Occasionally kinetic points in the runs with methanol, phenol or both were titrated for bromide as well as for hydrogen ion. Agreement within the limits of experimental error was always obtained, demonstrating that the reaction was entirely a solvolysis by the hydroxylic component and not at all the formation of a quaternary ammonium salt.

Pyridine hydrobromide or hydrochloride precipitates out in the usual procedure as the reaction progresses. In the analysis of one of the tubes in run 37 between 0.106 *M* trityl chloride, 0.112 *M* phenol and 0.108 *M* pyridine, the benzene layer, after extraction with alcohol and water and separation of the water layers for titration with sodium hydroxide, was further extracted with dilute sodium hydroxide, then water, and dried over sodium sulfate. The benzene was evaporated and the flask evacuated at 2 mm. for several hours. There was obtained 0.148 g. (83%) of white crystalline *trityl phenyl ether*, m. p. 93–98°. The recorded m. p. is 103°, as contrasted to 282° for the *p*-tritylphenol. The same treatment applied to a tube from run 40 between 0.106 *M* trityl chloride 0.109 *M* methanol and 0.108 *M* pyridine yielded 0.101 g. (70%) of white crystalline *trityl methyl ether*, m. p. 77–79°. The recorded m. p. is 82°.

Enhancement of Acidity of Hydrogen Chloride in Ether by Methanol, Phenol and a Mixture.—The solutions were prepared by adding a total of 2 cc. of various dry benzene solutions to each of a number of 10-cc. samples of a dry ether solution containing 0.001 *M* butter yellow plus enough dry hydrogen chloride gas to turn the indicator from yellow to a very pale yellow orange. The color was measured with a Cenco "Photelometer" (photoelectric colorimeter) using a Corning No. 401 primary green filter, which gave the largest difference between red and yellow solutions of a number of filters tested. The results are presented in Table VI.

TABLE VI

No.	*M* CH_3OH	*M* C_6H_5OH	Color	% transmission
1	...	...	Yellow-orange	100.0
2	0.036	...	Yellow-orange	89
3	.073	...	Yellow-orange	82
4	...	0.037	Orange	57
5	.036	.037	Orange	53.5
6	...	.075	Red	34.5

Acknowledgment.—The author wishes to thank Professors Linus Pauling, Paul D. Bartlett, Saul Winstein and Alwyn G. Evans for criticisms and suggestions which made a major contribution to this work.

Summary

Methanol reacts rapidly with triphenylmethyl chloride or bromide in benzene solution containing excess pyridine at 25° to give the methyl ether. When phenol is used instead of methanol, the phenyl ether is obtained at a slower rate. However, when both are present, the methyl ether is formed at a rate which is seven times as fast as the *sum* of the rates of reaction with methanol or phenol separately. Evidence is obtained to show that this cannot be a salt effect nor due to a complex between methanol and phenol. The kinetics are third order. In the mixed case this means that the rate is proportional to the product of concentrations of methanol, phenol and halide, although the phenol is not consumed in the rapid phase of the reaction.

This indicates that one molecule of alcohol or phenol hydrogen bonds with the halogen atom, weakening its bond to carbon, while another molecule simultaneously solvates the carbon which is becoming a carbonium ion. Phenol solvates halogen better than carbon; the converse is true for methanol. Therefore the concerted, termolecular attack proceeds at a high rate when both phenol and methanol are present and each can play the part to which it is best adapted.

The relative reactivity of a number of types of compounds toward triphenylmethyl bromide in benzene solution has been measured.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

The Chemical Properties of Elements 94 and 93

BY GLENN T. SEABORG AND ARTHUR C. WAHL[1a,b]

This report describes the chemical experiments which we have performed on elements 94 and 93 and the chemical properties which we have deduced from these experiments.

Although these chemical experiments have been under way for 94 since December, 1940, when element 94 was discovered,[2] and for 93 since somewhat earlier than this, the investigation has not been a very systematic one. In the case of element 93, we have repeated most of the experiments reported by McMillan and Abelson[3] in their original publication and have confirmed their results. It has been of paramount importance to develop as quickly as possible methods of isolating in very thin precipitates elements 94 and 93 from large amounts of uranium in order to study the properties of 94^{239},[4] and, therefore, the experiments have been of a very practical and explora-

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[1a] Now at Department of Chemistry, Washington University, St. Louis, Missouri.

[1b] This article was mailed as a secret report from Berkeley, California, to the "Uranium Committee" in Washington, D. C., on March 21, 1942. The experimental work was done throughout all of 1941 and the early part of 1942. Part of the original material is omitted in order to shorten the article to Journal length; otherwise it is unchanged from its original report form except for slight editing to make it conform to JOURNAL standards.

[2] G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl, *Phys. Rev.*, **69**, 366 (1946) (submitted January 28, 1941); G. T. Seaborg, A. C. Wahl and J. W. Kennedy, *ibid.*, **69**, 367 (1946) (submitted March 7, 1941).

[3] E. M. McMillan and P. H. Abelson, *Phys. Rev.*, **57**, 1185 (1940).

[4] J. W. Kennedy, G. T. Seaborg, E. Segrè and A. C. Wahl, *Phys. Rev.*, **70**, 555 (1946) (submitted May 29, 1941).

tory nature. It is only recently that we have begun a systematic investigation of the chemical properties; the description of these experiments is included also.

As the tracer for element 94 we have used the alpha-emitting, 50-year 94, whose production and properties are described elsewhere,[2] and for which the best isotopic assignment seems to be 94^{235} or 94^{238}.[5] As the tracer for element 93, we have used the beta-emitting 2.3-day 93^{239}.

The alpha-particles from 94^{238}, which have a range in air of about 4.1 cm., are detected with an ionization chamber connected to a linear amplifier and recording system. Only thin samples are prepared ($<$ 1 mg. carrier material per sq. cm.). The weak samples are counted by placing them on one electrode of the ionization chamber, the "inside" chamber, for which the counting efficiency, as determined with a weighed sample of uranium, is about 45%. The strong samples are counted with poor geometry sometimes with screens interposed, depending upon the strength of the samples, by placing them near an ionization chamber with a screen window.

Although the beta-particles from 93^{239} have an upper energy limit of 0.78 Mev. (aluminum absorption end-point 260 mg.), the major portion of the radiation being rather soft,[6] with a half thickness of 9 mg. of aluminum and therefore demanding thin samples, a correction for self-absorption of the beta-particles is made. Correction for the back-scattering of the beta-particles from the backing material upon which the samples are mounted is always made in the quantitative experiments. The beta radiation is detected with (1) a Geiger–Müller counter connected to an amplifier, scaling and recording system, (2) an ionization chamber connected to an FP-54 electrometer tube or (3) a Lauritsen electroscope, depending on the strength of the sample and the type of experiment.

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 ekarhenium and ekaosmium seem inappropriate in view of the marked dissimilarity of the chemical properties of elements 93 and 94 from those of rhenium and osmium.)

Experimental

General Remarks on Radiochemistry.—All of the experiments which we have performed have, of course, used exceedingly small amounts, in the macroscopic sense, of radioactive 94^{238} and 93^{239} as tracers, and great care must be exercised in deducing from these experiments the true chemical properties of macroscopic quantities of 94 and 93. Our experiments have employed amounts of 94^{238} and 93^{239} varying from about 10^{-7} microgram to about 1 microgram and concentrations of about 10^{-15} to 10^{-6} molal. The relationship of the chemical behavior of such small amounts to the behavior of macroscopic amounts of materials has been studied, using the natural radioactive isotopes as indicators, in the classical work of Fajans and Paneth and Hahn. The work of the numerous investigators in artificial radioactivity, which involves a great number of other elements, seems to lend confirmation to the rules of Hahn and Paneth and Fajans.

Precipitation reactions are among the most important reactions in studying the chemistry of an element by the use of microscopic amounts of a radioactive isotope of the element. It is well known that compounds of radioelements, though present in such dilution that their solubility is not exceeded, may be "carried down," even quantitatively, by a macroscopic precipitate of a non-isotopic element. Rules for this phenomenon have been formulated by Fajans and Paneth and Hahn. For example, Hahn[7] summarized Fajans' and Paneth's rule in a joint rule which he states as follows: "A radioelement, as cation, is more strongly adsorbed by a separating or a preformed precipitate, the less soluble is the compound it forms with the anion of the precipitate." From a study of these rules and the detailed discussion Hahn[7] gives them, it seems reasonably safe to assume that if a radioelement as cation is "carried down" by a precipitate formed in the presence of excess anion the compound between the radioelement and the anion is relatively insoluble, and if the radioelement is not "carried down" it is assumed that the compound is relatively soluble. That this is true has been confirmed in many instances since the discovery of artificial radioactivity in that many "pure" radioelements, that is, elements free from their stable isotopes, have been prepared and subjected to precipitation reactions of this sort. We believe that our conclusions as to the solubility and insolubility of the compounds of 94 and 93 are valid for macroscopic amounts, but it must be emphasized that in all the work there exists the possibility of drawing incorrect conclusions from such precipitation reactions.

It is remarkable, and it should be emphasized, that it has been found in many cases, when the radioelement is not "carried down" by the precipitate upon the addition of the precipitating

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(5) Note added at time of publication: This alpha radioactivity was later shown to be due to the isotope 94^{238} with a slight admixture of alpha radioactivity due to the isotope 94^{236}; the isotopic assignment, of course, makes no difference from the standpoint of this paper. In order to avoid confusion this paper has been edited so that it always refers to this radioactivity as due to the isotope 94^{238}.

(6) Our work has shown that there are roughly as many conversion electrons as there are disintegration beta-particles in the 93^{239} radiation.

(7) O. Hahn, "Applied Radiochemistry," Cornell University Press, Ithaca, N. Y., 1936.

agent, it is not necessary that there be present some carrier material in the solution to "stabilize" the radioelement in order to prevent its precipitation. Thus, we have found in the case of elements 94 and 93 that we can make precipitations from solutions containing these elements leaving them behind in the solution with no carrier material in the solution with them.

It is well established that in the distribution between solvents, in the cases where there is no chemical combination with the solvents, these extremely small amounts (concentrations as low as 10^{-15} M) obey the same distribution coefficient as do macroscopic amounts of material; therefore it is quite possible to make deductions as to true thermodynamic distribution coefficients from experiments with solutions of pure radioelements. Similarly, it has been found that the properties of volatility can be correctly deduced from experiments performed with such microscopic amounts of radioelements. In addition, it has been found that a great deal of information about the oxidation and reduction properties of an element, and of the ions of this element, can be deduced from experiments performed with these small amounts (concentrations as low as 10^{-15} M) of radioelement material, when proper account is taken of the concentration of the ions and of the possibility of slow reactions.

Precipitation Reactions.—Since one of the most common precipitating agents which we use is hydrofluoric acid, it is often necessary to use platinum ware where heat is necessary and waxed glassware for room temperature reactions and precipitations. Coating the glassware with a mixture of paraffin and beeswax has given very satisfactory results. However, it is possible to use ordinary Pyrex glassware, instead of waxed glassware, if, instead of hydrofluoric acid, potassium fluoride is used in solutions of low acidity and the solutions do not stand in the glass for more than an hour or two. We have used waxed glassware and bakelite almost always because we wanted to be absolutely sure that no silica appeared in our very thin samples.

We found it to be very advantageous to use a centrifuge[8] rather than to filter precipitates, and a great number of our precipitation reactions were carried out right in the centrifuge tube in order to avoid loss by transfer. Where hydrofluoric acid is employed, waxed centrifuge tubes or "lusteroid" tubes should be used. In some experiments, particularly in the final precipitation in which the sample is isolated, it has been found convenient to centrifuge onto a platinum or cellophane plate in a clear bakelite centrifuge tube with a removable bottom. Similarly, some electrolysis reactions have been performed with the metallic cathodes in bakelite tubes with removable bottoms.

A number of qualitative precipitation reactions were carried out using various carriers and always having an excess of the anion present. As stated above, the radioactive isotopes used to follow the behavior of elements 94 and 93 were the alpha-emitting 50-year 94^{238} and the beta-emitting 2.3-day 93^{239}.

We have found that, similarly to element 93, element 94 has two oxidation states; in its lower oxidation state 94 forms an insoluble fluoride, but the fluoride of its higher oxidation state is soluble. Peroxydisulfate ion ($S_2O_8^{--}$), in the presence of silver ion (Ag^+) as catalyst, has sufficient oxidizing power to oxidize 94 to its higher oxidation state. This reaction takes place in about fifteen minutes in an acid solution (few normal) at a temperature just below boiling when the concentration of peroxydisulfate ion is of the order of 0.2–1.0 g. and the silver ion of the order of 50 mg. per 100 cc. A number of precipitation experiments on the oxidized and reduced states of 94 and 93 are summarized in Table I, where (i) indicates that the activity was "carried down" with the precipitate and therefore the transuranium compound is considered to be insoluble, (s) that the activity was not "carried" and therefore that the compound is considered to be soluble. The experiments on the oxidized state of 93 took place in an acid solution (few normal) of bromate ion (BrO_3^-), with about 0.5 g. of BrO_3^- per 100 cc.

TABLE I

SOLUBILITY OF 93 AND 94 COMPOUNDS

	93		94	
	Reduced	Oxidized	Reduced	Oxidized
Fluoride	i	s	i	s
Sulfide (0.3 N H^+)	s	...	s	...
Sulfide (10^{-3} N H^+)	s	...	...	...
Iodate	i	s	i	...
Phosphate	s	...	...	...
Peroxyhydrate	...	...	i	...
Chloride	s	...	...	...
Hydroxide (NaOH)	i	i	...	...
Hydroxide (NH_4OH)	i	i	i	...
Hydroxide (NH_4OH and CO_3^{--})	...	s	...	...
Carbonate	i	...	...	...

Elements 94 and 93 are precipitated quantitatively, in their reduced states, with lanthanum or cerous fluoride even from rather strong acid (6 N) solutions. This is in rather sharp contrast to the behavior of thorium, where we have found, using UX_1 as tracer, that the precipitation is not quantitative from solutions in which the acidity is as high as 6 N.

An experiment was performed in which 0.5 mg. of lanthanum was added last to a hydrofluoric acid solution containing 94 and 93 in their reduced states, in order to determine whether 94 and 93 would be carried down into the lanthanum fluoride precipitate under these conditions. After the precipitate was digested in the hot solution

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[8] A convenient centrifuge, which handles 15 cc., 50 cc., 100 cc. and 250 cc. centrifuge tubes, is the Size 1 centrifuge of the International Centrifuge Company. This company also sells the "lusteroid," hydrofluoric-acid-proof, centrifuge tubes.

for about 20 min., the lanthanum fluoride precipitate was centrifuged out. It was found that this precipitate contained only about 50% of the 94 and about 90% of the 93. This would indicate that 94 and 93 are not precipitated quantitatively on "preformed" precipitates, and it is quite probable that the amount of 94 and 93 which is "adsorbed" would vary markedly with the conditions under which the precipitation was performed.

Oxidation and Reduction Reactions.—McMillan and Abelson[3] found that element 93 is not reduced to the metal by zinc. We have found the same to be true for element 94. To check the conditions of the experiment (stirring the acid solution over zinc amalgam for two hours at room temperature), very dilute solutions ($\sim 10^{-12}$ *M*) of polonium and 158-day $Cd^{107,109}$ were plated on zinc, proving (1) that if 94 had been plated out its alpha-particles could have been detected and (2) since no 94 was plated out it must be more difficult than cadmium to reduce to the metallic state.

The potential required to oxidize elements 94 and 93 from their "fluoride-insoluble" state to their "fluoride-soluble" state (see Table I) was studied in the following way: (1) 1 *M* sulfuric acid solutions of elements 94 and 93 were treated with various oxidizing agents (and with their reduction products) under varying conditions of time and temperature; (2) lanthanum fluoride, LaF_3, was precipitated from the solutions; and (3) the activity of the precipitate was measured on a Lauritsen electroscope to detect 93^{239} and ionization chamber plus linear amplifier to detect 94^{238}. The activity indicated whether the element had been in its lower, "fluoride-insoluble," state or its higher, "fluoride-soluble," state.

The results of these experiments are summarized in Table II. In this table "oxidized" indicates that less than 5% of the activity was carried with lanthanum fluoride; "not oxidized," that more than 85% was carried; "partially oxidized," that between 5 and 85% was carried.

Table II

Oxidation of 94 and 93 Solutions

0.1 *M* Oxidizing agent in 1 *M* H_2SO_4	Approx. temp., °C.	Approx. time, min.	Effect on	
			93	94
$S_2O_8^{--}$, SO_4^{--} (Ag$^+$ catalyst)	20	10	Oxidized	Partially ox.
$S_2O_8^{--}$, SO_4^{--} (Ag$^+$ catalyst)	80	15	Oxidized	Oxidized
H_5IO_6, IO_3^-	80	60	Oxidized	Oxidized
MnO_4^-, MnO_2	20	10	Oxidized	Not oxid.
MnO_4^-, MnO_2	80	30	Oxidized	Oxidized
BrO_3^-, Br_2	20	10	Oxidized	Not oxid.
BrO_3^-, Br_2	80	20	Oxidized	Not oxid.
Ce^{+4}, Ce^{+3}	80	30	Oxidized	Partially ox.
$Cr_2O_7^{--}$, Cr^{+3}	20	25	Oxidized	Not oxid.
$Cr_2O_7^{--}$, Cr^{+3}	80	11 hr.	Oxidized	Oxidized
Br_3^-, Br^-	20	2 hr.	Not oxid.	Not oxid.
Br_3^-, Br^-	80	15	Not oxid.	Not oxid.
HNO_3 (concd.)	80	15	Not oxid.	Not oxid.

In the few reduction experiments that were tried, it was found that 93 is reduced to the "fluoride-insoluble" oxidation state at room temperature by sulfur dioxide, SO_2, bromide ion, Br^-, manganous ion, Mn^{++}, and partially by thallous chloride, TlCl, while 94 is reduced by sulfur dioxide, partially by bromide ion and not by manganous ion or thallous chloride. The oxidized form of 93 in these experiments was obtained by the use of a small amount of permanganate ion, MnO_4^-, or bromate ion, BrO_3^- (in 1 *M* sulfuric acid). To these oxidized solutions, there was added an excess of the reducing agent and after separating out any manganese dioxide that formed (which did not carry the 94 and 93), lanthanum fluoride was precipitated and the activity measured.

Although there occurs no oxidation of 94 by bromate ion in 20 min. at 80° in the absence of cerium, some rough experiments indicate that partial oxidation of 94 by bromate ion occurs when cerium is present. This would suggest that bromate ion is capable of oxidizing 94 from its lower to its higher oxidation state and that it is a very slow reaction and is catalyzed by the $Ce^{+3} \rightarrow Ce^{+4}$ couple. In the separation of 94 and 93, bromate ion is used under conditions where it oxidizes 93 and not 94, advantage being taken of the apparently slow rate of reaction between 94 and bromate ion; therefore, this separation is carried out in the absence of cerium.

A reaction of the oxidized form of 94 which should be emphasized is the following. If a sulfuric acid solution of the oxidized form of 94 containing peroxydisulfate ion is heated until fumes of sulfur trioxide appear, so as to decompose all of the peroxydisulfate ion, the 94 is reduced to its lower, "fluoride-insoluble," form. Evidently in a solution of this acidity the 94 is reduced by water. This reaction is important in that, when an oxidizing agent is present which can be completely reduced by heating the solution, such as is true in the case of peroxydisulfate ion, the 94 can be reduced by heating the sulfuric acid solution until fumes of sulfur trioxide appear and the addition of a reducing agent is not necessary. Element 93 is likewise reduced from its higher to its lower oxidation state when a sulfuric acid solution of 93 containing peroxydisulfate ion is heated until fumes of sulfur trioxide appear. However, it is not entirely certain how quantitative these reductions are under varying conditions of evaporation and time of heating, and therefore in most of our experiments we add some reducing agent such as sulfur dioxide, even when the oxidizing agent which is present is completely decomposed during the evaporation procedure, in order to ensure the complete reduction of the 94 and 93.

Electrolysis Experiments.—The primary purpose of the experiments on the electrolysis of elements 94 and 93 was to develop a method of preparing very thin adherent layers, containing these elements, suitable for the performance of physical measurements upon them. The aim was not to use electrolysis as a method of isolating these elements free from all of the fission products in this manner, but experiments in the future may show that electrolysis can be helpful in such a separation. Haissinsky[9] has shown that actinium, thorium and uranium can be deposited electrolytically from absolute ethyl alcohol solution of their nitrates. It seems quite certain that it is the oxides of these elements, and not the elements themselves, that are deposited in these experiments. We have found that elements 94 and 93, with 0.2 mg. of lanthanum carrier, can be electrolyzed out of absolute alcohol solution quantitatively under conditions similar to the experiments of Haissinsky in which no acid may be present. This procedure, however, has not yet solved for us the problem of the preparation of very thin adherent layers of material containing 94 or 93 because, (1) in order to transfer 94 or 93 at all quantitatively from the water solution, where it is present just before the final stage of its isolation into a thin layer, it is necessary to use an amount as large as a few milligrams of rare earth carrier material and (2) the rare earths are deposited electrolytically along with the 94 and 93. When 0.2 mg. of rare earth, which is the maximum amount wanted on the final plate, has been used, the transfer to absolute alcohol, which involves an evaporation to dryness in order to eliminate all the water and acid, has not been quantitative due to the difficulty of redissolving all the material in the absolute alcohol. However, as stated above, all of the 94 or 93 that is put into the alcohol is deposited quantitatively in this electrolysis procedure, and the problem of transferring the 94 or 93 from a water to an anhydrous alcohol solution is a separate problem with which we happen to be concerned only because we want to transfer these elements, with practically 100% yield, to extremely thin layers.

Experiments were also undertaken to electrolyze 94 and 93 out of water solution, where the rare earths can be completely removed by making a rare earth fluoride precipitation from an oxidizing solution, and procedures for the electrolytic deposition of 94 and 93 were developed. It has previously been found in work in this laboratory that thorium, protactinium and uranium could be deposited from an acetic acid solution in which the acidity was kept very low by the addition of sodium acetate. We found that elements 94 and 93 could be deposited from such solutions when they were originally present in their oxidized form, but the conditions for quantitative deposition have not yet been perfected. Element 94 was put into its oxidized form by use of periodate ion and element 93 by the use of bromate ion in these experiments. Again it seems quite likely that it is the oxides of these elements and not the elements themselves that are deposited. In these experiments the electrolytically deposited layer is extremely thin, consisting only of a very small amount of what is probably platinum black and which is present also in the blank experiments. In experiments similar to these, elements 94 and 93 are not deposited when they are originally present in such an acetic acid–acetate solution in their reduced form.

Other Experiments.—Since ruthenium and osmium form volatile tetroxides and since element 94 is directly below these elements in the same column of the periodic table, it seemed important to establish whether 94 also forms a volatile tetroxide, even though it was not expected that it should do so in view of the dissimilarity between the chemical properties of 94 and osmium. Experiments were performed with both 94 and 93 to see whether they could be distilled, presumably in the form of their tetroxides, from a nitric acid solution containing peroxydisulfate ion and silver ion, in which these elements probably exist in their highest oxidation states. The delivery tube from the distillation flask was immersed in an alkaline solution in which the distillate of osmium tetroxide, which was used as a carrier material in this experiment, was absorbed. Upon acidification, reduction with sulfur dioxide, and precipitation of rare earth fluoride from the distillate solution, it was found that none of the 94 or 93 had distilled over.

Experiments have been performed to measure the distribution of 94 and 93 in the lower oxidation state as their nitrates between diethyl ether and neutral water. These experiments were performed in the presence of high concentrations of uranyl nitrate. Less than 1% of the 94 and 93 were found to be present in the ether in experiments of this type.

Chemical Properties of 94 and 93

Because of the similarity, in their reduced states, of 94 and 93, in their precipitation reactions, to the trivalent rare earths and actinium and to quadrivalent cerium, thorium and uranium, it is extremely probable that the reduced state of these elements has an oxidation number of +3 or +4, and the formulas NpF_3 and PuF_3 or NpF_4 and PuF_4 for the fluorides. Whether the oxidation number is +3 or +4 cannot be decided on the basis of the experiments which have been performed to date. Comparison with the neighboring elements thorium and uranium suggests +4, but 94 and 93 resemble the +3 rare earths in that they are carried quantitatively with lanthanum fluoride from quite acid solution whereas quadripositive UX_1 is not carried quantitatively with lanthanum fluoride from acid solution.

Although it is again not possible to assign with

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[9] S. Cotelle and H. M. Haissinsky, *Compt. rend.*, **206**, 1644 (1938).

certainty oxidation numbers to the oxidized states of 94 and 93 which exist in our experiments, it seems certain that the oxidation numbers will not exceed +7 and +8 for 93 and 94, respectively, and there may be intermediate oxidation states, such as, for example, +5 and +6 for 93 and +5, +6 and +7 for 94. It seems quite certain that the ions of the oxidized states of these elements will contain oxygen, similar to uranyl ion, UO_2^{++}, and because of their electropositive nature, the formulas may be of the type NpO_3^+ and PuO_3^{++}.

It should be possible, on the basis of our oxidation and reduction experiments, to assign some sort of values for the oxidation potentials of 94 and 93. We will attempt to assign values for these potentials in the system of standard oxidation potentials which is referred to the hydrogen–hydrogen ion couple as zero.[10] There are for each element the two oxidation potentials to be considered: (1) the potential for the oxidation of the element from its metallic to its reduced ionic (+3 or +4) state and (2) the potential for the oxidation of the element from its reduced ionic state (+3 or +4) to its oxidized ionic state (+5, +6, +7 or +8).

If the failure of zinc to reduce 94 and 93 to the metal is actually due to thermodynamic equilibria and not to slow rates, more than 0.75 volt must be needed to reduce the very dilute solutions ($\sim 10^{-12}$ *M*) of 94 or 93 to the metallic state. Assuming, for example, a three-electron change, more than 0.5 volt is required to reduce solutions at unit activities to the metals.

The experiments show quite strikingly that the reduced ionic state of 94 is oxidized very slowly and that the oxidized ionic state of 94 is reduced very slowly, while the corresponding reactions for 93 are quite rapid. Because 94 reacts so slowly with oxidizing and reducing agents, it is impossible from the existing data to assign an accurate potential to the change from the lower to the higher oxidation state of this element. However, since dichromate ion does oxidize 94 and bromide ion at last partially reduces it, some 1.0–1.4 volts must be needed to oxidize 94 from its "fluoride-insoluble" oxidation state to its "fluoride-soluble" state. These are not necessarily the "standard" oxidation potentials for these couples because we purposely neglected concentration effects which would be important if (1) the couple involves ions or molecules containing more than one 93 or 94 atom or (2) if the oxidation–reduction equilibrium is rapid enough so that it may be shifted by the adsorption of the reduced form (Np^{+4} or Pu^{+4}) by the rare earth fluoride. However, these are practical oxidation potentials in that they aid the experimenter in choosing a proper oxidizing agent when working with tracer amounts of these elements. The following couples summarize the oxidation–reduction data:

Couple	Volts
$Ac \longrightarrow Ac^{+3}$	+2.4 (?)
$Th \longrightarrow Th^{+4}$	~+2.0
$U \longrightarrow U^{+4}$	+1.4
$Np \longrightarrow Np^{+4}$	>+0.5
$Pu \longrightarrow Pu^{+4}$	>+0.5
$U^{+4} \longrightarrow UO_2^{++}$	−0.4
$Np^{+4} \longrightarrow NpO_3^{+}$ [11]	−1.35
$Pu^{+4} \longrightarrow PuO_3^{++}$ [11]	−1.0 to −1.4

In this table we have arbitrarily assigned an oxidation number of +4 to the "fluoride-insoluble" states and +7 and +8 to the "fluoride-soluble" states of 93 and 94, merely for the convenience of writing definite formulas.[11] The oxidation potentials for similar oxidations in actinium, thorium and uranium have been included for purposes of comparison.

The soluble and insoluble compounds of 94 and 93 in the reduced (+3 and +4) state are very similar to those of actinium, thorium and +4 uranium. For example, the fluorides and iodates and hydroxides of all five of these elements are insoluble in water and their sulfides are all soluble in acid. Likewise all five of these elements show quite a similarity in that their metals are all of an electropositive nature. On the other hand, there is little, if any, similarity between 94 and 93 and their homologs, osmium and rhenium. This supports McMillan and Abelson's suggestion and Mayer's calculations[12] that a new "rare earth" group may be starting at the upper end of the periodic table, *though from the present data we could just as well consider the group to be starting with actinium or thorium as with uranium.* In addition, it should be noted that uranium and 94 and 93 do differ in the values of their potentials for oxidation from the "fluoride-insoluble" to the "fluoride-soluble" state. It may be that in the chemistry that involves the higher oxidation states there will be marked differences between these three elements.

In the case of the electrolytic deposition of 94 and 93, it is probable that oxides of the formulas PuO_2 and NpO_2 are formed.

Yields

In this section we will discuss the yields of radioactive 94 and 93 which are obtained with the Berkeley 60-inch cyclotron. We have attempted no specific experiments to determine accurate yields, but, since it seems desirable to include in this report some yield data, we will summarize the rough yield data, obtained as incidental information, from our experiments. The isotope of 94 which can be formed most easily with the

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(10) See, for example, W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," Prentice-Hall, New York, N. Y., 1938, or the Table of W. M. Latimer and J. H. Hildebrand in the "Handbook of Chemistry and Physics," The Chemical Rubber Publishing Co., Cleveland, Ohio.

(11) Note added at time of publication: It is now known that the "fluoride-soluble" oxidation states studied here correspond to the formulas NpO_2^{++} and PuO_2^{++}.

(12) M. Goeppert Mayer, *Phys. Rev.*, **60**, 184 (1941).

most intensity is the 50-year 94. This alpha-emitting isotope is the decay product of the beta-emitting 2.0-day 93^{238} which is formed in the deuteron bombardment of uranium. The production of these isotopes is described in another report.[2] The yield of 2.0-day 93^{238} is about 10 microcuries per microampere-hour of 15 Mev. deuterons, and the corresponding yield of 94^{238} is, therefore, about 10^{-3} microcuries per microampere-hour. A 1000-microampere-hour bombardment produces about 1 microcurie of 94^{238}, corresponding to about 1×10^6 counts per min. (on a chamber with 45% counting efficiency), which is a sufficient amount of activity to serve as a tracer in a very large number of chemical experiments. There will be mixed with about 1 microcurie of 94^{238} about 0.02 microcurie of 94^{239} which is also formed during the deuteron bombardment of uranium. This other isotope of 94, namely, 94^{239}, might conceivably be used as a tracer, but the intensity of readily prepared samples is considerably less. In the bombardment with neutrons of a rather large amount, about 2 kg., of uranyl nitrate hexahydrate, placed directly behind the beryllium target of the Berkeley 60-inch cyclotron we have found that the yield of 94^{239} is about 0.02 microcurie per 1000 microampere-hours of deuterons. Thus, it is seen that the best tracer isotope for 94 is the 50-year 94^{238} formed in the deuteron bombardment of uranium.

On the other hand, it is the neutron bombardment of uranyl nitrate rather than the deuteron bombardment of uranium which is the more suitable for the production of radioactive 93 for tracer experiments. The yield of 93^{239} in the neutron bombardment of two kilograms of uranyl nitrate hexahydrate amounts to about 80 microcuries per microampere-hour of deuterons. The yield of 93^{239} in the direct deuteron bombardment of uranium is about 80 microcuries per microampere hour, which is about the same as that obtained in the bombardment of kilogram amounts of uranyl nitrate with neutrons; however, the 93 formed in the deuteron bombardment of uranium, being a complex mixture of some 90% 93^{239} and 10% 93^{238}, may be undesirable for some experiments involving 93 as a tracer because of the growth, during the experiments, of the highly alpha-active 94^{238} from the 2.0-day 93^{238}. In addition, it is more convenient to perform neutron bombardment of uranium; for example, an easily performed bombardment, 100 microampere-hours of beryllium plus 15 Mev. deuteron neutrons on 200 g. of uranyl nitrate hexahydrate, produces of the order of a millicurie of 93^{239}, which is ample for a set of tracer experiments. For these reasons we believe that the best tracer isotope for 93 is the 2.3-day 93^{239} formed by the neutron bombardment of uranyl nitrate hexahydrate.

S. G. English and J. W. Gofman have given us valuable help in some of the experiments described in this paper.

Summary[13]

The chemical properties of elements 94 and 93 have been studied by means of the tracer technique using the radioactive isotopes 94^{238} and 93^{239}. Plutonium is suggested as the name for element 94 following the convention used in the naming of neptunium (element 93) and uranium. The chemical symbols Pu and Np are suggested for plutonium and neptunium. In the reduced states the precipitation reactions of neptunium and plutonium are similar to those of the tripositive rare earths and actinium, and of the quadripositive cerium, thorium and uranium. Neptunium and plutonium resemble actinium, thorium and +4 uranium in that their fluorides, iodates and hydroxides are insoluble in water; their sulfides are soluble in acid; and their metals are electropositive. Neptunium and plutonium exhibit a higher oxidation state with properties similar to those of uranium of oxidation state +6.

Probably the reduced state of both elements has an oxidation number of +3 or +4 and the formulas of the fluorides are NpF_3 and PuF_3 or NpF_4 and PuF_4. For both elements the standard oxidation–reduction potential from the metal to the reduced ionic state is greater than +0.5 v. For the reduced to the oxidized ionic state the standard potential for neptunium is about −1.35 v. and for plutonium, −1.0 to −1.4 v. Probably PuO_2 and NpO_2 are the oxides formed by electrodeposition.

There is practically no resemblance in chemical properties between neptunium and plutonium and rhenium and osmium. The chemical properties of neptunium and plutonium indicate that a "rare earth" type group of elements is starting at the upper end of the periodic table, and from the present data we can just as well consider the group to be starting with actinium or thorium, rather than with uranium which has been previously suggested as the starting point.

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[13] Summary was written at time of publication, since the original report contained no summary.