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ABSTRACT

The first nuclear synthesis and identification (i.e., the discovery) of the synthetic transuranium element plutonium (isotope ^{238}Pu) and the demonstration of its fissionability with slow neutrons (isotope ^{239}Pu) took place at the University of California, Berkeley, through the use of the 60-inch and 37-inch cyclotrons, in late 1940 and early 1941. This led to the development of industrial scale methods in secret work centered at the University of Chicago's Metallurgical Laboratory and the application of these methods to industrial scale production, at manufacturing plants in Tennessee and Washington, during the World War II years 1942-1945. The chemical properties of plutonium, needed to devise the procedures for its industrial scale production, were studied by tracer and ultramicrochemical methods during this period on an extraordinarily urgent basis. This work, and subsequent investigations on a worldwide basis, have made the properties of plutonium very well known. Its well studied electronic structure and chemical properties give it a very interesting position in the actinide series of inner transition elements.

KEYWORDS

Plutonium; fortieth anniversary; discovery; fissionability; tracer chemistry; ultramicrochemistry; first isolation; industrial scale production; actinide.

INTRODUCTION

This year marks the fortieth anniversary of the synthesis and identification (i.e., the discovery) of plutonium. I believe that this "Actinides-1981" conference is an appropriate place to recount some of the history and describe the present status of this element.

The story of plutonium is one of the most dramatic in the history of science. For many reasons this unusual element holds a unique position among the chemical elements. It is a synthetic element, the first realization of the alchemist's dream of large-scale transmutation. It was the first synthetic element to be seen by man. One of its isotopes has special nuclear properties

which give it overwhelming importance in the affairs of man. It has unusual and very interesting chemical properties. It is rated as a dangerous poison. It was discovered and methods for its production were developed during World War II, under circumstances that make a fascinating and intriguing story.

HISTORICAL BACKGROUND

One can choose as a beginning for the story of the transuranium elements the discovery in 1934, by Fermi and co-workers (1934), that neutron irradiation of uranium leads to a considerable number of radioactive substances. The chemical investigation of these radioactivities led, however, to discovery of the fission process rather than of the transuranium elements. In their original work Fermi and his co-workers were led, on the basis of chemical experimentation, to assign some of these radioactivities to transuranium elements. The work of Hahn, Meitner and Strassmann (1936) and others appeared at first to confirm this point of view, and for several years the "transuranium elements" were the subject of much experimental work and discussion. However, early in 1939 Hahn and Strassmann (1939) described experiments which made it certain that they had observed radioactive isotopes of barium and other "light" elements as the result of the bombardment of uranium with neutrons. Subsequent work showed that practically all of the radioactivities previously ascribed to transuranium elements were actually due to fission products.

With poetic justice, the actual discovery of the first transuranium element in turn resulted from experiments aimed at understanding the fission process. Several experimenters, including McMillan (1939) of the University of California, measured the energies of the two main fission fragments by observing the distances they traveled from each other as a result of their mutual recoil when the nucleus explodes. McMillan noted that there was another radioactive product of the reaction, with a half-life of 2.3 days, which did not recoil, at least not sufficiently to escape from the thin layer of fissioning uranium. He suspected that this was a product formed by simple neutron capture--a process which does not release much energy--rather than by fission. In the spring of 1940 McMillan and Abelson (1940) deduced by chemical means that his product is surely an isotope of element 93, arising by beta decay from ^{239}U. The ^{239}U has a half-life of 23 minutes. Element 93 was given the name neptunium (Np) because it is beyond uranium, just as the planet Neptune is beyond Uranus.

McMillan's and Abelson's tracer investigations of the chemical properties of neptunium showed that it resembles uranium, and does not resemble rhenium, in its chemical properties. This was the first definite recognized evidence that the 5f electron shell undergoes filling in this region. Thus the discovery of neptunium was extremely important, not only from the standpoint of opening the transuranium field but also as the break-through to an eventual understanding of the electronic structure and the place in the periodic system of the heaviest elements.

DISCOVERY OF PLUTONIUM

In the fall of 1940 I asked a graduate student, A. 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 J. W. Kennedy, who, like myself, was at that time an instructor in the Department of Chemistry at the University of California. After McMillan's departure from Berkeley in November 1940, and his gracious assent to our continuation of the work he had

begun on the search for and possible identification of element 94, our group turned its major efforts to this problem.

Our first bombardment of uranium oxide with the 16-Mev deuterons from the 60-inch cyclotron was performed on December 14, 1940. Alpha-particle radioactivity was found to grow into the chemically separated element 93 fraction during the following weeks, and this alpha-particle activity was chemically separated from the neighboring elements, especially elements 90 to 93 inclusive, in experiments performed during the next two months. These experiments, which constituted the positive identification 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 first successful oxidation of element 94, which probably represents the key step in its discovery, was effected through the use of peroxydisulfate ion and silver ion catalyst on the night of February 23-24, 1941, in a small room (No. 307) on the third floor of Gilman Hall on the University of California campus in Berkeley. The particular isotope identified was later shown to have the mass number 238 (with a half-life of 88 years), and the reactions for its preparation are as follows:

$$^{238}_{92}U + ^{2}_{1}H \longrightarrow ^{238}_{93}Np + 2n$$

$$^{238}_{93}Np \xrightarrow[2.1\ \text{days}]{\beta^-} ^{238}_{94}Pu$$

In view of its apparent importance, the announcement of this discovery was withheld by the discoverers as a result of self-imposed secrecy, even though this work antedated the time of governmental support. It may be of interest to reproduce here the letters to the editor which were submitted for publication in the *Physical Review* but held in custody by one of their editors until publication after the war, in 1946. (Note that in these and following reproductions of early communications the isotopic designations follow the early convention of having the mass number come after the atomic number, e.g., 93^{239}, rather than precede it, e.g., $^{239}93$ as in the modern nomenclature.) The text of a communication (1946a) dated January 2 , 1941, read as follows:

We are writing to report some results obtained in the bombardment of uranium with deuterons in the 60-inch cyclotron.

The uranium was bombarded in the form of U_3O_8 and the deuterons had to pass through a 2-mil thickness of aluminum foil before hitting the uranium target. The carefully purified element 93 fraction contained a beta-activity whose aluminum absorption curve *(taken on an ionization chamber connected to a FP-54 tube and also on a Lauritsen electroscope) was distinctly different from the absorption curve of a sample of the 2.3-day 93^{239} (formed from uranium plus neutrons) taken under identical conditions. The upper energy limit of the beta particles from this new 93 activity is about 1 Mev, compared with about 0.5 Mev for 93^{239}. The ratio of gamma-ray to beta-particle ionization is about five times larger than for 93^{239}. The initial part of the absorption curve of this 93 from uranium plus deuterons is very similar to the initial part of the absorption curve of 93^{239}. Of course the production of 93^{239} is expected in the deuteron bombardment of uranium, from the reaction $U^{238}(d,n)$ 93^{239}. It is impossible to deduce from the absorption curve the relative intensities of the new 93 and of 93^{239}, since the initial parts of the individual absorption curves of these two activities might well be nearly identical. The rate of decay of the high energy beta-particles (0.5--1 Mev) and gamma-rays from the 93 of uranium plus deuterons was determined. This gave a half-*

life of about 2 days for the new 93. This activity is probably to be assigned to 93^{238}, 93^{236}, or 93^{235} formed in the reaction $U^{238}(d,2n)93^{238}$, $U^{235}(d,n)93^{236}$, or $U^{235}(d,2n)93^{235}$, respectively.

The growth of alpha-particles, which might be due to the element 94 daughter of the 2-day 93, was then looked for. We did observe the growth of alpha-particles in the very carefully purified, as well as in the semi-purified 93 fractions, and the growth curves indicate a half-life of roughly 2 days for the parent o. the alpha-emitter. The final alpha-particle count amounts to several hundred counts per minute for a bombardment of 200 microamperehours. This work was done with a proportional type counter. We plan to redetermine the alpha-particle growth curve more accurately, using an ionization chamber and linear amplifier with the help of a magnetic field to bend out the very strong beta-particle background. The alpha-particles have a range of approximately 3.9 cm in air.

The alpha-activity is chemically separable from uranium and 93. The chemical experiments so far indicate a similarity to thorium and the activity has not yet been separated from thorium. More chemical experiments definitely must be performed before it can be regarded as proved that the alpha-particles are due to an isotope of element 94.

The report (1946b) dated March 7, 1941, on the oxidation experiment which occurred on February 24, 1941, read as follows:

We should like to report a few more results which we have found regarding the element 94 alpha-radioactivity formed in the 16-Mev deuteron bombardment of uranium. We sent a first report of this work in a Letter to the Editor of January 28, 1941. We have in the meantime performed more experiments in order to study the chemical behavior of this alpha-radioactive isotope. The radioactivity can be precipitated, in what is probably the +4 valence state, as a fluoride or iodate by using a rare earth or thorium as carrier material and as a peroxyhydrate by using thorium as carrier material. However, in the presence of the extremely strong oxidizing agent persulfate ion ($S_2O_8^{=}$), plus Ag as a catalyst, this radioactive isotope is oxidized to a higher valence state which does not precipitate as a fluoride. The oxidizing agent bromate ion (BrO_3^-) is not sufficiently powerful to oxidize it to this higher valence state and hence the radioactivity comes down as a fluoride even in the presence of bromate ion. With the help of persulfate ion it has been possible to separate quantitatively this radioactivity from thorium, by using the beta-active UX_1 as an indicator for thorium. These experiments make it extremely probable that this alpha-radioactivity is due to an isotope of element 94. The experiments are being continued.

CHEMICAL INVESTIGATIONS AT BERKELEY

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," or by code names, until the spring of 1942, at which time the first detailed reports on them were written. The early work, even in those days, was carried on under a self-imposed cover of secrecy--as a matter of fact, I recall that a code name was often used for element 94, even in oral references. Throughout 1941 we referred to it by the code name of "copper," which was all right until we found it necessary to introduce the element copper into some of our experiments; we were then faced with the problem of distinguishing between the two. For a while we referred to plutonium

as "copper" and the real copper as "honest-to-God copper." This seemed clumsier as time went on and we finally christened the element "plutonium" and began to call it that. In order to write the original report on the chemical properties, it became necessary to have chemical symbols for the two elements.

This report, by Wahl and myself, dated March 19, 1942, was mailed as a secret report from Berkeley, California, to the Uranium Committee (the group, headed by L. J. Briggs, that had been coordinating the early United States work on possible practical energy from nuclear fission) in Washington, D.C., and it was issued as Report No. A-135. Although it was published (Seaborg and Wahl, 1948) in its original form after the war, it may be interesting to quote the section in which the name plutonium was first suggested:

Naming the Elements. Since formulas are confusing when the symbols "93" and "94" are used, we have decided to use symbols of the conventional chemical type to designate these elements. Following McMillan, who has suggested the name "neptunium" (after Neptune, the first planet beyond Uranus) for element 93, we suggest "plutonium" (after Pluto, the second planet beyond Uranus) for element 94. The corresponding chemical symbols would be Np and Pu. The names "eka-rhenium" and "eka-osmium" seem inappropriate in view of the marked dissimilarity of the chemical properties of elements 93 and 94 to those of rhenium and osmium.

As a result of these tracer investigations during 1941 and early 1942 at the University of California, to which Wahl made the major contributions, a great deal was learned about the chemical properties of plutonium. It was established that it had at least two oxidation states, the higher of which was not carried by lanthanum fluoride or cerium fluoride, while the lower state was quantitatively coprecipitated with these compounds. It was established that the higher oxidation state could be obtained by treatment of the lower state with oxidizing agents such as persulfate and argentic ions, dichromate, permanganate, or periodate, and that the upper state could be reduced to a lower (rare earth fluoride-carriable) state by treatment with sulfur dioxide or bromide ion. The approximate oxidation potential of the couple plutonium (reduced) → plutonium (oxidized) was shown to be between -1.0 and -1.4 volts. It was established that plutonium in aqueous solution is not reduced to the metal by zinc, and that plutonium does not form a volatile tetroxide. It was shown that a stable lower state of plutonium--probably plutonium (Pu^{IV})--was carried by $Th(IO_3)_4$. Ether extraction had been used to separate large amounts of uranyl nitrate from plutonium. Methods had also been devised for the separation of plutonium from elements 90, 91, and 93.

On the basis of these facts and others not mentioned here, it was speculated that plutonium in its highest oxidation state is similar to uranium (VI) and in a lower state is similar to thorium (IV) and uranium (IV). It was reasoned that if plutonium existed normally as a stable plutonium (IV) ion, it would probably form insoluble compounds or stable complex ions analogous to those of similar ions, and that it would be desirable (as soon as sufficient plutonium became available) to determine the solubilities of such compounds as the oxalate, phosphate, fluoride, iodate, and peroxide. Such data were needed to confirm deduction based on the tracer experiments.

We conceived the principle of the oxidation-reduction cycle, as applied to the separations processes that were to become so useful later. This principle applied to any process involving the use of a substance which carried plutonium in one of its oxidation states but not in another. By use of this principle, for example, a carrier could be used to carry plutonium in one oxidation state and thus to separate it from uranium and the fission products. Then the

carrier and the plutonium could be dissolved, the oxidation state of the plutonium changed, and the carrier reprecipitated, leaving the plutonium in solution. The oxidation state of the plutonium could again be changed and the cycle repeated. With this type of procedure, only a contaminating element having a chemistry nearly identical with the plutonium itself would fail to separate if a large number of oxidation-reduction cycles were employed. This principle, of course, applies to other types of processes, such as solvent extraction, adsorption, or volatility methods.

DEMONSTRATION OF FISSIONABILITY OF ^{239}Pu

The plutonium isotope of major importance is the one with mass number 239. The search for this isotope, as a decay product of ^{239}Np, was being conducted by the same group, with the collaboration of E. Segrè, simultaneously with the experiments leading to the discovery of plutonium. The isotope ^{239}Pu was identified, and its possibilities as a nuclear energy source were established during the spring of 1941, using a sample prepared by the decay of ^{239}Np produced by neutrons from the 60-inch cyclotron and later purified by taking advantage of the then-known chemistry of plutonium.

A sample of uranyl nitrate weighing 1.2 kilograms was distributed in a large paraffin block placed directly behind the beryllium target of the 60-inch cyclotron and was bombarded for two days (terminating on Mar. 3, 1941) with neutrons produced by the full deuteron beam. This uranyl nitrate was placed in a continuously operating glass extraction apparatus and the uranyl nitrate was extracted into diethyl ether. The ^{239}Np was isolated by use of the oxidation-reduction principle with lanthanum and cerium fluoride carrier and reprecipitated six times in order to remove all uranium impurity. For each of the numerous centrifugation procedures it was necessary to carry the material in a heavy lead shield from the chemistry building to Crocker Laboratory, which contained the only centrifuge available for this work. Measurement of the beta-particle radiation from the ^{239}Np made it possible to calculate the amount of ^{239}Np that was present to yield ^{239}Pu upon decay.

In order to capture more completely the spirit of this rather extensive chemical separation procedure, carried out in a way to avoid as much as possible exposure to radiation, the original notebook entries are reproduced here. These were written before the experiment in the manner of instructions for guidance in the conduct of the rather complicated chemical procedure and were annotated as the separation progressed. Since the guidance instructions were followed faithfully, they serve as an actual account of how the chemical separation was carried out.

1. Put 2 liters of ether in flask, add the uranium nitrate to the extractor, and run the extractor for several hours. Wear goggles! (Started boiling at about 10:00 a.m. and stopped at about 2:30 p.m., Monday, March 3, 1941.)

2. Boil down aqueous phase in nickel coated Pt dish outside on porch, cool and add 10 mg La and 10 mg Ce, 1/2 cc 36 N. H_2SO_4, transfer to wax tube and add enough 27 N. HF to make soln. 6 N. in HF (15 cc of soln. = 65 cc total).

3. Carry the centrifuge tube to Crocker Lab in Pb beaker in wooden box (also containing 2nd tube, wax beaker and wax bottle and 6 N. HF) wearing Pb gloves. Balance behind Pb shield. Centrifuge for 20-30 minutes, pour liquid into beaker and then into wax bottle. Pour about 65 cc 6 N. HF into centrifuge tube and stir and centrifuge, add wash water to same wax bottle. Carry box to room 305 and put wax bottle into Pb cylinder on porch. (Completed this at

5:30 p.m.).

4. Wash precipitate into Ni coated Pt dish, using about 10 cc H_2O and bakelite stirring rod, add 5 cc 36 N. H_2SO_4 and heat to fuming behind Pb shield in room 305, add about 50 cc H_2O and 1 cc sat. $NaBrO_3$ and heat and wait 10 minutes while warm and then cool soln. Transfer to 2nd wax tube, add 15 cc 27 N. HF.

5. Carry to Crocker Lab in Pb beaker in wooden box (also containing 1st wax tube), balance behind Pb and centrifuge. Carry box to room 305 and pour liquid into Ni coated Pt dish. Wash rare earth precipitate into wax bottle marked R.E. ppt. and put in Pb cylinder on porch. (Finished at about 10:00 p.m.).

6. Evaporate soln. to H_2SO_4 fumes in room 305 behind Pb shield. (Finished at 12:00 a.m.) Add about 40 cc H_2O and cool in ice bath, add 100 cc sat. SO_2 in ice water and heat, add 3 mg La and 3 mg Ce. Transfer to 2nd wax centrifuge tube and add 18 cc 27 N. HF and stir. (Approximately 11:00 a.m. Tuesday, March 4, 1941.)

7. Carry to Crocker Lab (with 1st tube and 6 N. HF and wax bottle marked "1st 93 filtrate"), centrifuge, pour into wax bottle, wash in centrifuge with about 65 cc 6 N. HF, pour into same wax bottle, carry to room 305.

8. Wash ppt. with about 10 cc H_2O and new bakelite rod into old Pt dish in old end of room 305 behind old Pb shield on old electric heater. Add 5 cc 36 N. H_2SO_4, heat to fumes, add about 35 cc H_2O, 1 cc sat. SO_2 in ice water, transfer to clean 3rd centrifuge tube. Add 15 cc 27 N. HF and stir.

9. Carry to Crocker Lab (with 2nd tube, 6 N. HF and wax bottle marked "2nd 93 filtrate") and continue as in step 7. (Approximately 4:00 p.m. Tuesday, March 4, 1941.)

10. Repeat step 8 but use all new stuff at clean end and 4th centrifuge tube.

11. Carry to Crocker Lab (with 3rd centrifuge tube, 6 N. HF, and wax bottle marked "3rd 93 filtrate") and continue as in step 7. (Approx. 10:30 p.m. Tuesday, March 4, 1941.)

12. Repeat step 8.

13. Carry to Crocker Lab (with other centrifuge tube, 6 N. HF and wax bottle marked "4th 93 filtrate") and continue as in step 7. (Approx. 11:55 a.m. Wednesday, March 5, 1941.)

14. Repeat step 8.

15. Repeat step 13. (Approx. 5:00 p.m. Wednesday, March 5.)

16. Repeat step 8.

17. Repeat step 8, except use final bakelite tube. (Approx. 12:30 p.m. Thursday, March 6, 1941.)

18. Ppt. put into Pt dish (1.5 cm diameter and 1/2 to 1 cm deep), solution evap. off, sides snipped off, covered with thin layer Duco cement. (Approx. 5:00 p.m. Thursday, March 6, 1941.)

This is called Sample A.

Using neutrons produced by the 37-inch cyclotron in the University of California Old Radiation Laboratory, the group first demonstrated on March 28, 1941, with the sample estimated to contain about 0.5 microgram of ^{239}Pu, that this isotope undergoes slow neutron-induced fission with a cross section even larger than that of ^{235}U. The sample, labelled "Sample A," was placed near the screened window of an ionization chamber, which was imbedded in paraffin near the beryllium target of the 37-inch cyclotron. This gave a small but detectable fission rate when a six-microampere beam of deuterons was used. In order to increase the accuracy of the measurement of the fission cross section, this sample, which had about five milligrams of rare-earth carrier material, was subjected to an oxidation-reduction chemical procedure that reduced the amount of carrier to a few tenths of a milligram.

Kennedy, Segrè and I made our definitve measurements on the thinned "Sample B" on May 18, 1941. The measurements were again made at the 37-inch cyclotron using the neutrons produced by the bombardment of the beryllium target by 8 Mev deuterons. Sample B was placed near the screened window of our ionization chamber imbedded in an improved paraffin arrangement near the beryllium target.

Comparison of its fission rate was made with that of a more accurately determined sample containing 200 micrograms of natural uranium, and hence 1.46 micrograms of ^{235}U (U Standard No. 4) prepared by electrodeposition by Wahl. A deuteron beam of about 9 microamperes was used at the 37-inch cyclotron and measurements with both Sample B and U Standard No. 4 were made, with and without the slow neutron shielding material cadmium plus boron. Sample B gave a fission rate with slow neutrons of 80 per minute, while our 1.46 microgram ^{235}U sample, when placed in an identical position, gave a fission rate with slow neutrons of 140 per minute.

This enabled us to calculate the slow neutron fission cross section of ^{239}Pu compared to that of ^{235}U. For this we needed a more accurate weight for the ^{239}Pu in sample B. Our measurement of the intensity of beta particles from the ^{239}Np in Sample A (from which Sample B was derived) was 52 millicuries when measured at 5:35 p.m. on March 6, 1941. When this was corrected for decay, this corresponded to 120 millicuries at 10:00 p.m. on March 3, the time when the ^{239}Np was separated from the ^{239}Pu which had grown in up to that time. 120 millicuries of ^{239}Np with its 2.3 day half-life corresponded to 0.5 micrograms, which was also the weight of the daughter ^{239}Pu.

The slow neutron fission cross section of ^{239}Pu was therefore found to be equal to $\frac{1.46}{0.5} \times \frac{80}{140} = 1.7$ times that of ^{235}U.

With the thin sample it was also possible to measure the alpha-particle counting rate of ^{239}Pu. This was 800 counts per minute compared to 240 counts per minute before the thinning. Correcting for the geometrical factor (1.3%) for our ionization chamber-magnetic field setup, as determined with a known amount of uranium of the same thickness as the sample, the total alpha-particle emission of the sample now amounted to about 60,000 per minute. This corresponded to an alpha half-life for ^{239}Pu of about three times 10^4 years. Our absorption measurements on the alpha-particles indicated a range in air (15° C.) of the order of 3.6 or 3.7 cm corresponding to an energy of about 5.2 MeV.

Our fission cross section for ^{239}Pu was in remarkable agreement with the accurate values which were determined later. A report (1946c) of this work was registered on May 29, 1941, for publication in the *Physical Review*, but again the information was voluntarily withheld from actual publication until after the end of the war in 1946. This demonstration that ^{239}Pu undergoes fission

with thermal neutrons with a large probability, showing that all the neutrons emitted in the process are eligible to cause further fissions, established the great value of this isosope, and the recognition of this by E. O. Lawrence and others led to the wartime Plutonium Project for its production on a large scale, looking toward its possible use in a nuclear weapon.

PRODUCTION OF ^{239}Pu

One of the questions which posed itself immediately was the following: Is it possible by use of the mixture of the uranium isotopes as it occurs in natural uranium, consisting of about 0.7 per cent of ^{235}U and 99.3 per cent of ^{238}U by weight, to cause a chain reaction to occur on a very large scale? If so, the extra neutrons produced in the fission of ^{235}U would be absorbed by ^{238}U to form the desired isotope, ^{239}Pu, in large quantity.

The other question which of necessity came up for immediate discussion was: Would it be possible to devise, in a reasonable period of time, chemical means for separating this ^{239}Pu from the uranium and from the tremendous quantity of fission-product elements that would be present with it?

These were the two staggering problems which formed the basis of the Plutonium Project. Their solutions were to a large extent unrelated, and the development program in connection with each of these problems was, of course, in the hands of research men in different fields, physics and chemistry.

Early in 1942, following a high-level decision made in Washington, D.C., on December 6, 1941, physicists who had been working on the development of the chain reaction and chemists who had been working on the development of separation processes for the plutonium assembled at the Metallurgical Laboratory of the University of Chicago. In time, other scientists--chemists, physicists, engineers, biologists, and medical men--assembled here, to solve problems related to those described above.

During the first months at the Metallurgical Laboratory, intensive effort was directed toward defining the chemical-separation process to be used in the production plants which were then being planned. Among the possible procedures that were investigated were precipitation, solvent-extraction, volatility, adsorption-elution, and pyrometallurgical and pyrochemical processes; in fact, all of the types of processes now in use or under investigation were included in this early scouting program of the year 1942. The solvent-extraction approach was investigated by D. E. Koshland, Jr., the volatility approach by H. S. Brown and O. F. Hill and later E. G. Bohlmann, pyrochemical and pyrometallurgical procedures by T. T. Magel and M. Cefola, and the adsorption-elution method by J. E. Willard and E. H. Turk as well as G. E. Boyd, A. W. Adamson, E. E. Motta, E. R. Russell, J. Schubert, and their co-workers. However, it was decided before the end of 1942 to use a precipitation process because this seemed to offer the greatest certainty of at least limited success in the short time interval involved, even though it did not seem to offer the greatest ultimate efficiency and would not lead to the recovery of the uranium for reuse.

The problem of separating the new element plutonium from uranium and fission products might not at first seem difficult, for it was, indeed, primarily a chemical problem. However, it differed in a great many ways from ordinary chemical problems, and these differences made the solution of the problem as a whole much more difficult, even though some of the differences actually helped the solution. From the beginning, our limited time seemed the most

nearly insurmountable difficulty. It was by no means possible to complete the design and testing of the process before it had to be placed in operation. Even a simple chemical process usually requires a much longer time to place in large-scale operation than did the plutonium-separation process, even though the latter cannot be regarded as either simple or short.

The problem which had to be met during the fall of 1942 was that of developing a separation process which would meet the demanding requirements. The process had to accomplish a separation of plutonium in high yield and purity from many tons of uranium in which the plutonium was present at a maximum concentration of about 250 parts per million. Because of this low concentration, compounds of plutonium could not be precipitated, and any precipitation-separation process had to be based upon coprecipitation phenomena, i.e. the use of so-called "carriers" for plutonium. At the same time, the radioactive fission products produced along with plutonium in the uranium (as a result of the fission of ^{235}U) had to be separated so that less than one part in 10^7 parts orginally present with the plutonium would exist with the final product from the process. This requirement was necessary in order to make it safe to handle the plutonium, for without a separation of the fission products, the plutonium from each ton of uranium would have more than 10^5 curies of energetic gamma radiation associated with it. The process of separating fission products was called "decontamination." Thus a unique feature of the process was the necessity of separating a wide variety of elements completely from the final product and of accomplishing these separations by remote control behind large amounts of shielding in order to protect operating personnel from the hazards of the radiation. The finally decontaminated plutonium compound that was to be provided to those responsible for its ultimate use had to be one that would facilitate those final steps; it had to be a compound or solution of small bulk that could be shipped without difficulty, and it had to be of a composition that could be easily subjected to further purification. The separation process had to meet the further requirement that a "critical mass" of plutonium, which would lead to a disruptive nuclear chain reaction, would not accumulate at any step of the procedure.

If large amounts of plutonium had been available in the fall of 1942 and if its chemistry had been as well known as the chemistry of the more familiar elements, the task of developing the chemical process would still have been a formidable undertaking. Essentially all that was known about plutonium at this time was based upon secondary evidence from tracer experiments involving the infinitesimal amounts of the element which had been produced entirely by cyclotron bombardments. All of the plutonium (in the form of the isotopes ^{238}Pu and ^{239}Pu) used in the experiments up until the time of the operation of the Clinton reactor, with the exception of an experimental test of the separation process on the semiworks scale using some plutonium-containing uranium oxide from the reactor at Argonne Forest, was cyclotron produced, using the cyclotrons at the University of California and Washington University. Tracer chemistry itself was a relatively new science; many of its phenomena were not clearly understood; and deductions based on it were often subject to doubt, particularly when applied to a new element. Added to the difficulty of devising the chemical process was the fact that only a few of the fission products had been identified, and many of these proved to be among the least well known of the chemical elements.

Operation of a chemical process by remote control behind massive shielding in an area which would become so highly radioactive after use that operating and maintenance personnel would not be able to enter the area for even brief periods of time to adjust and service equipment, made it imperative that the process be thoroughly tested in advance in the type of equipment to be used in the

plant, in order to minimize the possibility of errors in the design of the process or the equipment. Furthermore, operational errors had to be kept to a minimum, and careful chemical control of the operations had to be maintained. In all of these considerations it was obviously desirable that the process to be operated be as short and simple as possible. Similarly, the process from the standpoint of plant design should consist of a number of similar steps requiring the same sort of equipment rather than consisting of steps which were so fundamentally different as to require many different types of equipment. At the same time, it seemed advisable to design the process and the equipment in such a way as to facilitate changes in case of failure. All of these requirements were met; in fact, the process was operated more successfully than even the most optimistic dared to hope and from the beginning gave high yields and decontamination factors.

Although it was felt that such a 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. S. G. Thompson (1956) is largely responsible for the conception and early development of the process which was finally chosen. The key to the process is quantitative carrying of plutonium (IV) from acid solution by bismuth phosphate, an unexpected phenomenon which was discovered in December 1942, and the expected noncarrying of plutonium (VI) by the same carrier material. This method, known as the Bismuth Phosphate Process, operated as follows: Neutron-irradiated uranium is dissolved in nitric acid, and, after the addition of sulfuric acid to prevent the precipitation of uranium, plutonium (IV) is coprecipitated with bismuth phosphate. The precipitate is dissolved in nitric acid, the plutonium (IV) is oxidized to plutonium (VI), and a by-product precipitate of bismuth phosphate is formed and removed, the plutonium (VI) remaining in solution. After the reduction of plutonium (VI) to plutonium (IV), the latter is again coprecipitated with bismuth phosphate, and the whole "decontamination cycle" is repeated. At this point the carrier is changed to lanthanum fluoride, and a similar "oxidation-reduction cycle" is performed, using this carrier, thereby achieving further decontamination and concentration. The plutonium at this point is sufficiently concentrated that final purification can be accomplished without the use of carrier compounds and plutonium peroxide is precipitated from acid solution.

One of the most remarkable features of the Process is the limited time in which it was developed. The element plutonium was discovered in December 1940, and the first compound was isolated in August 1942, as will be described. The unusual properties of bismuth phosphate as a carrier for plutonium were discovered in December 1942, and the Bismuth Phosphate Separation Process was placed in successful operation in the pilot plant at Clinton Laboratories in Tennessee in December 1943. Thus in actually less than one year the process development work was almost completed before the total quantity of plutonium available from cyclotron bombardments had reached two milligrams. Additional developmental work preceded the beginning of operation of the vast processing plants at Hanford, Washington, in December 1944. Finally, it is significant that only four and one-half years elapsed between the discovery of plutonium and its first use as a source of nuclear energy for military purposes. Accomplishment of this objective during World War II required not only tremendous financial resources, engineering and chemical skill, careful planning and organization, high priorities for material, skilled manpower, and construction facilities, but also imagination and (perhaps as much as anything else) a considerable measure of good fortune.

As a result of early work at Berkeley, one separation process had evolved

already, based on the oxidation and reduction of plutonium and its nonprecipitation and precipitation with a lanthanum fluoride carrier. This was called the "Lanthanum Fluoride Process," and it later became an integral part of the Bismuth Phosphate Process. Although the Lanthanum Fluoride Process seemed to be sound chemically, there were many potential difficulties inherent in its operation in the plant.

ULTRAMICROCHEMICAL INVESTIGATIONS

The isolation of plutonium at the Metallurgical Laboratory, after initial contributions by M. Cefola, was carried on chiefly by Cunningham and Werner, (1949) who had previously been occupied in the biochemical field. The first pure chemical compound of plutonium, free from carrier material and all other foreign matter, was prepared on August 20, 1942, after starting with a plutonium concentrate in about 10 milligrams of rare earths prepared by A. C. Wahl and co-workers at Berkeley. This historic day marks man's first sight of the element plutonium and, in fact, the first sight of a synthetically produced isotope of any element. The excitement throughout the laboratory, which was situated in a guarded area on the fourth floor of the Jones Chemical Laboratory on the University of Chicago campus, was great indeed, as person after person came to view the historic sight under the microscope. The achievement was described by B. B. Cunningham, Cefola and L. B. Werner in their contribution to the Metallurgical Laboratory Report CN-250, covering the period August 16-31, 1942, entitled "Ultra Microchemical Investigations on 94," and which I quote here:

A. Isolation of compounds of pure element 94. In our last report (CN-239), we described our preparations for experiments with pure element 94, in which the 30,000-year 94^{239} is to be used. Although larger amounts of 94^{239} will be available soon, we had on hand about 1 μg for immediate experimentation. Using this quantity of 94^{239}, we have prepared some compounds of pure element 94. The sample containing this 94^{239}, which originally had about 10 mg of rare earths (Ce^{+4} and La^{+3}) with it as carrier, was carried through a series of oxidation-reduction cycles using fluoride precipitations and Ag^{++}, $S_2O_8^{--}$ oxidations. In four such cycles, the amount of carrier was successively reduced from 10 mg to 1 mg to 20 μg to 5 μg, and finally to 0 μg, with the interpolation of a hydroxide precipitation at the 5 μg of carrier stage. The volumes in which precipitation took place in the last three steps were from 100 to 15 λ, and only La^{+3} was used as carrier in these steps.

B. Precipitation of 94 as fluoride or double fluoride. After all of the rare earth carrier had been eliminated as described above, the fluoride, or perhaps a double fluoride, of pure element 94 was precipitated by adding HF to the solution in which 94 was present in its lower oxidation state. This precipitate of 94, which was viewed under the microscope and which was also visible to the naked eye, did not differ visibly from the rare earth fluorides. (Shortly after the 94 was precipitated, a considerable quantity of K_2SiF_6 was observed to separate, as a result of the fact that precipitation has been performed in glass vessels. This will be avoidable in future work because we have now developed suitable fluoric-resistant micro vessels.)

From the alpha-activity remaining in the supernatant liquid after the final precipitation as a fluoride, it can be calculated, using 30,000 years as the half-life of 94^{239}, that this salt of 94 has a solubility of the order of magnitude of 10 mg of the element per liter of 6 N HF solution. This value is necessarily somewhat tentative.

C. Precipitation of 94 as iodate. The mixed precipitate of 94 fluoride and

K_2SiF_6 was treated with H_2SO_4 and heated to the appearance of fumes of SO_3. Because of the large volume of water required to dissolve the residue, 20 μg of La^{+3} were added as carrier and mixed $La(OH)_3$ and 94 hydroxide were precipitated. This was dissolved in a minimum volume of 6 N H_2SO_4. In this operation some of the La^{+3} as $La_2(SO_4)_3$ failed to dissolve, and this was centrifuged off. Excess potassium iodate was added to the filtrate and mixed iodates of 94 and Ag^+ (the Ag coming from traces of silver oxide which had precipitated with the hydroxides) were obtained. The silver iodate was dissolved away from the precipitate by using 6 N NH_4OH, which was subsequently removed. A small amount of brownish crystalline precipitate remained, and upon treatment with a little H_2O_2 in ∿ 3 N HNO_3 and 1/4-saturated KIO_3, the color of this precipitate changed to white without any other visible change in its characteristics. This remaining precipitate presumably was the iodate of pure element 94. From the alpha-activity remaining in the supernatant liquid in equilibrium with the 94 iodate it appears that the iodate in 1/4-saturated KIO_3 solution in ∿ 3 N HNO_3 has a solubility of the same order of magnitude as the fluoride or somewhat less. This value also is a tentative one.

Accurate data on the solubility of pure compounds of pure element 94 will be available from our experiments shortly.

Note the use of "94" rather than "plutonium" as the name of the element at this time. The name "plutonium" had been suggested only a few months earlier and was not yet in general use by the scientists at the Metallurgical Laboratory. The code name "49" was by this time being used to designate the isotope 94^{239}, following the general (not very subtle) code which used the last digits of the atomic and mass number to represent an isotope.

The first weighing of a pure compound of plutonium occurred on September 10, 1942, when 2.77 micrograms of the oxide (PuO_2) were weighed by Cunningham and Werner. It was part of the plutonium, mentioned below, produced in the large undertaking of the summer of 1942. A contribution by Cunningham, Cefola and Werner, also entitled "Ultra Microchemical Investigation of 94," to Metallurgical Laboratory Report CN-261, covering the period September 1-15, 1942, describes the earliest work on plutonium compounds and the first and second weighings of pure plutonium compounds.

Introduction. In our last report (CN-250), we described the isolation of compounds of essentially pure 94^{239}. Further work, which is described in this report, has been done upon the isolation of larger amounts of 94^{239}. This larger amount of 94^{239} has made it possible to investigate the properties of some of the compounds of 94 and the results of this investigation are described in this section. The method of purification used in order to obtain the pure 94^{239} is described immediately below.

A. Isolation and purification of plutonium. A sample containing plutonium equivalent to 8 x 10^6 alpha disintegrations per minute, in a volume of 19 cc, was treated with 1 mgm La^{+3} carrier, and mixed La and 94 fluorides precipitated by the addition of HF. The fluorides were dissolved by heating with H_2SO_4 to the appearance of fumes of SO_3. The sulfate solution was taken up in a volume of approximately 1 ml, made 1 M in HNO_3, saturated with $(NH_4)_2S_2O_8$ and treated with approximately 5 mgm AgO. After 10 minutes, the solution was made 6 M in HF and the precipitated LaF_3 centrifuged out. Two drops of 30% H_2O_2 were added to reduce the 94 and then 100 γ La^{+3} carrier was added. The solution was centrifuged after 30 minutes. The mixed fluorides of La and 94 were dissolved as before, taken up in ∿250 γ of H_2O, oxidized as above, and the La^{+3} again precipitated out. The supernatant liquid was transferred to a platinum microcrucible, treated with a few drops of 6 N H_2SO_4, and the fluoride

expelled by heating in the usual way. The H_2SO_4 digest was treated with 5 drops of concentrated NH_4OH, and the resulting hydroxide precipitate packed by centrifugation in a micro cone. The hydroxide was washed 3 times with approximately 40 λ portions of concentrated NH_4OH (in order to remove any silver). The hydroxide was then dissolved in a minimum volume of concentrated HNO_3, and the iodate was precipitated from this solution by the addition of an excess of saturated KIO_3 solution. The iodate was washed 3 times with 6 M HNO_3 1/4-saturated with KIO_3 (to remove the La impurity) and was then converted to the chloride by several evaporations with 6M HCl. The chloride was converted to the nitrate by repeated evaporation with concentrated HNO_3. The hydroxide was precipitated once more with concentrated NH_4OH, the supernatant liquid removed, the nitrate formed by adding HNO_3 and a portion of this nitrate was converted to the oxide by ignition. The oxide was weighed and its specific alpha-activity determined. Assuming the formula of the oxide to be PuO_2, a specific activity of 110,000 alpha disintegrations per minute per microgram Pu was found. The rest of the plutonium nitrate solution was then treated with concentrated NH_4OH, the hydroxide washed 3 times as before, then converted to the iodate and again washed 4 times with 6 M HNO_3-iodate solution. The oxide (assumed PuO_2) prepared from this compound showed a specific activity of 167,000 disintegrations per minute per microgram Pu (see Section H), and it was considered probable that the plutonium was reasonably pure.

B. Plutonous nitrate. Using some of the pure plutonium whose purification is described in the section above, pure solid plutonous nitrate was prepared. This compound was prepared by the evaporation of a concentrated solution of the metal with excess HNO_3. The resulting solid was a lemon-yellow crystalline material, probably deliquescent and highly hydrated. It melted easily on warming. The formula is presumably $Pu(NO_3)_4 \cdot xH_2O$. Solutions of plutonous nitrate of concentrations about 2-4 grams plutonium per liter appear pale-green in color.

C. Plutonous oxide. This compound was prepared by ignition of the plutonous nitrate. This compound was yellow-brown in color; crystalline form was not evident. It was virtually insoluble in 6 N HNO_3, either at room temperature or at boiling temperature. It dissolved fairly readily in hot concentrated H_2SO_4, presumably due to the formation of the stable soluble complex of Pu^{+4} with sulfate (Reports CN-239 and CN-250). It also dissolved in 6 N HNO_3 when Ce^{+4} was present, presumably being aided by the oxidation of the Pu^{+4} to its higher oxidation state. The formula may very well be PuO_2.

D. Plutonous iodate. This compound was formed by precipitation upon addition of KIO_3 to a plutonous nitrate solution. The precipitate was a white, bulky crystalline material. The solubility in a solution 6 N in HNO_3 and containing approximately 4 g KIO_3/ liter is about 0.020 grams plutonium per liter. The solubility was determined from the alpha-activity remaining in solution after the precipitation of the plutonous iodate. This is a practical solubility and may not necessarily be a true solubility, since there is no assurance that equilibrium had been attained between the two phases. The formula, again upon the assumption that the lower oxidation state has an oxidation number of $^{+}4$, is presumably $Pu(IO_3)_4$.

E. Plutonous hydroxide. This was prepared in these experiments by treating the iodate with concentrated NH_4OH. The more insoluble plutonous hydroxide was formed and from the alpha-activity remaining in the solution after this transformation it can be deduced that the solubility corresponds to 0.004 grams plutonium per liter. Again there is no assurance that this is the true solubility, in that it was not certain that there was equilibrium between the two phases. The plutonous hydroxide, presumably of formula $Pu(OH)_4 \cdot xH_2O$, appeared

as a pale yellowish-green flocculent precipitate. Figure A [not reproduced here] *shows a positive photo-micrograph of about 0.5 gammas of Pu as the hydroxide under a magnification of approximately 30 diameters taken with reflected light. The dark material in the photograph is the glass micro centrifuge cone in which the precipitate appears as a white mass which is slightly dislodged from the barely discernible apex of the centrifuge cone.*

F. Plutonous fluoride. This has not yet been prepared in a completely pure state. Plutonous fluoride is, however, very insoluble, and appears as a white (or pale yellow) flocculent precipitate.

G. Plutonium peroxide. This compound was prepared by precipitation from a plutonous chloride solution which had in turn been prepared by dissolving plutonous hydroxide in HCl and evaporating to dryness. After the solution of the chloride in about 20 mλ of distilled water, excess H_2O_2 was added. A small white precipitate (perhaps slightly yellow) rather more crystalline than the hydroxide, appeared. On the basis of this experiment, the plutonium peroxide appears to be insoluble, although further experiments under controlled pH conditions are necessary to make the information useful.

H. Half-life of 94^{239}. A sample of plutonous oxide, obtained by igniting the nitrate described in section B at about 700°C for 20 minutes was weighed on the Salvioni balance by the technique previously described (Report CN-239). 4.45 γ of the oxide (assumed PuO_2) showed an alpha-activity of 672,000 disintegrations per minute. The activity per microgram of plutonium was calculated as 167,000 disintegrations per minute. From this determination the half-life of Pu would appear to be 20,000 ± 2000 years. Additional purifications and determinations of the specific activity will be necessary before this figure can be considered as final.

In this communication it was already more convenient to refer to the element as "plutonium" (with symbol Pu) rather than as "94."

During the summer of 1942, large amounts of uranium (hundreds of pounds) were bombarded for several months with the neutrons from the cyclotrons of the University of California, Berkeley, under the supervision of J. G. Hamilton; and Washington University, St. Louis, under the supervision of A. S. Langsdorf, Jr. The initial large-scale operations at the Metallurgical Laboratory for the isolation of plutonium were carried out by T. P. Kohman, A. H. Jaffey, D. E. Koshland, Jr. and E. H. Turk and co-workers. In these operations diethyl ether was used to separate the bulk of the uranium, as uranyl nitrate hexahydrate, from the plutonium (IV) and fission products; it is the success of this method that led to the above-mentioned consideration of solvent extraction as a possible chemical procedure to be used in the manufacture of plutonium. The lanthanum fluoride oxidation-reduction procedure was used for the separation of the plutonium from the fission products and for its concentration. These operations resulted in the production of several hundred micrograms of plutonium, a great deal more that had been anticipated. This was used in the tracer-scale investigations of the chemical separation processes for plutonium and other tracer-scale investigations of plutonium, and also made it possible to carry on the program of ultramicrochemical investigation at Chicago (including the work described just above). In September 1942 Cunningham and Werner (1949) were able to prepare a number of compounds of pure plutonium and to determine with certainty, by means of chemical analysis, that the oxidation number of the most stable state of the element in solution is the IV state. M. Cefola, R. L. Patton, and C. Smith also made contributions to the program at the Metallurgical Laboratory, at this time as well as somewhat later.

The first unequivocal production of plutonium metal was made in November, 1943 by Baumbach and co-workers (1958). About 35 micrograms of PuF_4 in a small thoria crucible in a high vacuum was reacted with barium metal at 1400° C to yield plutonium metal. The metal had a silvery lustre, a density of about 16 grams per cubic centimeter and rapidly absorbed hydrogen at about 210° C to form a black powder subsequently identified as PuH_3 (a proof that metal had been produced).

The group remaining in Berkeley with W. M. Latimer also contributed to this ultramicrochemical program of investigation. During the summer of 1942, A. C. Wahl, independently, was also processing cyclotron-irradiated uranium in order to isolate pure plutonium. He succeeded in isolating 200 micrograms of chemically pure plutonium in 92 per cent yield from 45 kilograms of uranium that had been irradiated for two months with neutrons from the Berkeley 60-inch cyclotron. He employed the Lanthanum Fluoride Process and measured yields and decontamination factors at every step, collecting data which proved very valuable in evaluation of this separations process, then the only practical method for isolation of plutonium. The chemistry was started in July, but progress was slow because of the care exercised in evaluation of the separations process, and a pure compound of plutonium (IV) hydroxide, was not isolated until September 29, 1942. However, it was with great elation that Wahl showed the 0.2 milligram plutonium sample, easily visible to the naked eye, to E. O. Lawrence, whose cyclotron had produced the plutonium. This plutonium was used in an ultramicrochemical program of investigation at Berkeley, by Wahl, J. W. Gofman, R. E. Connick, J. W. Hamaker, G. E. Sheline, and W. H. McVey. Among other accomplishments, this group was able to establish in 1943 that the oxidation number of the highest state is VI (Connick and co-workers, 1949).

From this time until the fall of 1943, cyclotron bombardments were the sole source of plutonium, and over this period of time about 2,000 micrograms, or 2 milligrams, of plutonium, were prepared. This material was used to maximum advantage by the ultramicrochemists to prepare compounds of plutonium and to measure properties such as solubilities and oxidation potentials. In particular, it was possible--and this was of inestimable importance--to test the Bismuth Phosphate Process which was under consideration for use at Hanford. The various parts of the complicated separation and isolation procedures were tested at the Hanford concentration of plutonium in the careful and crucial experiments performed by B. B. Cunningham, L. B. Werner, D. R. Miller, I. Perlman, and others. Without the possibility of these tests early in 1943, I believe it is fair to say that this process, which went into use at the plutonium production plant at Hanford in the state of Washington, and which turned out exceedingly well, would not have been chosen.

I want to emphasize that the scale-up between the ultramicrochemical experiments to the final Hanford plant amounts to a factor of about 10^9, surely the greatest scale-up factor ever attempted. In spite of these difficulties the chemical separations process at Hanford was successful from the beginning, and its performance exceeded all expectations. High yields and decontamination factors (separation from fission activity) were achieved in the very beginning and continued to improve with time.

CHEMICAL PROPERTIES AND ELECTRONIC STRUCTURE

The successful operation of the reactor and plutonium extraction plant at Oak Ridge, Tennessee led to the availability of first milligram, and then gram, amounts of plutonium early in 1944. The availability of milligram amounts of

plutonium led to the immediate discovery of the III oxidation state. The early tracer work at the University of California in 1941 had established the existence of a lower oxidation state (IV and/or III state) and a higher state (VI and/or higher state); and the ultramicrochemical work late in 1942 and in 1943, as mentioned above, had defined the existence of the IV and VI states. The III oxidation state was discovered early in 1944 by Connick, McVey and Sheline (1949), who actually worked with about 0.25 milligram of cyclotron-produced plutonium, at the University of California, Berkeley, and, essentially simultaneously, by Hindman and co-workers (1949) at the Metallurgical Laboratory and Mastick and Wahl (1944) at the Los Alamos Laboratory; the latter two groups utilized the milligram amounts of plutonium made available at that time through the operation of the reactor and chemical separation plant at the Clinton Laboratories in Tennessee. The existence of the V oxidation state was established in the summer of 1944, through the use of plutonium obtained from the Clinton Laboratories, by Connick, Kasha, McVey and Sheline (1949), at the University of California, Berkeley.

In July of 1944, based on the chemical evidence available up to that time, I made the suggestion that plutonium might be the fifth of a 14-member "actinide" series of transition elements in which the 5f electron shell is being filled. This suggestion appeared in Metallurgical Project Report CK-1968, pp. 55-57, (July 17, 1944), in a section entitled "Electronic Structure of the Heaviest Elements":

Plutonium is the eighth element in the seventh period of the periodic table. The correlation of its chemical properties with its atomic structure can best be accomplished by considering it together with a number of the other elements in the seventh period (elements 89 to 94) in a discussion involving the chemical and physical properties of these elements.

It seems very probable that some kind of a transition group should begin in the neighborhood of these elements. The elements 90 to 94 lie in corresponding positions just below the sixth-period transition elements hafnium to osmium (atomic numbers 72 to 76), in which the 5d shell is being filled. The transition elements hafnium to osmium are very similar in their chemical properties to the corresponding 4d transition elements of the fifth period (zirconium to ruthenium, atomic numbers 40 to 44). Although the first members ($_{90}$Th, $_{91}$Pa) of the group 90 to 94 show a great deal of resemblance in chemical properties to the first members ($_{72}$Hf, $_{73}$Ta) in the 5d transition series and to the first members ($_{40}$Zr, $_{41}$Cb) in the 4d transition series, the later members ($_{93}$Np, $_{94}$Pu) show practically no resemblance to $_{75}$Re and $_{76}$Os or to element 43 and $_{44}$Ru. Neptunium and plutonium are much more electropositive in character than the noble elements rhenium, element 43, osmium, and ruthenium. There is no evidence for a volatile plutonium tetroxide in contrast with the volatile osmium and ruthenium tetroxides, and there is no evidence for an oxidation number of VIII in plutonium. Thus it seems certain that the transition in the elements 89 to 94 does not involve the simple filling in of the 6d shell.

On the other hand, the chemical properties of neptunium and plutonium are very similar to those of uranium and thorium and are such as to suggest that the 5f shell is being filled and that we are dealing with another rare-earth series similar to the well-known lanthanide series, $_{58}$Ce-$_{71}$Lu, in which the 4f shell becomes filled. Many people had suggested, on the basis of considerations of electronic structure, that a rare-earth-like series should begin in this region. There has been a large degree of uncertainty in these predictions with regard to the starting point of this series. The two principal choices have been between a thoride and a uranide series. From the standpoint of the chemical properties of $_{90}$Th, $_{91}$Pa, and $_{92}$U considered alone, the evidence for such a

series was not strong. However, with the discovery of neptunium and plutonium and the observation of the marked similarity of these elements to uranium and thorium in chemical properties, the chemical evidence for a rare-earth-like series has become very strong.

The persistence of the IV oxidation state through the elements thorium, uranium, neptunium, and plutonium is certainly good evidence that electrons are going into the 5f shell. The observation by Zachariasen of the isomorphism of the compounds ThO_2, UO_2, NpO_2, and PuO_2 and his observation of the regular decrease in radius of the metallic ion in these oxides in the anticipated manner are also very good evidence that the electrons are going into the 5f shell. A number of other crystallographic observations by Zachariasen lend support of this view. There are other points of evidence, for example (1) magnetic susceptibility measurements on uranium and plutonium, (2) the sharpness of the optical absorption in aqueous solutions of uranium and plutonium, and (3) evidence for organic complexes of U^{+4} and Pu^{+4} in which these elements have a coordination number of 8 (indicating that the 6d, 7s, and 7p orbitals are available), which facts also give strong support to this conclusion. It seems very probable from these lines of evidence that uranium and plutonium (and neptunium) have electrons in the 5f shell; however, it is not possible to deduce whether or not uranium is the first element in the series for which this is the case. It would be consistent with this evidence for thorium and protactinium to have no electrons in the 5f shell and for uranium to have two electrons in this shell.

An attractive hypothesis is that this rare-earth-like series begins with actinium in the same sense that the lanthanide series begins with lanthanum. On this basis it may be termed the "actinide series," and the first 5f electron may appear in thorium. Thus, the ground state of thorium may have the structure $5f^1 6d 7s^2$ beyond the radon core. With an actinide series, uranium may have the electron configuration $5f^3 6d 7s^2$, neptunium the configuration $5f^4 6d 7s^2$ and plutonium the configuration $5f^5 6d 7s^2$. It is very interesting to note that Kiess, Humphreys, and Laun give a preliminary description of the analysis of the spectrum of neutral uranium atoms and come to the conclusion that the electron configuration of the lowest state of uranium is $5f^3 6d 7s^2$ (with the term symbol $^5L_6$), which supports the above view.

It may be that, as in the lanthanide series, electrons do not tend to occupy the 6d orbital; rather, an additional electron goes into a 5f orbital and gives, for example, the configuration $5f^2 7s^2$ for thorium and the configuration $5f^4 7s^2$ for uranium. There is evidence that thorium emits a complex spectrum corresponding to a rare earth with an electron structure like that of $_{58}Ce$, whose ground state is known to have the configuration $4f^2 6s^2$, and that uranium has a spectrum similar to that of the rare-earth element $_{60}Nd$, whose ground state is known to have the configuration $4f^4 6s^2$.

It may be, of course, that there are no 5f electrons in thorium and protactinium and that the entry into a rare-earth-like series begins at uranium, with three electrons in the 5f shell. It would still seem logical to refer to this as an actinide series.

In an actinide series it may seem rather peculiar at first sight that the persistent oxidation number of IV should be in this region. The IV oxidation state seems to be most prevalent and generally most stable among these elements. However, as referred to above, in the lanthanide series there are usually only two electrons present in the 5d and 6s shells, whereas the persistent oxidation state is certainly III. This generally involves the removal of a 4f electron. There are also a number of cases in the lanthanide series where the

oxidation number IV is found. In the "actinide" series, although the oxidation number IV is perhaps prevalent, the oxidation number III seems also to be found in most of the members of the series. Zachariasen has recently reported crystallographic evidence for tripositive thorium compounds (ThF_3 and ThOF), although magnetochemical experiments by Selwood have failed to confirm this report.

There is one way in which the actinide series definitely differs from the lanthanide series. This is in the existence of oxidation states higher than IV [protactinium(V), uranium(VI), neptunium(VI), plutonium(VI)] in the series. It must be concluded that the 5f electrons are not so tightly bound as the 4f electrons. This is certainly reasonable. However, the evidence so far is in favor of a maximum oxidation number of VI in this series, so that the removal of three electrons, or four if there are no electrons in the 6d orbitals, from the 5f orbitals is the maximum that occurs in ordinary chemical reactions.

It is interesting to speculate a little about the chemical properties of the series members which we have not yet had an opportunity to study. The element $_{91}Pa$ is obviously interesting to study from a chemical and crystallographic point of view in order to throw further light on the situation. It seems very likely that this element will have oxidation states of IV and III in addition to the V state, and probably at least the IV state will have a reasonable amount of stability. It seems almost certain, also, that neptunium will have an oxidation state of III, intermediate in stability between U^{+3} and Pu^{+3}. If the picture of the actinide series is correct, the configuration $5f^7 6d^1 7s^2$ may be reached with element 96 (similar to the configuration of $_{64}Gd$); this configuration should be especially stable. The prediction may be made that with element 96 it will be very difficult, if not impossible, to reach any oxidation states above III or IV. In the case of element 95 the configuration $5f^7 7s^2$, similar to $_{63}Eu$, may be possible, and it may be expected that the oxidation state II will exist. Oxidation states higher than IV may also be difficult or impossible to reach in the case of element 95. There already seems to be some evidence for a trend toward greater stability for the lower oxidation states in the members of the series that have been studied so far. Thus, in going from uranium to plutonium, there seems to be a trend toward greater stability of the III oxidation state and greater difficulty in reaching the VI state. If the series is truly a thoride or a uranide series, the most stable lower oxidation states will occur at elements beyond 95 and 96; however, even in this event some tendency may be expected in this direction at elements 95 and 96. It would obviously be of great interest and value in elucidating the nature of this series to study the chemical properties of elements such as 95 and 96.

The production early in 1945 of larger amounts came as a result of operation of the Hanford plant. Continuing investigations of the chemical properties of plutonium in many laboratories throughout the world, as it has become available, has led to the situation where the chemistry of this relative newcomer is as well understood as is that of most of the well-studied elements. Thus, plutonium has the four oxidation states--III, IV, V, and VI--leading to a chemistry which is as complex as that of any other element. In fact, it is unique among the elements in that these four oxidation states can all exist simultaneously in aqueous solution at appreciable concentration. As a metal, too, its properties are unique. It has six allotropic forms, in the temperature range from room temperature to its melting point (640°C), and some of these have properties not found in any other known metal.

During the intervening years, plutonium has been prepared in ton quantities in nuclear reactors and chemically isolated, using much more efficient procedures.

The nuclear properties of plutonium are also very interesting (Seaborg, 1978). All of the isotopes from ^{232}Pu to ^{246}Pu are known. Research in laboratories throughout the world has given us much information about their radioactive decay, and fission properties, and their methods of production by nuclear transmutation reactions.

PRESENCE IN NATURE

As early as 1942, only a short time after the first synthesis of Pu^{238} and Pu^{239}, Seaborg and Perlman (1948) found plutonium (Pu^{239}) in extremely small trace concentrations in the uranium-bearing mineral Canadian pitchblende. Later in 1942, C. S. Garner, N. A. Bonner, and Seaborg reported the similar presence of Pu^{239} in the uranium ore carnotite (Garner and co-workers, 1948). The half-life of Pu^{239} of less than 25,000 years precludes the presence of this isotope of plutonium as a primordial element. Its existence is predicated on the capture of neutrons by U^{238}, resulting in U^{239} that leads by beta particle emission through Np^{239} to the Pu^{239}. The neutrons originate from either the spontaneous fission of U^{238}, (α,n) reactions on elements of low atomic number, or fission or spallation reactions induced by cosmic rays. Some neutron multiplication undoubtedly arises from neutron-induced fission of U^{235} as well.

In 1951, Levine and Seaborg (1951) published a paper describing the observation of trace quantities of plutonium in a number of uranium-bearing ores and the variation in its concentration. In the same year, Peppard and co-workers (1951), isolated microgram quantities of Pu^{239} from uranium process waste solutions and established its concentration as approximately one part in 10^{11} parts of the Belgian Congo pitchblende concentrate. A year later Peppard and co-workers (1952) established the presence of about one part of Np^{237} (half-life 2×10^6 years) in 10^{12} parts of Belgian Congo pitchblende, produced by the reaction of fast neutrons with U^{238}.

Longer-lived ^{244}Pu (half-life 8.3×10^7 years), possibly from a primordial source, has been found in very small concentration (1 part in 10^{18}) in a rare earth mineral (bastnasite) by Hoffman and co-workers (1971). This work provides the only established example of a transuranium element in nature present as a part of our initial inheritance of elements in our solar system.

In this brief commemorative account of *The Plutonium Story* it has not been possible to do justice to the forty years of investigation of this interesting element. My emphasis has been placed on its early history and especially those aspects with which I am most familiar.

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