CHEMISTRY OF THE TRANSURANIC ELEMENTS

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The elements which have now been discovered beyond uranium [atomic number (Z) = 92] are neptunium (Z = 93), plutonium (Z = 94), americium (Z = 95), and curium (Z = 96). Thus the last three periods of the Periodic Table start as follows :

Number of places beyond inert gas	0	1	2	3	4	5	6	7	8	9	10
2nd long period . . .	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
3rd long period . . .	Xe	Cs	Ba	La	Ce	Pr	Nd	61	Sm	Eu	Gd
Last period	Rn	Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm

Written in this way the Periodic Table shows the contrast between the second and third long periods caused by the presence of the rare earths. The reason for this difference, as is well known, is that in the rare-earth series the fourth quantum shell is filled up from 18 at lanthanum to 32 at lutecium, where it is complete, whilst in the second long period the third quantum shell cannot expand beyond 18. The availability of the $4f$ orbits gives the rare earths their characteristic properties. In the last period a similar expansion of the fifth quantum group could take place ; and the evidence is very strong that in fact $5f$ electrons occur in uranium and the succeeding elements. If no $5f$ electrons were present we should expect the elements neptunium, plutonium, americium, and curium to be analogous to rhenium and the platinum metals. What is perhaps not so clear is the behaviour we should expect for elements containing $5f$ electrons. In the first place it by no means follows that, because the first $4f$ electron appears in the fourth element beyond the inert gas (in cerium), the first $5f$ electron will appear in thorium. However, we might reasonably expect that when $5f$ orbits were occupied the properties of the elements would deviate from the sequence found in the first and second long periods ; and, because an electron in a $5f$ orbit might to some extent be removed from the region of chemical attack, as $4f$ electrons are, that the deviations from first- and second-long-period behaviour would be in the direction of a series of elements of similar chemical properties. These remarks will be amplified later in the comments on the observed chemical behaviour of the transuranic elements. Since the rare-earth series starts in effect at lanthanum, the chemistry of the elements from actinium onwards will have to be taken into account, though this will be done very briefly for the elements before uranium. The resemblances of the chemistry of neptunium and plutonium to that of uranium are so extensive that a rather more extended account of uranium will have to be given.

Solution Chemistry

All the elements from actinium to curium are base metals, and with the possible exception of protoactinium form compounds which give simple hydrated ions in aqueous solution. In this it is at once seen that they resemble the rare earths whose most characteristic compounds are their tervalent salts, which in solution give hydrated M^{3+} ions ; the platinum metals, and also tungsten and rhenium, on the other hand, give little indication of simple cations in solution. The simple ions of the heavy elements are :

—	—	—	—	—	—	Am^{2+}	—
Ac^{3+}	—	—	U^{3+}	Np^{3+}	Pu^{3+}	Am^{3+}	Cm^{3+}
—	Th^{4+}	—	U^{4+}	Np^{4+}	Pu^{4+}	—	—

In addition the characteristic oxy-ions are known :

$$UO_2^{2+} \qquad NpO_2^{2+} \qquad PuO_2^{2+}$$
$$UO_2^{+} \qquad NpO_2^{+} \qquad PuO_2^{+}$$

and there are compounds such as $UOCl_2$ and $NpOCl_2$ which possibly give quadrivalent oxy-ions in solution. Some of these ions are somewhat unstable, but where the stability is sufficient a series of salts can be prepared by the ordinary methods, and the ions of any element can be converted into each other by suitable oxidising or reducing agents. In considering ·the stability of these ions in aqueous solution, we must take into consideration the following types of reaction which might remove the ion in question : (i) oxidation or reduction by water or the associated anion, (ii) disproportionation to a higher and lower valency state, (iii) hydrolysis, and (iv) formation of a covalent complex with the anion. (i) and (ii) can conveniently be considered together since they are both dependent on the oxidation–reduction potentials.

All the compounds of actinium are tervalent,[1] and there can be little doubt that the hydrated Ac^{3+} ion, with a rare-gas structure, is present in solution. Thorium gives the well-known series of quadrivalent salts, such as thorium(IV) nitrate, $Th(NO_3)_4$. Though tervalent and bivalent thorium compounds, such as thorium tri-iodide, can be obtained by dry methods, these are decomposed by water to give quadrivalent thorium.[2] The equilibrium,

$$Th^{3+}(aq.) + H_2O \ \rightleftharpoons \ Th^{4+}(aq.) + OH^- + \tfrac{1}{2}H_2$$
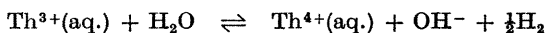
is evidently very much in favour of the right-hand side. In other words the oxidation–reduction potential of the Th(III/IV) couple is very positive. In this thorium resembles hafnium as opposed to cerium. Little is known of protoactinium ions in solution ; the few protoactinium compounds that have been characterised are quinquevalent, but it is very improbable that protoactinium forms a simple quinquevalent ion in solution. Recently indications of a lower valency state of protoactinium, produced by reduction

[1] S. Fried and F. Hagemann, AECD 1891 (References to MDDC or AECD numbers here and later are to American atomic energy declassified reports).

[2] J. S. Anderson and R. W. M. D'Eye, Chemical Society Symposium, Oxford, April 1949 ; J., 1949. s244.

with zinc amalgam, have been obtained. In this state protoactinium gives an insoluble fluoride, which is taken as an indication of ter- or quadrivalent protoactinium.[3] The formation of this compound might also explain the cathodic deposition of protoactinium when electrolysed in solutions containing fluoride.[4]

Uranium forms two well-known series of salts, the uranyl salts of UO_2^{2+}, and the uranous salts of U^{4+}. Moderately strong reducing agents are needed to reduce uranyl to uranous compounds, e.g., amalgamated zinc ; and conversely most oxidising agents convert uranous into uranyl salts. The evidence that uranyl solutions do in fact contain UO_2^{2+}, presumably hydrated, comes, first, from the formulæ of the salts which always contain a bivalent UO_2 group, e.g., $UO_2SO_4,3H_2O$, $NaUO_2(OAc)_3$, and, secondly, from the vibrational fine structure of the spectrum of the solutions,[5] which indicates a cation containing more than one atom that is unchanged by considerable variations of pH, and thirdly from the electrochemistry of the solutions, which is described below. The Raman spectrum [6] can be explained in terms of a bent ion $(O-U-O)^{++}$. If the uranyl solution is reduced electrolytically, the first stage of the reduction involves a single electron transfer, and occurs at a half-wave potential that is little affected by acidity [7, 8, 9, 10] so that evidently this process is $UO_2^{2+} + e^- \rightarrow UO_2^+$. This is confirmed by the diffusion constants of these ions, calculated from the diffusion current at a dropping mercury electrode by the Ilkovic equation, $i_d = 605nD^{\frac{1}{2}}m^{\frac{2}{3}}t^{\frac{1}{6}}$, where i_d is the diffusion current per g.-mol., n is the number of charges transferred in the electrode process, D is the diffusion constant, m is the mercury flow rate, and t the time of formation of the mercury drops. If n is assumed to be 1, the value of D becomes 0.65×10^{-5} cm.^{2}/sec., whilst the value of D obtained from the conductance of UO_2Cl_2 solutions is 0.5×10^{-5} cm.^{2}/sec. The UO_2^+ ion readily disproportionates to sexi- and quadri-valent uranium. The rate is proportional to the square of the UO_2^+ concentration and to the H^+ concentration. The rate constant is 130 (moles/l.)$^{-1}$.sec.$^{-1}$, when the H^+ activity is unity, so that disproportionation is rapid at UO_2^+ concentrations above about $M/1000$, though the stability increases in less acid solutions. H. G. Heal [7] calculates that at equilibrium in a M-solution of UO_2^{2+} and of U^{4+}, N. with respect to H^+, the concentration of UO_2^+ would be only 10^{-6}.

The polarographic reduction of UO_2^{2+} gives a second wave which is a two-stage reduction, uranium(V) to uranium(III), which shows signs of a kink at half its height. Before the kink, which presumably corresponds to reduction to uranium(IV) the wave is irregular, whilst its second half is

[3] M. Haissinsky and G. Bouissières, *Compt. rend.*, 1947, **226**, 573.
[4] G. Bouissières, *J. Phys. Radium*, 1941, [viii], **2**, 72.
[5] R. E. Connick, M. Kasha, W. H. McVey, and G. E. Sheline, MDDC 892.
[6] H. W. Crandall, MDDC 1294.
[7] *Nature*, 1946, **157**, 225 ; *Trans. Faraday Soc.*, 1949, **45**, 1.
[8] I. M. Kolthoff and W. E. Harris, *J. Amer. Chem. Soc.*, 1945, **67**, 1484.
[9] D. M. H. Kern and E. F. Orlemann, MDDC 1703.
[10] K. A. Kraus and F. Nelson, AECD 2394.

logarithmic. Hence the reduction uranium(V) to uranium(IV) is not reversible at a dropping mercury electrode, whilst the uranium(IV) to uranium(III) stage is. This is consistent with the view that we have a change of ion type in passing from uranium(V) to uranium(IV), but not from uranium(IV) to uranium(III), *i.e.*,

$$UO_2^+ + 4H^+ + e^- \longrightarrow U^{4+} + 2H_2O$$
$$U^{4+} + e^- \longrightarrow U^{3+}$$
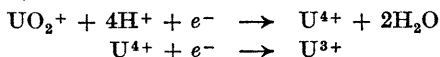
This change is confirmed by the formulæ of the quadrivalent salts, which are not those of an oxy-ion, and by the fact that the interchange of uranium between uranium(IV) and uranium(VI) compounds (*e.g.*, UCl_4 and UO_2Cl_2) occurs at a measurable rate.[11] Further the U(VI/IV) couple is not reversible at a platinum electrode, and so far as it can be observed appears to be strongly dependent on the acid concentration. The U(IV/III) couple is reversible and not acid dependent [7, 10, 12] at a mercury electrode. (A platinum electrode, however, takes up the potential of a hydrogen electrode.) Both the UO_2^+ and U^{3+} ions are very easily oxidised, for instance by air at room temperature ; UO_2^+ can be titrated with ferric salts.

Neptunium almost certainly gives the same series of ions as uranium, namely NpO_2^{2+}, NpO_2^+, Np^{4+}, and Np^{3+} (all hydrated), but their relative stabilities are altered.[13, 14] In particular quinquevalent neptunium is stable in aqueous solution. Sexivalent neptunium requires more vigorous oxidation to prepare it than is necessary for sexivalent uranium, but less than for sexivalent plutonium. Cold bromate solutions, for instance, oxidise neptunium(IV) solutions to neptunium(VI), the reaction passing through neptunium(V), and it is believed that it is the first stage that is the rate controlling step ; but the kinetics of the reaction are not simple. Ceric or argentic solutions will also oxidise it to neptunium(VI), as will potassium permanganate. Neptunium(VI) is reduced by stannous chloride, rapidly to neptunium(V), and then more slowly to neptunium(IV). The same is true of reduction by hydrazine, hydroxylamine, or sulphur dioxide. Ferrous iron also reduces neptunium(VI) or neptunium(V) to neptunium(IV) at a rate proportional to the neptunium(V) concentration and to rather more than the first power of the hydrogen-ion concentration, suggesting that the slow stage is :

$$NpO_2^+ + Fe^{2+} + H_3O^+ \longrightarrow Fe^{3+} + H_2O + NpO_2H^+$$
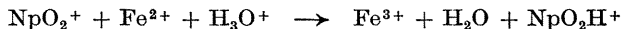
followed by a faster conversion into Np^{4+}. Hydrogen peroxide will reduce neptunium(VI) to neptunium(V), and sodium nitrite also effects reduction only as far as neptunium(V). Chlorine oxidises neptunium(IV) to neptunium(V), whilst chloride ion will slowly reduce neptunium(VI) to neptunium(V). Strong reduction (*e.g.*, electrolytic) is required to produce neptunium(III) solutions and they are oxidised by air.

That sexivalent neptunium solutions do indeed contain NpO_2^{2+} ions is shown by the isolation of $NaNpO_2(OAc)_3$, isomorphous with the corre-

[11] E. Rona, AECD 1909.   [12] B. J. Fontana, MDDC 1453.
[13] L. B. Magnusson, J. C. Hindman, and T. J. La Chapelle, MDDC 1266, 1267, 1381 ; *J. Amer. Chem. Soc.*, 1949, **71**, 687.
[14] S. Fried and N. R. Davidson, MDDC 1332.

sponding uranium compound, and by the electrochemistry of the neptunium ions. Neptunium(VI) solutions on reduction with one equivalent of a reducing agent give solutions, that are quite stable, of a neptunium ion with a characteristic absorption spectrum. This is presumably the NpO_2^+ ion ; this conclusion is supported by the fact that the Np(VI/V) couple is reversible, and is only slightly dependent on the hydrogen-ion concentration (this apparent slight dependence may in any case be due to liquid-junction potentials). The absorption spectrum of the NpO_2^+ ion is very similar to that of the iso-electronic PuO_2^{2+} ion. The Np(V/IV) couple on the other hand is not reversible at a platinum electrode, and it has only been measured indirectly by means of the equilibrium,

$$NpO_2^+ + Fe^{2+} + 4H^+ \rightleftharpoons Np^{4+} + 2H_2O + Fe^{3+}$$
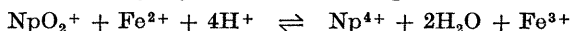
As with uranium, the irreversibility of this couple is attributed to the slowness of removal of the covalently-bound oxygen atoms in the quinquevalent ion. The Np(IV/III) couple is reversible and acid independent, so that the ions in these valency states are probably hydrated Np^{4+} and Np^{3+}. The disproportionation of quinquevalent neptunium, analogous to the rapid disproportionation of UO_2^+ does occur ; but in M-sulphuric acid the rate constant k (from $d[NpO_2^+]/dt = k[NpO_2^+]^2$) $= 5 \cdot 3 \times 10^{-2}$ (moles/l.)$^{-1}$.min.$^{-1}$ at 25°. For the reverse reaction the rate constant is $2 \cdot 15$ (moles/l.)$^{-1}$.min.$^{-1}$. Hence in M-sulphuric acid the equilibrium constant of the reaction

$$2NpO_2^+ + 4H^+ \rightleftharpoons NpO_2^{2+} + Np^{4+} + 2H_2O$$

is $K = [NpO_2^+]^2/([NpO_2^{2+}][Np^{4+}]) = 40$. It is also found from measurements of the " reproportionation " rate at two temperatures, and from a study of the kinetics of oxidation of neptunium(IV) by bromate, that the activation energy of the reaction, $Np(IV) + Np(VI) \rightarrow 2Np(V)$, is 27 kcals./g.-mol.

Plutonium in aqueous solution also gives a similar series of ions, PuO_2^{2+}, PuO_2^+, Pu^{4+}, and Pu^{3+}. The tervalent ion is, however, much more stable than with uranium or neptunium ; PuO_2^+ is intermediate in stability between UO_2^+ and NpO_2^+. Plutonium(IV) is probably the most stable valency state of plutonium ; to obtain plutonium(VI) it is necessary to use hot bromate [15] or permanganate [16] solution (though these will oxidise plutonium(IV) slowly in the cold), but ceric nitrate, argentic ions, hot perchloric acid,[17] potassium dichromate,[18] nitric acid [19] at moderate concentrations, or in fact any vigorous oxidising agent can be used. Conversely, plutonium(VI) is reduced by a variety of reducing agents (e.g., ferrous ions, hydroxylamine, or sulphur dioxide), initially to plutonium(V), which disproportionates and is further reduced. The reduction of plutonium(IV) to plutonium(III) is much easier than the corresponding process for uranium or neptunium, and, as will be seen, is not much more difficult than the reduction of plutonium(VI). Sulphur dioxide, hydrazine, iodide ion, or

[15] R. E. Connick and W. H. McVey, MDDC 335.
[16] B. G. Harvey, H. G. Heal, A. G. Maddock, and E. Rowley, J., 1947, 1010.
[17] M. Kahn, MDDC 391.
[18] R. E. Connick, W. H. McVey, J. W. Gofman, and G. E. Sheline, MDDC 587.
[19] R. E. Connick and W. H. McVey, MDDC 337 ; K. A. Kraus, MDDC 1378.

hydrogen and a platinum catalyst will all give plutonium(III) solutions. The oxidation of plutonium(III) to plutonium(IV) needs a moderate oxidising agent and is, for instance, not effected by air.[20]   There is no sign of a lower ion than Pu^{3+}.

That the plutonium(VI) solutions do in fact contain PuO_2^{2+} ions is shown (i) by the formulæ of their salts, e.g., $NaPuO_2(OAc)_3$, isomorphous with the uranium and neptunium compounds [21] or the 8-hydroxyquinoline derivative $PuO_2(C_9H_6NO)_2,C_9H_7NO$; [16] (ii) by the fact that the absorption spectrum shows vibrational fine structure in the same wave-length region and with nearly the same separation of the lines as does that of UO_2^{2+} ; [5] and (iii) by the electrochemistry of plutonium solutions.   Electrolytic reduction of a plutonium(VI) solution leads in the first place to a solution with a different absorption spectrum from either that of plutonium(VI) or plutonium(IV), and this must be plutonium(V) since only one equivalent is needed to reduce plutonium(VI) to this state.   Similarly it can be made under the right conditions by oxidation of plutonium(IV) [22], [23] [this generally leads directly to plutonium(VI)].   The plutonium(VI/V) couple is reversible and the potential is independent of the acid concentration,[22], [23], [24] which indicates that the quinquevalent ion is PuO_2^+.   It has been found that this ion disproportionates, and no well-defined compound derived from it has been obtained (or at least described), though it is believed to be present in a complex carbonate precipitated from alkaline solution.   The kinetics and equilibria involved in the disproportionation of plutonium(V) have been examined.[22], [23], [25]   It is found that plutonium(V) is fairly stable at pH values from about 2 to 5 ; but at all acidities it slowly disproportionates to plutonium(IV) and plutonium(VI).   The concentrations of the various plutonium ions can be followed by their absorption spectra ; the initial process in the disappearance of plutonium(V) appears to be

$$2PuO_2^+ + 4H^+ \;\rightleftharpoons\; PuO_2^{2+} + Pu^{4+} + 2H_2O \qquad . \qquad . \quad (1)$$

at least in effect, though presumably (as with neptunium) there is an intermediate stage involving an oxy-ion of plutonium(IV) (e.g., PuO_2H^+) which then reacts with more hydrogen ion.   A faster equilibrium than the above reaction is then set up :

$$PuO_2^+ + Pu^{4+} \;\rightleftharpoons\; PuO_2^{2+} + Pu^{3+} \qquad . \qquad . \qquad . \quad (2)$$
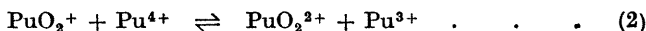
As soon as appreciable amounts of Pu(III) are present, the reaction

$$PuO_2^+ + Pu^{3+} + 4H^+ \;\longrightarrow\; 2Pu^{4+} + 2H_2O \qquad . \qquad . \quad (3)$$
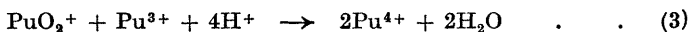
occurs [again probably with some intermediate stage involving an oxy-ion of plutonium(IV)], and this reaction is believed to be in practice the most important one in removing plutonium(V).[22], [25], [26]   Thus the mechanism of disproportionation of plutonium(V) is more complicated than that of

[20] R. E. Connick and W. H. McVey, MDDC 338.
[21] W. H. Zachariasen, MDDC 67.
[22] R. E. Connick, M. Kasha, W. H. McVey, and G. E. Sheline, MDDC 749.
[23] L. H. Gevantman and K. A. Kraus, MDDC 1251.
[24] J. C. Hindman, AECD 1893.   [25] R. E. Connick, MDDC 566.
[26] M. Kasha, MDDC 904.

uranium(V) or neptunium(V) because of the production of plutonium(III) as well as plutonium(IV) and plutonium(VI) ; and it is one of the main peculiarities of the plutonium ions in aqueous solution that the 3-, 4-, and 6-valency states can exist together in comparable concentrations in solutions of moderate acidity. Consequently the study of the mechanism of disproportionation of plutonium(V) has to be carried out in solutions containing more than negligible amounts of plutonium(III), (IV), and (VI), so that the precise elucidation of the mechanism is difficult. R. E. Connick [25] finds for the equilibrium constant of (2) above, in 0·5M-hydrochloric acid :

$$K_2 = \frac{[Pu(III)][Pu(VI)]}{[Pu(IV)][Pu(V)]} = 8\cdot5$$

Kasha [26] finds $K_2 = 10\cdot7$ in 0·1M-perchloric acid. Combining this with the constant obtained for the disproportionation of Pu(IV) (see below)

$$K = [Pu(III)]^2[Pu(VI)]/[Pu(IV)]^3 = 0\cdot05$$

we get for the disproportionation of plutonium(V) to plutonium(IV) and (VI)

$$K_1 = [Pu(V)]^2/\{[Pu(IV)][Pu(VI)]\} = 7 \times 10^{-4}$$

(in 0·5M-hydrochloric acid at 25°). This may be compared with the value of 10^{-12} for uranium(V), and 40 for neptunium(V) (both in M-acid). Consequently, in fairly acid solution very little plutonium(V) will be present at equilibrium, but as can be seen from the reaction (1) above [which assumes that plutonium(V) is present as the oxy-ion PuO_2^+], the stability of plutonium(V) would be much favoured by higher pH. This is in fact found by L. H. Gevantman and K. A. Kraus,[23] who also found decreasing stability with rising temperature. The interpretation of these kinetic measurements is complicated by the reduction of plutonium(VI) by the products of the alpha-particle bombardment of the solution, which destroys plutonium(VI) at the rate of 1—2% per day. Gevantman and Kraus attribute this reduction to hydrogen peroxide, which is known to reduce plutonium(VI) ; plutonium(V) reacts with hydrogen peroxide much more slowly.

Quadrivalent plutonium in sufficiently acid solution (more than about 0·2N.) is probably largely present as hydrated Pu^{4+}. Thus the Pu(III/IV), but not the Pu(IV/V) or (IV/VI), couple is reversible and reasonably independent of acid concentration. Plutonium(III) gives under these conditions the simple hydrated ion Pu^{3+}. This is confirmed by the formulæ of the salts of plutonium in these valencies, e.g., $Pu(IO_3)_4$, $Pu_2(C_2O_4)_3$. As was mentioned above, the plutonium ions are remarkable in that at moderate acidities the oxidation–reduction potentials of the Pu(III/IV) and (IV/VI) couples are not very different. Consequently all three ions can exist in solution simultaneously in equilibrium :

$$3Pu^{4+} + 2H_2O \rightleftharpoons PuO_2^{2+} + 4H^+ + 2Pu^{3+} \qquad . \qquad . \quad (4)$$
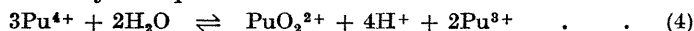
The equilibrium constant, written as $K_4 = [Pu(III)]^2[Pu(VI)]/[Pu(IV)]$, was found [26] to have the following values, using plutonium concentrations about 0·001M. :

K_4 :	252	40·2	0·195	0·0405
Molarity of $HClO_4$:	0·052	0·102	0·516	0·994

K_4 is of course dependent on the hydrogen ion concentration, and equation (4) suggests that it should be inversely proportional to its fourth power ; in fact it is inversely proportional to the third power of the perchloric acid concentration, but it must be remembered that no account has been taken of activity coefficients. However, these results are more consistent with this equation, involving only the simple hydrated ions, than with those based on hydrolysed ions [e.g., in particular, plutonium(IV) as $PuOH^{3+}$]. It will be seen from these values of K_4 that if the acidity falls below about 0·2M. considerable disproportionation of plutonium(IV) occurs. At low acidities plutonium(V) is also formed, possibly by the reverse of equilibrium (2) above, or possibly directly thus :
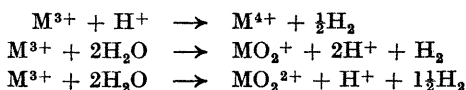
$$2Pu^{4+} + 2H_2O \rightleftharpoons PuO_2^+ + Pu^{3+} + 4H^+$$
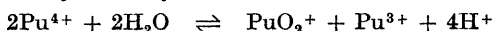
The latter mechanism is supported by the observation that the rate of disproportionation of plutonium(IV) is proportional to $[Pu(IV)]^2$; the rate constant is 0·053 $(mole/l.)^{-1}.min.^{-1}$ at 25° in 0·48M-perchloric acid.

The oxidation–reduction potentials of the uranium, neptunium, and plutonium ions have been measured in various solutions. The results in some cases indicate considerable complex formation with the anion, but as is usual the potentials in perchlorate solutions appear to give the most reliable figures for the simple hydrated cations ; the potentials in chloride solutions are not much different. The most thorough investigation of the plutonium redox potentials is that of Kraus,[27] who has studied their dependence on hydrogen-ion concentration (cf. also ref. 28) ; the following table gives the potentials relative to the normal hydrogen electrode ; a smaller negative value for the potential indicates that the oxidised state of the couple is relatively more stable. The uranium potentials are for M-hydrochloric or -perchloric acid solutions ; somewhat different values have also been reported for uranium(IV/V).

Couple.	U.	Np (in M-HCl).	Pu (in M-HClO₄).	Pu (in M-HCl).
III/IV . . .	+ 0·63	− 0·14	− 0·96	− 0·97 volts
IV/V	− 0·55	− 0·74	− 1·20	− 1·13
V/VI	− 0·06	− 1·14	− 0·93	− 0·91

These results show the increasing stability of the lower valency states as we pass from uranium to plutonium, and also the relatively large stability of neptunium(V). The same trends are evident from measurements of the heats of formation of the ions in M-hydrochloric acid.[29, 30] The following table gives values of ΔH (in kcals./g.-mol.) for the reactions

$$M^{3+} + H^+ \rightarrow M^{4+} + \tfrac{1}{2}H_2$$
$$M^{3+} + 2H_2O \rightarrow MO_2^+ + 2H^+ + H_2$$
$$M^{3+} + 2H_2O \rightarrow MO_2^{2+} + H^+ + 1\tfrac{1}{2}H_2$$

[27] K. A. Kraus, MDDC 814.
[28] B. J. Fontana, MDDC 1603 ; K. A. Kraus, and G. E. Moore, MDDC 906 ; and refs. (9), (12), (13), (22), and (24).
[29] L. Brewer, AECD 1899.   [30] E. F. Westrum, AECD 1903.

Ion formed.	U.	Np.	Pu.
M^{4+}	$-$ 23·6	$-$ 5·9	$+$ 12·9
MO_2^+	$+$ 12·8	$+$ 33·1	$+$ 62·9
MO_2^{2+}	$+$ 9·5	$+$ 55·4	$+$ 79·7

The lower the value of ΔH, the more stable is the ion relative to tervalent M^{3+}.

Neither americium nor curium forms the series of ions given by uranium, neptunium, or plutonium. Both elements are predominantly tervalent, and there can be little doubt that in solution they give the ions Am^{3+} and Cm^{3+}. Americium cannot be oxidised by argentic ions in 2N-nitric acid, nor by potassium permanganate or sodium bromate,[31] suggesting that its oxidation potential is more negative than $-$ 2 v. (for the III/IV couple). In alkaline solution it can be oxidised by strong oxidising agents such as sodium hypochlorite ; but the higher oxidation state has not been definitely characterised. Americium(III) can be reduced by sodium amalgam, but not by zinc amalgam.[32] The product of the reduction is believed to be Am^{2+}, as it can be co-precipitated with europous and samarous sulphates, presumably as $AmSO_4$; americium(III) is not carried on these precipitates. Curium so far has been obtained only as tervalent compounds and is not affected by the reagents which oxidise or reduce americium.
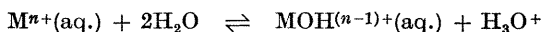
These oxidation–reduction potentials show an analogy with the behaviour of the rare-earth ions. If we consider the 3+ rare-earth ions, starting with Ce^{3+} where the first $4f$ electron appears, it becomes progressively more difficult with increasing atomic number (and, in fact, after praseodymium impossible) to remove a further $4f$ electron by chemical means. The rising nuclear charge holds the $4f$ electrons progressively more firmly, though it is somewhat screened by the other $4f$ electrons. Eventually in samarium a point is reached where the electrons are so firmly held that the bivalent ion Sm^{2+} can be obtained in solution by strong reduction, and in europium this reduction is easier. In gadolinium the trends of the redox potentials are sharply interrupted : gadolinium is only tervalent, and the next element terbium shows signs of quadrivalency. Thereafter the elements are only tervalent until ytterbium is reached, which can be bivalent. Thus the trends of the first half of the rare-earth series are repeated. This break at gadolinium is no doubt because in Gd^{3+}, with seven $4f$ electrons, another electron (to give the unknown Gd^{2+}) would have to be paired with one of the previously-held electrons and it is known from the spectroscopic and magnetic properties of the rare-earth ions that this pairing involves a relatively higher energy, i.e., a more. unstable ion. In the heavy elements more electrons can be involved in chemical reaction than in the rare earths ; that is to say, the outermost electrons are not so firmly held, as is generally the case with elements of high atomic number. As with the rare earths, the tervalent ions become progressively more stable relative to the quadri-
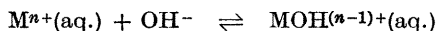
[31] B. B. Cunningham, AECD 1879.
[32] S. G. Thompson, R. A. James, and L. O. Morgan, AECD 1907.

valent, and further on the bivalent relative to the tervalent.   This is also true of the MO_2^{2+} ions relative to the M^{4+} ions : the M(IV) becomes more stable relative to M(VI).   The changes are more rapid than in the rare-earth series, and it is to this that we owe the far less uniform chemistry of the heavy-element series.   The $5f$ electrons seem to provide a less efficient screening of the nuclear charge than do the $4f$ electrons.   Finally, in Cm^{3+} a point is reached where the $5f$ shell is half full (assuming no $6d$ electrons), and the Cm^{2+} ion, like the Gd^{2+} ion, is unknown.   It should also be mentioned at this point that the relative energy levels of $4f$ and $5d$, as compared with $5f$ and $6d$, electrons are probably somewhat different, the $6d$-electron levels being relatively of lower energy.   As will be seen later, the ground state of the atom (un-ionised) of thorium is $6d^2 7s^2$; and there is some, not entirely conclusive, magnetic evidence for $6d$ electrons in some uranous compounds.   At present no very definite assignment of the un-shared electrons in heavy element *compounds* can be made in all cases, and the position on this question appears to be as follows.   It is still possible to maintain that all unshared electrons in *compounds* of the heavy elements, beyond the radon core, are in $5f$ orbits ; but it seems more probable that at the beginning of the series we have $6d$ orbits, which become relatively less stable as we go to higher atomic numbers.   By the time uranium is reached, the $5f$ orbits are probably somewhat the more stable, and beyond uranium there is no evidence of unshared electrons in $6d$ levels.   Thus the only compounds likely to contain unshared $6d$ electrons are the lower valency compounds of thorium and protoactinium.

Mention was made earlier that the heavy-element ions were probably of a simple hydrated type in acid solution.   In fact of course an equilibrium of the type :

$$M^{n+}\text{(aq.)} + 2H_2O \;\rightleftharpoons\; MOH^{(n-1)+}\text{(aq.)} + H_3O^+$$

or

$$M^{n+}\text{(aq.)} + OH^- \;\rightleftharpoons\; MOH^{(n-1)+}\text{(aq.)}$$

is set up in solution for any n-valent ion.   Investigations have been made of the equilibrium constants of these reactions for the heavy-metal ions, by measurements of the pH of solutions of their salts when titrated with alkali,[27] and by changes in the absorption spectra and redox potentials in solutions of various pH.   The values of the hydrolytic constants so obtained[24, 27, 33,34,35] are given in the table following, where $K = [H_3O^+].[MOH^{(n-1)+}]/[M^{n+}]$ and $pK = -\log_{10} K$, so that pK is equal to the pH at which 50% hydrolysis occurs.

Mention[37] may be made for comparison of the ceric ion which is largely hydrolysed to $CeOH^{3+}$ and so is a much weaker base than Th^{4+} or Pu^{4+}, and of the tervalent rare-earth ions where pK ranges from roughly 8 (in lanthanum) to 6.

Plutonium tetrahydroxide is thus a base of very much the same strength as uranium tetrahydroxide.   Plutonium(IV) also readily polymerises at pH values above about 1, so that in its solutions, if the pH is raised by the

[33] K. A. Kraus and F. Nelson, AECD 1864.   [34] *Idem*, AECD 1888.
[35] J. C. Hindman and D. P. Ames, MDDC 1213.

Ion.	U.	Np.	Pu.
M^{3+}	—	—	6·95 (in M-ClO_4^-) (27) 7·1 (35) 7·2 (34)
M^{4+}	1·44 1·15 (10)	—	1·53 (34) 1·4 (in M-Cl^-)
MO_2^+	—	9·0	9·7
MO_2^{2+}	4·7 (36)	—	5·7

(Figures in parentheses are references.)

addition of alkali, there is a rapid initial change as the monomeric hydroxide complex is formed, followed by a slow drift in pH to lower values as the polymer is formed. On acidification the polymer is only slowly destroyed, though this can be hastened by heating the solution. The solution of the polymer has a characteristic absorption spectrum, different from that of monomeric plutonium(IV). On further addition of alkali to a polymeric plutonium(IV) solution a polymeric hydroxide is precipitated, different from that obtained by rapid addition of excess of alkali to monomeric plutonium(IV). The composition of these polymeric precipitates is often approximately $(Pu(OH)_{3·85}X_{0·15})_n$, where X is the anion initially present.[27, 34] Uranium(IV) also polymerises. It is not clear at present whether the polymeric plutonium(IV) is simply a mixture of a number of ions containing various numbers of Pu atoms combined by Pu–O–Pu links and with varying numbers of hydroxyl groups attached, or whether it is a definite compound, but in spite of the relative constancy of the amount of associated anion it is probably the former. Ions containing more than one metal atom occur also in somewhat basic uranyl and, probably, plutonyl solutions, e.g., $U_2O_5^{2+},xH_2O$.

Analogous to the hydrolysis of the heavy-metal ions is their combination with anions, other than hydroxyl, in the solution. Some evidence of such combination comes from the formation of double salts, such as $(NH_4)_2Pu(NO_3)_6$, but this is not by itself a proof of complexity as X-ray examination has shown many double salts, e.g., $RbUO_2(NO_3)_3$, not to contain complex anions. More definite evidence of complexity comes from electrical migration experiments, and from observed changes in absorption spectra, solubilities, and cell e.m.f.s when various anions are added. Qualitatively it is found that sulphate, acetate, oxalate, and probably fluoride combine strongly with Pu^{4+}, the nitrate moderately, and the chloride and perchlorate still less.[38] In perchloric acid solution, plutonium(IV) and (VI) show no signs of migration as an anion, even at 10M-concentration. In hydrochloric acid, plutonium(III) migrates chiefly as a cation even in

[36] H. Guiter, *Bull. Soc. chim.*, 1947, 64.
[37] M. S. Sherrill, C. B. King, and R. C. Spooner, *J. Amer. Chem. Soc.*, 1943, **65**, 170.
[38] C. K. McLane, J. S. Dixon, and J. C. Hindman, MDDC 1215.

10M-acid ; plutonium(IV) begins to migrate chiefly to the anode when the acid concentration reaches about 5—6M., and the same is found for plutonium(VI). In nitric acid plutonium(IV) migrates as an anion at concentrations above about 6M-acid, and plutonium(VI) does so above about 10M-acid. In sulphuric acid plutonium(III) migrates as an anion at concentrations above about 4M-, plutonium(IV) above about 0·1M-, and plutonium(VI) above about M-acid. The behaviour of neptunium(VI) is very like that of plutonium(VI), though anionic complexes are slightly more easily formed. Acetate and oxalate both readily give anionic complexes with plutonium(IV), but fluoride does not do so even at 10M-concentration in transference experiments, although there is other evidence showing that a positively charged plutonium(IV) fluoride complex is formed.

Since plutonium(III) combines less readily with these anions than does plutonium(IV), the potential of the Pu(III/IV) couple should be lowered by complex formation, and this is found to occur. The extent of this effect is shown by the following values : [39]

E.m.f., v. :	− 0·966	− 0·953	− 0·92	− 0·74	− 0·50
Acid, M. :	HCl	HClO$_4$	HNO$_3$	H$_2$SO$_4$	HF

It is interesting to note that both thorium and cerium(IV) have been shown to form complex anions with nitrate, and this has been rarely found elsewhere. These results, and the absorption spectra,[35, 40, 41] can be interpreted by assuming that at least initially a complex of the general formula PuX^{3+} is formed by Pu(IV) with an anion X$^-$, and the value of its association constant, $K = [PuX^{3+}]/([Pu^{4+}].[X^-])$, is about 3 (mole/l.)$^{-1}$ for X = nitrate, and about 0·2 for chloride. For sulphate the value is probably about 2000, and for fluoride [42] 6×10^6 (mole/l.)$^{-1}$. These figures apply only to the first complex formed by association with an anion ; it was shown by the transference measurements described above that in many cases further combination occurs leading presumably to ions such as Pu(NO$_3$)$_6{}^{2-}$.

Compounds of the Transuranic Elements

From the solutions of these ions of the transuranic elements various solid salts have been obtained by the usual methods of evaporation and precipitation. In certain cases solutions have been described (e.g., in work on absorption spectra) without an actual separation of a solid salt having been made, the nature of the salt present being inferred from the method of preparation of the solution. In this section an account will be given of the compounds actually isolated from solution. In addition to preparation from solution, many compounds have been obtained by dry methods, and these will also be described here. The analogous thorium, uranium, or rare-earth compounds will be briefly noted.

Metals.—Neptunium and plutonium metal have both been prepared by methods which show that these elements, like uranium and unlike the

[39] J. J. Howland, J. C. Hindman, and K. A. Kraus, MDDC 1260.
[40] J. C. Hindman, MDDC 1256.   [41] *Idem*, MDDC 1257.
[42] C. K. McLane, MDDC 1147.

platinum metals, are base metals, and vigorous methods have to be used for their isolation. Neptunium [14] is prepared by the reduction of the fluoride by barium vapour at 1200°. Plutonium, uranium, and americium [43] can be obtained similarly. The heats of formation (given in the table below, in kcals./g.-mol.) of the ions of these elements from the metal [29] also show that we are not dealing with noble metals [compare, *e.g.*, $Pt + 2Cl_2 \rightarrow PtCl_4$ (solid) $- 56$ kcals./g.-mol.] :

Ion formed.	Th.	U.	Np.	Pu.
M^{3+}	—	$- 123.6$	$- 159.8$	$- 141.9$
M^{4+}	$- 185.5$	$- 147.2$	$- 165.7$	$- 129.0$

Curium metal has not been described. The density of americium metal is given as 10—11, which makes the atomic volumes in the series roughly :

Th	Pa	U	Np	Pu	Am
20·9	—	12·8	13·5	—	22—24

Ce	Pr	Nd		Sm	Eu
20·6	20·8	20·6	—	21·7	29·0

It is interesting to notice that a sudden increase occurs at europium, and (presumably) americium, an increase which is attributed in the case of europium to packing of essentially Eu^{2+} with two valency electrons, as compared with, say, Ce^{3+} with three such electrons. Thorium does not fit the expected trend, but this may be due to electrons in $6d$ orbits.

Oxides.—The transuranic elements, like uranium, form a number of oxides, though it has not always proved possible to obtain all the oxides corresponding to all the valency states known in solution. If we exclude peroxides, the following oxides have been described :

UO	NpO	PuO	AmO	
		Pu_2O_3		(Cm_2O_3)
		Pu_4O_7		
UO_2	NpO_2	PuO_2	AmO_2	
U_3O_8	Np_3O_8			
UO_3				

The oxides UO, NpO, and PuO have been obtained, usually in relatively small amounts, by vigorous reduction of the higher oxides—for example, when traces of oxygen are present as an impurity during reduction of the fluoride to metal,[44] or by reactions such as $U + UO_2 \rightarrow 2UO$ at temperatures above 2000°. Uranium mono-oxide is a brittle, high-melting substance with a metallic appearance ; the monoxides of neptunium and plutonium are apparently similar. They all have a crystal structure of the sodium chloride type. These oxides correspond to valency states that are not known in solution ; they are presumably semi-metallic compounds. Americium monoxide is obtained from the dioxide and hydrogen at 800° ;

[43] S. Fried, AECD 1930.
[44] R. C. L. Mooney and W. H. Zachariasen, AECD 1787.

it can be sublimed to give black crystals, isomorphous with uranium or plutonium mono-oxide, and is probably a normal oxide though it has not been obtained directly from the americious salts.

The compound Pu_2O_3 was obtained by reduction of the dioxide by atomic hydrogen, or by heating the dioxide to 1700°. It forms body-centred cubic crystals, isomorphous with the C modification of the rare-earth sesquioxides. The lattice constant is somewhat variable in different preparations, and this is attributed to variable composition over the range $PuO_{1.5}$ to $PuO_{1.75}$, but the system does not seem to have been examined in detail. Its direct preparation from tervalent plutonium solutions has not been reported, presumably because plutonium trihydroxide is too readily oxidised to be dehydrated to the sesquioxide Pu_2O_3 The same applies to the preparation of sesquioxides from uranium(III) or neptunium(III) solutions. It is however remarkable that americium trihydroxide on ignition in air gives americium dioxide, and this on reduction in hydrogen gives americium monoxide, and not the sesquioxide. Curium, so far as is known, forms only the sesquioxide Cm_2O_3.

The dioxides ThO_2, UO_2, NpO_2, PuO_2, and AmO_2 all have the fluorite-type structure with lattice constants (A.) as follows :

ThO_2	UO_2	NpO_2	PuO_2	AmO_2
5·586	5·457	5·425	5·386	5·372

All except uranium dioxide are the normal oxides formed by ignition of their other oxides or decomposable salts, such as nitrates, in air at not too high a temperature. Plutonium dioxide is the highest plutonium oxide [45] known, and attempts to oxidise it further by nitrogen dioxide or atomic oxygen were unsuccessful. Neptunium dioxide can, however, be oxidised under these conditions to give a compound of composition about $NpO_{2.64}$, presumably Np_3O_8 with a slight deficiency of oxygen. It is isomorphous with the uranium analogue U_3O_8. Uranium is remarkable for the range of oxides intermediate between UO_2 and UO_3 that it forms.[46] Triuranium octaoxide U_3O_8 is of course the oxide formed by heating other oxides in air, but this can be converted into uranium trioxide UO_3 by heating it in oxygen under pressure. Low-temperature oxidation of uranium dioxide goes about as far as $UO_{2.3}$ with small change in the crystal structure, and magnetic measurements [47] show that the U(IV) oxidised in this range becomes sexivalent uranium. From U_2O_5 to UO_3 we have another range of stability with progressive change of crystal structure, and magnetic measurements can best be interpreted in terms of quinquevalent uranium being present.[47, 48]

Hydroxides.—These are formed by the addition of aqueous ammonia or other alkali to solutions of the transuranic elements. Tri- and tetra-hydroxides of plutonium, neptunium tetrahydroxide, and americium tri-

[45] D. M. Gruen and J. J. Katz, AECD 1892.
[46] E.g., K. B. Alberman and J. S. Anderson, Chemical Society Symposium, Oxford, April 1949; J., 1949, s303.
[47] J. K. Dawson and M. W. Lister, unpublished.
[48] H. Haraldsen and R. Bakken, Naturwiss., 1940, 28, 127.

hydroxide are all obtained as insoluble precipitates, redissolving in acids to give the corresponding salts, and insoluble in excess of aqueous ammonia. There is no sign of ammine formation. The trihydroxides of the elements before plutonium are too easily oxidised to be isolated ; $Pu(OH)_3$ is easily oxidised, whilst americium trihydroxide is quite stable. The latter is a pink gelatinous material. Plutonium tetrahydroxide has been examined in some detail by Kraus,[49] who finds that the dark-brown precipitate formed by addition of alkali to aqueous plutonium tetranitrate contains, after thorough washing, nitrate in the proportion $Pu(OH)_{3\cdot85}(NO_3)_{0\cdot15}$. It will be remembered that polymeric plutonium(IV) precipitates contain anions in roughly this proportion, so that polymerisation is presumably occurring. Kraus, by following the pH changes on precipitation and washing, also obtained evidence of basic nitrates.

In its sexivalent state plutonium, like uranium, has acidic properties. Barium hydroxide precipitates a compound of composition about $BaPu_3O_{10}$ —at least this is the Ba : Pu ratio.[27] This is no doubt a polyplutonate, analogous to the polyuranates. A similar precipitate can be obtained with sodium hydroxide, which is considerably more soluble ;[15] the precise composition is uncertain. There is evidence from the pH titration curves of MO_2^{2+} solutions with alkali, where M is uranium, neptunium, or plutonium, that polymerisation of all these ions occurs in slightly alkaline solution, and on addition of acid again depolymerisation occurs only slowly.

Peroxides.—Various peroxides may be mentioned. Uranyl solutions with hydrogen peroxide precipitate a uranium(VI) peroxide, hydrated UO_4. Plutonyl solutions on the other hand are reduced by hydrogen peroxide, rapidly to plutonium(V) and then more slowly to plutonium(IV).[50] Plutonium(IV) with amounts of hydrogen peroxide comparable to the plutonium present gives two soluble peroxido-complexes, which can be distinguished by their absorption spectra. The brown complex, which is formed first contains two plutonium atoms and one peroxido-group —O—O— per molecule ; the red compound contains one more peroxido-group. It can be shown that the dissociation constant of the brown compound, $K_1 = [\text{brown compound}]/([Pu^{4+}].[H_2O_2]) = 7 \times 10^7$ (moles/l.)$^{-1}$ in 0·5M-hydrochloric acid at 25°, whilst for the red compound the constant $K_2 = [\text{red compound}]/([\text{brown compound}].[H_2O_2]) = 145$ (moles/l.)$^{-1}$. It is thus evident that most of the plutonium in these solutions will be combined with the hydrogen peroxide. The structure of these complexes has not been elucidated in detail. If an excess of hydrogen peroxide is added a green precipitate is obtained [51, 52] which contains some of the anion present, particularly if this is sulphate. Its composition varies somewhat owing to decomposition, but approximates to Pu_2O_7,xH_2O, or Pu_2O_6,SO_4,xH_2O ; somewhat different forms are precipitated depending on the relative amounts of plutonium and hydrogen peroxide. These compounds con-
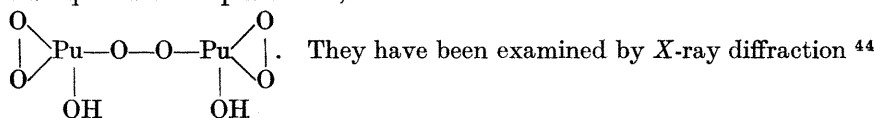
[49] K. A. Kraus, MDDC 1377.
[50] R. E. Connick and W. H. McVey, MDDC 619.
[51] E. D. Koshland, J. C. Kromer, and L. Spector, MDDC 1263.
[52] H. H. Hopkins, MDDC 1334.

tain quadrivalent plutonium, so we must write formulæ for them such as

$$\begin{array}{c}\mathrm{O} \diagdown \qquad\qquad \mathrm{O}\\ \quad \diagup\!\!\!\diagdown\!\!\mathrm{Pu}\!-\!\mathrm{O}\!-\!\mathrm{O}\!-\!\mathrm{Pu}\!\diagdown\!\!\!\diagup\\ \mathrm{O}\diagup \quad | \qquad\quad | \quad \diagdown\mathrm{O}\\ \quad\ \ \mathrm{OH}\qquad\ \ \mathrm{OH}\end{array}$$ They have been examined by X-ray diffraction [44]

and shown in one case to resemble closely thorium peroxide, which forms a compound of empirical formula Th_2O_6,SO_4 ; but detailed structures have not been determined.

Salts.—*Halides and oxy-halides.* The following simple halides of the heavy elements have been described (in this table X = any halogen) :

| Valency.	Th.	U.	Np.	Pu.	Am.	Cm.
6 . . .	—	UF_6 ; UCl_6	NpF_6	(PuF_6)	—	—
5 . . .		UF_5 ; UCl_5	—	—	—	—
		U_2F_9				
4 . . .	ThX_4	UX_4	$NpF_4, NpCl_4$	$NpBr_4, PuF_4$	—	—
3 . . .	ThI_3	UX_3	NpX_3	PuX_3	AmX_3	CmX_3
2 . . .	ThI_2					

The volatile, easily hydrolysed uranium hexafluoride has long been known ; it is made from uranium tetrafluoride and fluorine. Neptunium trifluoride with fluorine at red heat gives neptunium hexafluoride, which melts at 53° and is easily volatile ; this is isomorphous with uranium hexafluoride and is a white solid, easily hydrolysed ; its stability is less than that of uranium hexafluoride. Uranium hexachloride, made by the reaction $2UCl_5 \longrightarrow UCl_6 + UCl_4$, is much less stable than the hexafluoride ; as would be expected, therefore, neptunium hexachloride is unknown. Plutonium hexafluoride is not known for certain, though traces of it may have been obtained. The uranyl halides are well-known, stable compounds, UO_2X_2. The corresponding neptunyl and plutonyl fluorides, chlorides, and bromides must all have been obtained in solution ; iodide reduces these cations. PuO_2F_2,xH_2O is a white, fairly soluble solid.

Quinquevalent uranium fluoride and chloride are known, and U_2F_9, but no corresponding transuranic compounds. Quinquevalent salts of the type NpO_2Cl must occur in solution, but the solids have not been described.

The tetrahalides of uranium are all stable. Neptunium tetrafluoride has been made as a light-green solid on the micro-scale by the reaction [53] $4NpF_3 + O_2 + 4HF \longrightarrow 4NpF_4 + 2H_2O$ at about 500°. Neptunium tetrachloride and tetrabromide can be obtained by interaction of the dioxide with carbon tetrachloride and aluminium tribromide, respectively. The tetrachloride is a yellow solid, volatile at high temperatures ; the tetrabromide is a reddish-brown solid, volatile at about 500°. No tetraiodide could be made. Plutonium tetrafluoride is the only tetrahalide of plutonium that can be isolated, though the tetrachloride must exist in solution, but attempts to separate it have led only to the trichloride. Plutonium tri-

[53] S. Fried and H. R. Davidson, *J. Amer. Chem. Soc.*, 1948, **70,** 3539 ; MDDC 1332.

chloride does not react with chlorine at 170°.[54]   The hydrate, $PuF_4,2H_2O$, is precipitated from aqueous solution ; [55] the tetrafluorides of all of this group of elements are insoluble, but the other halides are soluble.   No tetrahalides of americium are known, so that we have a regular decrease in the stability of the tetrahalides in passing from uranium to americium. The oxyhalides $UOCl_2$ and $NpOCl_2$ are known.   The series of the trihalides of these elements is known more or less completely, except of course with thorium.   They are obtained in the earlier elements (uranium and nep-tunium) by heating the higher halides in hydrogen, or in the later elements by heating the oxides with an aluminium or carbon halide.   Neptunium trifluoride has been made by heating the dioxide with hydrogen and hydrogen fluoride, and americium trifluoride has similarly been made by heating the trihydroxide in gaseous hydrogen fluoride.   Plutonium tri-fluoride can be precipitated from aqueous solution.   The fluorides are in general insoluble, but the other halides dissolve to give M^{3+} solutions. Their relative stability, like that of the $3+$ ions, rises in passing from uranium to americium and curium.   It is interesting to note [56] that, although plutonium tetrachloride cannot be obtained, the tetrafluoride can be made by use of the equilibrium :
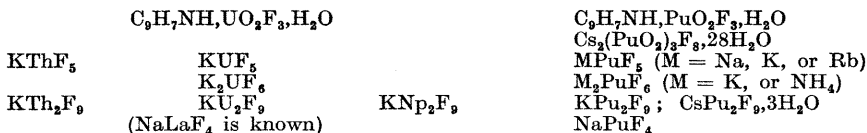
$$4PuF_3 + O_2 \rightleftharpoons 3PuF_4 + PuO_2$$
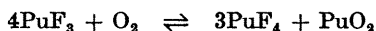
Plutonium trichloride with 6, 3, or 1 molecule of water of crystallisation can be obtained from aqueous solution.   On heating it gives the oxy-chloride $PuOCl$, not the anhydrous trichloride.   The oxybromide can similarly be prepared from the tribromide hexahydrate or by the following reaction at high temperatures : [57]

$$PuO_2 + \tfrac{1}{2}H_2 + HBr \rightleftharpoons PuOBr + H_2O$$
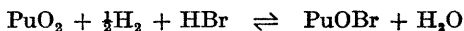
The equilibria, $PuX_3 + H_2O \rightleftharpoons PuOX + 2HX$ (where X = Cl or Br), have been measured at 500—700°.   The oxyiodide behaves similarly.[58]

Complex halides.   A number of complex halides [59, 60] has been prepared from solution.   These consist of a variety of fluorides and one series of double chlorides ; the fluorides are as follows :

	C_9H_7NH,UO_2F_3,H_2O		C_9H_7NH,PuO_2F_3,H_2O
			$Cs_2(PuO_2)_3F_8,28H_2O$
$KThF_5$	KUF_5		$MPuF_5$ (M = Na, K, or Rb)
	K_2UF_6		M_2PuF_6 (M = K, or NH_4)
KTh_2F_9	KU_2F_9	KNp_2F_9	KPu_2F_9 ; $CsPu_2F_9,3H_2O$
	(NaLaF$_4$ is known)		$NaPuF_4$

Other complex thorium and uranium fluorides are known, but the table shows only those analogous to the transuranic compounds.   It is uncertain whether these plutonyl fluorides contain true complex ions ; and the same is true of the lower complex fluorides since, though combination of plu-tonium and fluoride certainly must occur in solution, as was mentioned

[54] B. M. Abraham, MDDC 1574.   [55] H. H. Anderson, MDDC 1130.
[56] S. Fried and N. R. Davidson, MDDC 1250.
[57] N. R. Davidson, MDDC 1578.
[58] I. Sheft and N. R. Davidson, MDDC 1712, 1713.
[59] H. H. Anderson, MDDC 1129, 1130, 1362.   [60] E. S. Maxwell, AECD 2134.

above, there is no evidence from electric migration experiments of complex anions. The compounds KMF_5 and KM_2F_9 form isomorphous series.[61]

A small number of complex chlorides has been prepared, of the general formula M_2PuCl_6, where M was cæsium, tetramethylammonium, pyridinium, or quinolinium (cf. $Cs_2ThCl_6,8H_2O$ and Cs_2UCl_6). No double chlorides could be isolated with potassium, rubidium, or zinc. The complex anion $PuCl_6{}^{2-}$ has been shown to be present in the crystal, by X-ray diffraction.

Sulphides. Transuranic sulphides have been prepared by dry methods ; they are all lower-valency compounds :

ThS	US		(PuS)
Th_2S_3	U_2S_3	Np_2S_3	Pu_2S_3 ; Pu_2O_2S
	UOS	NpOS	(Pu_3S_4)
ThS_2	US_2		

Triuranium octaoxide, when heated in hydrogen sulphide at 1300—1400°, gives uranium disulphide US_2, and some of the sesquisulphide U_2S_3. The disulphides ThS_2 and US_2 are normal covalent compounds, but the sesqui-sulphides Th_2S_3 and U_2S_3 are semi-metallic.[63, 64] Neptunium dioxide on heating to 1000° in hydrogen sulphide gives first an oxysulphide NpOS, and at 1200° a sesquisulphide Np_2S_3, which is isomorphous with U_2S_3 and also apparently semi-metallic. Plutonium dioxide and hydrogen sulphide at 1300° give a compound Pu_2O_2S with a metallic lustre. On further treat-ment at 1340° a black compound with a composition intermediate between Pu_3S_4 and Pu_2S_3 is obtained which gives a different X-ray diffraction pat-tern from the sesquisulphide obtained from plutonium trichloride and hydrogen sulphide at 800—1000°. Plutonium sesquisulphide is not semi-metallic in character, so that as usual we have a progressive increase in the stability of the lower valencies in passing from uranium to plutonium. There are some indications of a lower sulphide, probably PuS, obtained when plutonium trifluoride and calcium vapour react in a barium sulphide crucible.[65]

Nitrates. A nitrate, $Pu(NO_3)_4,xH_2O$, has been prepared [66] as light-green crystals. No double salts could be obtained with nickel, cobalt, or manganese nitrates, but the salt $(NH_4)_2Pu(NO_3)_6$ has been prepared,[40] isomorphous with the corresponding thorium and ceric compounds. The compounds $M_2Pu(NO_3)_6$ are also known, where M is Cs, Rb, Tl, K, or quinolinium. These probably contain the complex anion $Pu(NO_3)_6{}^{2-}$, as is shown by the uniformity of their formulæ, by the electric-migration experiments, and by analogy with the corresponding thorium compounds, $Rb_2Th(NO_3)_6$ and $Cs_2Th(NO_3)_6$, whose diamagnetic susceptibilities [67] are much less than the sum of those of their components, suggesting that new bonds are formed in the double salts.

[61] W. H. Zachariasen, *J. Amer. Chem. Soc.*, 1948, **70**, 2147.
[63] E. F. Strotzer and M. Zumbusch, *Z. anorg. Chem.*, 1941, **247**, 215.
[64] E. D. Eastman, MDDC 193.
[65] B. M. Abraham, N. R. Davidson, and E. F. Westrum, AECD 1788.
[66] H. H. Anderson, MDDC 1130.
[67] C. Braselitin, *Compt. rend.*, 1941, **212**, 193.

Sulphates. Quadrivalent plutonium gives the reddish-brown sulphate $Pu(SO_4)_2,4H_2O$, which on heating loses water to $\frac{1}{3}H_2O$. H. H. Anderson [68] could not obtain the anhydrous salt without decomposition. Uranium disulphate also gives a tetrahydrate, which loses water on heating to give a hemihydrate which cannot be completely dehydrated without hydrolysis. Plutonium gives a greyish-green basic sulphate, $Pu_2O(SO_4)_3,8H_2O$. Double sulphates, $M_4Pu(SO_4)_4 + 1$ or $2H_2O$, with $M = NH_4$, K, or Rb, have been prepared, and there are thorium and uranium salts of the same composition. The electric-migration experiments make it probable that these are true complex salts.

Tervalent plutonium gives light-blue crystals of composition $Pu_2(SO_4)_3,xH_2O$. A number of double sulphates are known, $MPu(SO_4)_2,4H_2O$, where M is Tl, Na, Rb, Cs, or NH_4; potassium gives a pentahydrate. Double salts $K_5Pu(SO_4)_4$ and $Tl_5Pu(SO_4)_4$ can be made, but no compounds of the type $M_3Pu(SO_4)_3$ known. The rare earths, of course, give numerous double sulphates of the type $M(R.E.)(SO_4)_2$, but of somewhat variable hydration.

Iodates. The light-brown iodate plutonium tri-iodate and the light-pink tetraiodate are both insoluble. Plutonyl iodate is somewhat more soluble.[69]

Oxalates. Diplutonium trioxalate is a slightly soluble salt,[70] and the compound $Pu(C_2O_4)_2,6H_2O$ is also insoluble (about 10^{-4} g.-mol./l. at $25°$).[71] With excess of oxalate it gives a more soluble complex ion $Pu(C_2O_4)_3{}^{2-}$, and it is found that the constant of the equilibrium

$$Pu(C_2O_4)_2 + H_2C_2O_4 \rightleftharpoons Pu(C_2O_4)_3{}^{2-} + 2H^+$$
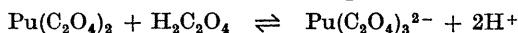
in water at $25°$ is $K = \dfrac{[Pu(C_2O_4)_3{}^{2-}][H^+]^2}{[Pu(C_2O_4)_2][H_2C_2O_4]} = 25$ (concentrations in

g.-mols./l.). Thorium oxalate is similarly soluble in excess of oxalate. Neptunium dioxalate is also known.[42]

Acetates. The sexivalent ions of uranium, neptunium, and plutonium form isomorphous, easily-crystallised compounds $NaMO_2(OAc)_3$. This is a relatively insoluble salt of these ions, whose compounds are generally easily soluble. The solubility of sodium plutonyl acetate is 19·5 g./l. in water at $25°$, and is less in the presence of excess of sodium acetate.[60]

Acetylacetonates. The tetra-acetylacetonate of plutonium has been prepared and is isomorphous with the thorium compound. It is soluble in benzene or chloroform and can be sublimed under reduced pressure.[72]

8-Hydroxyquinoline (oxine) derivatives. The plutonyl oxine compound $PuO_2(oxine)_2,H(oxine)$, analogous to the uranyl compound,[16] and the dark-red $Pu(oxine)_4$ are known.[73]

Ferri- and ferro-cyanides.[74] Plutonyl nitrate gives a reddish-brown precipitate with potassium ferricyanide, probably $(PuO_2)_3[Fe(CN)_6]_2,xH_2O$. Potassium ferrocyanide reduces plutonium(VI) rapidly, but reduces plu-

[68] H. H. Anderson, MDDC 1127.   [69] *Idem*, MDDC 1407.
[70] D. F. Mastick and A. C. Wahl, MDDC 1761.   [71] W. H. Reas, MDDC 1218.
[72] J. S. Dixon and C. Smith, MDDC 1205.
[73] R. L. Patton, MDDC 1385.   [74] H. H. Anderson, MDDC 1434.

tonium(IV) only very slowly. Aqueous plutonium(IV) and potassium ferricyanide give a greyish-brown precipitate $Pu_3[Fe(CN)_6]_4,15H_2O$. Plutonium(IV) and potassium ferrocyanide, or plutonium(III) and potassium ferricyanide, give black precipitates, of apparently different solubility and water content ; they are both $PuFe(CN)_6,xH_2O$. The individuality of these two compounds is said to be uncertain, and indeed it would seem probable that they are the same compound with the resonance forms $Pu(III)Fe(III)(CN)_6$ and $Pu(IV)Fe(II)(CN)_6$, analogous to the Prussian blues, $NaFe(II)Fe(III)(CN)_6$. This is supported by the black colour of the compound. Plutonium(III) and potassium ferrocyanide gave a precipitate, from acid solution, of $HPuFe(CN)_6$.

Hydrides.—Uranium and plutonium metal both combine with hydrogen to give solid hydrides whose formulæ approximate to UH_3 and PuH_3. The hydrogen content is frequently lower than that required by these formulæ, but there is no evidence of a definite lower hydride. The absorption isotherms and kinetics of the reaction $2Pu + 3H_2 \rightleftharpoons 2PuH_3$ have been examined.[75, 76] It is remarkable that the decomposition pressure of plutonium(III) deuteride may be 1·4 to 1·5 times that of the hydride at certain temperatures. The heat of reaction, calculated from the pressure–temperature curve, is 4·4 kcals./Pu atom at moderate temperatures. The structure of uranium(III) hydride has been examined by X-ray diffraction ; the uranium atoms have a cubic (β-tungsten) arrangement ; the hydrogen atoms cannot of course be located directly. R. E. Rundle [77] believes that U–H–U bridges occur, with one pair of valency electrons available in each bridge, $i.e.$, to the two U–H bonds. This conclusion is supported by L. Pauling and F. J. Ewing [78] who calculate that such a structure would agree with the observed cell dimensions.

Nitrides.—Plutonium nitride PuN can be made by the action of ammonia on the trichloride, trihydride, or metal at high temperatures.[79] Under these conditions no other nitride is formed. Uranium [80] gives a nitride UN, and also U_2N_3 and UN_2.

Carbides.—Carbides PuC and UC are known. All these mono-nitrides carbides, and oxides have the sodium chloride type of structure [43, 81] with the following lattice dimensions (in A.) :

	U.	Np.	Pu.	Am.
MC	4·951	—	4·910	—
MN	4·880	—	4·895	—
MO	4·92	5·00	4·948	4·95

[75] I. B. Johns, MDDC 717.
[76] J. E. Burke, AECD 2124.
[77] J. Amer. Chem. Soc., 1947, **69, ** 1719.
[78] Ibid., 1948, **70, ** 1660.
[79] B. M. Abraham, N. R. Davidson, and E. F. Westrum, MDDC 1640.
[80] R. E. Rundle, N. C. Baenziger, and A. S. Wilson, J. Amer. Chem. Soc., 1948, **70, ** 3299.
[81] W. H. Zachariasen, AECD 2195.

Borohydrides.—Aluminium borohydride reacts with heavy-metal tetrahalides to give volatile borohydrides, of which the following have been identified :

$Th(BH_4)_4$	$U(BH_4)_4$	$Np(BH_4)_4$	? $Pu(BH_4)_4$
	$U(BH_4)_3$		
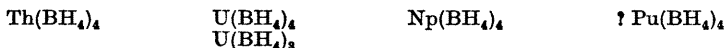
These borohydrides are stable in the cold and in air, but are hydrolysed by water with evolution of hydrogen. When heated they decompose to give borides. Their vapour pressures are of the order of 0·1 mm. Hg at room temperature. The composition of the plutonium compound is uncertain ; it was prepared from plutonium tetrafluoride and aluminium borohydride, but its formula has not been definitely established.

Structure of the Heavy-metal Atoms

As was mentioned in the introduction, the heavy elements from actinium onwards might follow the sequence of the second long period owing to filling of $6d$ orbits, or the sequence of the third long period (rare earths) owing to filling of the $5f$ shell, or some modification of the sequence of the third long period owing to the filling of the $5f$ shell starting at some relatively later element. In the chemistry of these elements it is evident that thorium behaves as a group 4 element, protoactinium (probably) as a group 5 element, and uranium predominantly as a member of group 6. After this the sequence differs entirely from the second long period, and neptunium to curium are not analogues of rhenium and the platinum metals, but instead resemble uranium and to some extent the rare earths. There is a strong similarity between these elements when they are in the same valency state ; thus uranium(VI), neptunium(VI), and plutonium(VI) are similar ; so are thorium(IV), uranium(IV), neptunium(IV), and plutonium(IV) ; and actinium(III), plutonium(III), americium(III), curium(III), and, to a lesser extent, the easily oxidised uranium(III) and neptunium(III). Thus the properties of, for instance, uranium(IV), apart from its oxidation to uranium(VI), closely resemble those of thorium(IV), and are not very like those of tungsten(IV). We have good chemical evidence for the presence of $5f$ electrons in uranium and the succeeding elements. The oxidation–reduction relations, as was explained above, are also consistent with the presence of $5f$ electrons if these are assumed to be less firmly held than $4f$ electrons (at least at first) and to provide relatively less screening of the nuclear charge, so that the oxidation–reduction relations alter more rapidly along the series.

Finally we may review briefly the physical evidence that bears on this point. The atomic spectra of thorium and uranium have been examined. Thorium [82] has its four valency electrons in $6d^27s^2$; uranium [83] has its six valency electrons in $5f^36d^17s^2$. Thus in uranium, and presumably in succeeding elements, $5f$ levels are in fact occupied. The fact that uranium

[82] W. F. Meggers, *Science*, 1947, **105,** 514 ; quoting P. Schuurman, Thesis, Amsterdam, 1946.

[83] C. C. Kiess, C. J. Humphreys, and D. D. Laun, *J. Res. Nat. Bur. Stand.*, 1946, **37,** 57.

has three $5f$ electrons suggests that the starting place of the series is two places earlier, namely at thorium ; but this is largely an artificial point of view, since it assumes a regularity that need not, and in fact does not, exist.

Further evidence for $5f$ structures comes from the absorption spectra of the heavy-element compounds and, particularly, from their resemblances therein to the rare earths. It is well known that the colours of the ter-valent rare-earth ions are due to transitions amongst $4f$ levels ; this is shown by the great sharpness of the absorption bands, since the $4f$ levels are shielded by the $5s$ and $5p$ electrons from disturbance by the fields of surrounding molecules ; and by their relatively low intensity, having regard to the narrowness of the bands, since these are " forbidden " transitions in the sense that the l quantum numbers do not change. The absorption spectra of the heavy-element ions also give narrow absorption bands, which are to be interpreted as transitions between $5f$ levels. (See, for instance, plutonium,[5] neptunium,[13] or americium spectra.[31]) The spectra of the tervalent ions in some cases somewhat resemble those of the " correspond-ing " rare-earth ions, i.e., uranium(III) and neodymium(III) ; plutonium(III) and samarium(III) ; and, particularly, americium(III) and europium(III).[84] The resemblance of the spectra of americium and europium trichloride, which were examined in the crystal, is evidence of six $5f$ electrons in the former, but no detailed analysis of the spectra has yet been published.

The ions of the heavy elements, like those of the rare earths, are fre-quently paramagnetic.[85, 86, 87] Thorium(IV) ions, having a rare-gas struc-ture, are, of course, diamagnetic, and the uranyl ion has a small, temperature-independent paramagnetism. As a result of measurements in solution the following values of the magnetic moments, in Bohr magnetons, were obtained :

Ion.	No. of electrons above Rn core.	Moment.	Ion.	No. of electrons above Rn core.	Moment.
NpO_2^{2+} . .	1	2·40	U^{3+} . . .	3	3·20
NpO_2^+ . .	2	2·96 [a, b]	Np^{4+} . . .	,,	3·03
,,	,,	3·08 [b]	Pu^{4+} . . .	4	1·85
PuO_2^{2+} . .	,,	2·95	Pu^{3+} . . .	5	0·90
U^{4+} . . .	,,	2·91	Am^{3+} . . .	6	0·8 [c]

[a] Measured at 0—55° ; $\Delta = 18\cdot5°$.
[b] Refs. 85 and 86.   [c] Small sample used.

These results are mostly from measurements at room temperature only, and the calculated values of the moment assume that Δ in the Weiss–Curie law is zero. Analogous measurements on the rare-earth ions show

[84] S. Fried and F. J. Leitz, AECD 1890.
[85] J. J. Howland and M. Calvin, AECD 1895.
[86] C. A. Hutchison and N. Elliot, AECD 1896.
[87] R. W. Lawrence, J. Amer. Chem. Soc., 1934, 56, 776.

that Δ may be appreciable even in magnetically-dilute materials, so that the values of some of these moments may need some modification, probably upwards. The general trend of these values closely follows that of the rare-earth ions :

Ion (all 3+) :	Ce	Pr	Nd	—	Sm	Eu
Electrons above xenon core :	1	2	3	4	5	6
Moment :	2·39	3·47	3·52	—	1·58	3·54

In addition to these results in solution various solid compounds have been measured : e.g., uranous oxalate trihydrate [88], 3·66 ; uranous sulphate [86], 3·46 ; uranous acetylacetonate [86], 3·39 ; UF_4 [89], 3·30 ; UO_2 [47], 3·19. These moments are all given in Bohr magnetons ; the susceptibilities were measured over a range of temperature and obeyed the Weiss–Curie law, $\chi(T + \Delta) = C$, where χ is the magnetic susceptibility.

The moments of the rare-earth ions have been well explained by H. J. Van Vleck [90] on the assumption that all electrons above the inert-gas core are in $4f$ orbits, and that the spin-orbital coupling is not disturbed. The agreement of the moments of the ions NpO_2^{2+} and Ce^{3+} makes it probable that neptunium here has one $5f$ electron (ground state $^2F_{5/2}$). The moments of the U^{4+}, NpO_2^+, and PuO_2^{2+} compounds differ somewhat, but in general they are lower than that of Pr^{3+} compounds. This may be due to the strong interaction of neighbouring atoms suppressing the contribution of the orbital momentum, so that only the spin is effective. In such a case an atom containing n unpaired electrons will have a moment of $\sqrt{n(n+2)}$ which is 2·83 in these ions, and the moments of various uranium(IV), neptunium(V), and plutonium(VI) compounds are not much above this value. However, such interaction would be more probable for $6d$ than for $5f$ electrons, and these low values provide some support therefore for $6d$ structures. On the other hand, if the uranous ion had a $6d^2$ structure in which L–S coupling were preserved, ground state $^3F_2$, the calculated moment would be 1·63, much lower than any of the observed values. The observed values are indeed usually somewhat higher, particularly for the uranous compounds, than the " spin only " moment ; and also the Δ values, where these are known, are large and positive, so that unless this constant is also measured the observed moments will really be too low. Moments of uranium tetrafluoride and dioxide are undoubtedly nearer the spin-only value, but these are of course the most magnetically concentrated substances. The uranous sulphate and oxalate moments are in agreement with a $5f^2$ structure. The values for the Np^{4+} and U^{3+} ions are also lower than that calculated for three $5f$ electrons and L–S coupling, ground state $^4I_{9/2}$, namely 3·62 ; and here the spin-only formula gives a higher value of 3·87, whilst structures involving $6d$ electrons would give values much lower than those observed. This is also true of the Pu^{4+} ion. The values for Pu^{3+} and Am^{3+} ions fall much below those of Sm^{3+} and Eu^{3+} ; but it will be

[88] C. A. Hutchison and N. Elliot. Phys. Reviews, 1948, 73, 1229.

[89] N. Elliot, ibid., 1949, 76, 431.

[90] " Theory of Electric and Magnetic Susceptibilities ", Oxford, 1932.

remembered that Van Vleck and Frank in their calculation of the moments of latter ions had to assume that the multiplet intervals were comparable with kT, so that states above the ground state are appreciably contributing. The other moments are calculated assuming multiplet intervals large compared with kT : this would lead to a value of 0·84 for Sm^{3+} and 0·0 for Eu^{3+}. Consequently the moment of Pu^{3+} agrees with a $5f^5$ structure (ground state $^6H_{5/2}$) with wider multiplet spacing ; and the value for Am^{3+} is probably also best explained as a $5f^6$ structure (ground state $^7F_0$) with multiplet intervals somewhat wider than those of the europium ion ; but detailed calculations have not yet been published. Thus the magnetic evidence taken as a whole undoubtedly supports the $5f$ structures for the transuranic compounds.

The crystal structures of a number of series of analogous heavy-element compounds have been determined by X-ray diffraction, and from these radii for the heavy-element ions have been deduced assuming values for the radii of the associated ions.[21, 91] The series most fully investigated are the trifluorides, trichlorides, tribromides, and dioxides. The radii (A.) so obtained are as follows :

	Ac.	Th.	Pa.	U.	Np.	Pu.	Am.
3+ ion . . .	1·11	—	—	1·04	1·02	1·01	1·00
M–O distance in MO$_2$ . . .	—	2·42	—	2·36	2·35	2·33	2·32

Whilst these absolute radii depend on the values chosen for the radii of the halide ions, their relative values are unambiguously determined by the X-ray data. It will be seen that a steady fall takes place with rising atomic number, and this of course parallels the behaviour of the rare-earth compounds.

Corresponding figures for the rare-earth 3+ ions, using the same halide radii, are :

	La.	Ce.	Pr.	Nd.	—	Sm.	Eu.
3+ ion . . .	1·04	1·02	1·00	0·99	—	0·98	0·97

In addition, the cell dimensions have been found to show a similar contraction in other series of heavy-metal compounds, such as $NaMO_2(OAc)_3$, KM_2F_9, where M is the heavy element ; and indeed this contraction seems to be quite general. The cause of this phenomenon is no doubt the same as in the rare-earth group, *viz.*, that the ionic size is determined by the quantum numbers of the outermost electrons and by the effective nuclear charge (*i.e.*, the nuclear charge minus the screening effect of the other

[91] W. H. Zachariasen, MDDC 1572.

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electrons) in which they are held.   In the heavy-metal ions, if we assume that their structure is similar to that of the rare-earth ions, the outermost electrons are always in the completed $6p$ sub-shell, and the effective nuclear charge rises with the atomic number, since the screening effect of the extra electrons in the $5f$ shell does not entirely compensate for the increased nuclear charge.   Hence this contraction is in fact evidence for the $5f$ theory of the structure of the heavy-metal compounds.   It will also be seen that the contraction is somewhat more rapid in the heavy metals than in the rare earths, which is at least consistent with the more rapid alteration of the oxidation–reduction potentials.