotopes of this type the most

certain. For isotopes with an odd number of protons or an odd number of neutrons or an odd number of both protons and neutrons, the rate of decay by both alpha decay and by spontaneous fission is slower than for the regular even type. Slide No. 18 shows the predicted half lives (indicated by a broken line) of the longest lived isotopes for elements up to element 110. Unless unexpected island of stability due to closed neutron or proton shells are found, the predictions based on the regularities in the decay properties suggest that it should not be possible to produce and detect additional elements beyond another half dozen or so.

By the time elements 104 and 105 are reached we shall probably find that the longest-lived isotopes that can be prepared will exist barely long enough for chemical identification, which will undoubtedly be made on isotopes with an odd number of nucleons. It is probable that the present criteria for the discovery of a new element, chemical identification by traditional methods and separation from all previously known elements, will have to be changed at some point. Careful investigations of decay properties and reaction yields and mechanisms, together with the use of the recoil technique combined in some cases with the chemical identification of daughter isotopes, should provide means for the satisfactory identification of isotopes with very short half lives. Decay properties may have to be measured at the target area, on recoil-product nuclei, during the bombardment. In some cases, it may be possible to make a satisfactory identification of a new element isotope by using simple and fast methods involving the migration of gaseous atoms or ions, volatility properties, reactions with surfaces, or gas-flow reactions. It is likely that the identification of the first isotopes of all the new elements that will be discovered

in the future will be accomplished by such methods, and the production of isotopes of these new elements with sufficiently long half lives to allow chemical identification by traditional methods will follow later if this is possible at all. Regardless of the method used, evidence for the discovery of a new element should include a reasonable establishment of the atomic number and this requires more than the observations of predicted decay properties and yields.

The prediction of the chemical properties of the elements beyond mendelevium seems to be quite straightforward. The position in the periodic table of undiscovered elements up to element 118 can be predicted as a consequence of having determined the point of filling of the 5f electron shell which occurs at element 103, even though many of them will never be produced. The chemical properties of all of these elements can be estimated to the extent that membership of any element in a certain group or column in the periodic table foretells its chemical properties. It is expected that the actinide series will be completed at element 103 and that elements 104, 105, 106, etc. will be fitted in under hafnium, tantalum, tungsten, etc., including the positions occupied by thorium, protactinium, and uranium in the pre-World War II periodic tables. (Slide No. 2) The filling of the 6d electron shell should be followed by the addition of electrons to the 7p shell, with the rare gas structure being attained at element 118.

It seems probable that the chemical identification of element 103 and of isotopes of element 102 with sufficiently long half lives will be made by the ion exchange method. Element 102 might be expected to have, in addition to a stable III oxidation state, a somewhat unstable II state in aqueous solution. This lower oxidation state may well be important in the eventual chemical identification of longer-lived isotopes of element 102.

If the stability of this II state is comparable to the stability of the II state of ytterbium, then a rapid separation of this element from the other actinide elements may be effected through electrolytic or amalgam reduction, using ytterbium as a carrier. It is expected that the metallic form of element 102 will have a low density and high volatility relative to the preceding actinide elements.

Element 104 should be exclusively tetrapositive in aqueous solution and should resemble its homologues hafnium and zirconium. The fluoride of element 104 would be expected to be soluble, thus permitting separation from the actinide elements by precipitating the insoluble flurides of the tripositive actinides, leaving element 104 in solution. Solvent extraction may also prove to be a rapid and effective method of separating element 104 from the heavier actinide elements.

Element 105 should resemble niobium and tantalum, and to some extent, protactinium, with the V oxidation state expected to be the most important. Although it is not a true chemical homologue of protactinium, element 105 might resemble protactinium in its carrying and solvent extraction properties. Element 105 is expected to have troublesome hydrolysis properties. The chemical properties of element 106 can be deduced from those of tungsten and molybdenum. Thus we might expect to find the III, IV, V, and VI oxidation states. Elements 107, 108, 109, 110, etc. would be expected to have chemical properties similar to those of rhenium, osmium, iridium, and platinum, etc., respectively, although such elements may not have any isotopes sufficiently long-lived to permit much study of their chemical properties.

So far we have given no consideration to the methods by which these undiscovered elements might be prepared. The process of multiple slow

neutron capture as a result of intense neutron irradiation over a long period of time offers little promise for the first synthesis of transformium elements. Some of the necessary intermediate isotopes have half lives too short to be present in appreciable concentrations as required. The production of new transuranium isotopes and possibly even new elements by thermonuclear explosions is an interesting possibility. The products must, however, be recovered in better yield than has yet been possible. This method of synthesis is similar to that which occurs in some stars.

Synthesis by heavy ion bombardments offers promise for the production of elements of high atomic number. Isotopes of californium, einsteinium, and fermium have been produced by the bombardment of uranium with carbon, nitrogen, and oxygen ions, respectively, and element 102 was discovered as a product of the bombardment of curium with carbon ions. These heavy ions can be accelerated in cyclotrons of the conventional type, but specifically designed cyclotrons and linear accelerators which will be devoted to the acceleration of heavy ions to energies sufficient to transmute the heaviest nuclei are also coming into operation in several laboratories throughout the world. Slide 19 shows a line drawing of the new heavy ion linear accelerator (Hilac) at the University of California Radiation Laboratory in Berkeley, California, and Slides 20-22 show pictures of this machine. In the U.S.S.R. the heavy-ion cyclotron at the Atomic Energy Institute in Moscow is soon to be supplemented with a new, superior, and more versatile one designed to produce large beams of heavy ions, including ions as heavy as those of magnesium and aluminum; this should greatly extend the range of experimental work that can be done in this laboratory. Even with the use of heavy ions, the lack of availability of target materials of high atomic number and the small reaction yields present very serious problems. The

reaction yields are small due to the competition of the fission reaction and this competition is the more severe the higher the atomic number and the heavier the projectile; the heavier projectile requires more energy to surmount the potential barrier, and this gives more excitation energy to the nucleus, which leads to more steps of competition with fission as successive neutrons are boiled out. In order to prepare milligram amounts of berkelium and californium, and microgram amounts of einsteinium for target materials on a more reasonable time scale, new, expensive, high-flux reactors producing 10^{15} to 10^{16} neutrons per square centimeter per second are needed.

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In conclusion, it appears that the addition of new transuranium elements to the periodic table can be expected and that their study will add much to our knowledge of atomic and nuclear structure.