corresponds to a mean distance of about 8.5 Å. between neighboring ions. This value of mean distance is not unreasonable if we recall that the crystallographic ionic radii of Na^+, K^+ and Cl^- are 0.95 1.33 and 1.81 A., respectively, and that the average length of water molecules in pure water is about 3 Å.

When the concentration of salt solution is so high that the ions can no longer get enough water molecules from the system to become fully hydrated, one may expect the oppositely charged ions to share their water of hydration or even to form pairs by direct contact of bare ions. Under such circumstances, one may expect the activation energy for "tracer-diffusion" to be so high that the diffusion coefficients may be very much smaller than the corresponding values at infinite dilution. However, since in these highly concentrated solutions the ions are no longer fully hydrated, they would diffuse with a smaller mass, and hence faster inherent velocity. It is not possible to decide which of these two effects dominates by making "tracer-diffusion" measurements in potassium chloride solution in this concentration range because of it low solubility. Preliminary measurement shows that the "tracer-diffusion" coefficient of Na^+ in 12 molal lithium chloride solution is about one-fifth as large as that in infinitely dilute solution, indicating that the effect of increase of activation energy discussed above is the dominating one. However, more experimental work is desirable before definite conclusions can be drawn for "tracer-diffusion" in concentrated electrolytic solutions. Measurements of the diffusion of various tracer-ions in different salt solutions at various concentrations and temperatures are in progress in this Laboratory. The results will be reported in subsequent articles of this series.

Acknowledgment.—The author is indebted to Professor H. S. Harned whose constant encouragement and support made the present work possible, and to Professor J. G. Kirkwood who read and commented on the manuscript. He should thank Professor H. C. Thomas for kindly providing facilities for handling radioactivity. He is also indebted to Professor J. W. Kennedy and Mr. A. M. Friedman who first brought to his attention the problem of Δl-correction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Heats of Reaction of Some Oxides of Americium and Praseodymium with Nitric Acid and an Estimate of the Potentials of the Am(III)–Am(IV) and Pr(III)–Pr(IV) Couples[1]

BY L. EYRING,[2] H. R. LOHR AND B. B. CUNNINGHAM

The heats of reaction at 25° of $Pr_2O_{3(c.C\ form)}$ with 6.02 *M* and 1.00 *M* nitric acid, of $PrO_{2(c)}$ with 6.02 *M* nitric acid and 6.02 *M* nitric acid–0.1 *M* fluoboric acid, and of AmO_2 with 6.02 *M* nitric acid–0.1 *M* fluoboric acid have been measured. From these measurements and other thermodynamic data heats of formation of $Pr^{+3}{}_{(aq)}$, $Pr(NO_3)_{3(aq)}$, $Pr(NO_3)_{3(aq.\ in\ HNO_3.54H_2O)}$, $Pr(NO_3)_{3(aq.\ in\ HNO_3\cdot 7.5H_2O)}$, $Pr(NO_3)_{3(aq,\ in\ HNO_3\cdot 0.017HBF_4\cdot 7.5H_2O)}$, $PrO_{2(c)}$, $Am^{+4}{}_{(aq)}$ and $AmO_{2(c)}$ are calculated. From these data and estimated entropy values the potentials of the couples: $Am^{+3}{}_{(aq)} + H^+{}_{(aq)} = Am^{+4}{}_{(aq)} + {}^1/_2H_{2(g)}$, and $Pr^{+3}{}_{(aq)} + H^+{}_{(aq)} = Pr^{+4}{}_{(aq)} + {}^1/_2H_{2(g)}$ are estimated to be −2.4 volts and −2.9 volts, respectively, with an uncertainty of about ±0.2 volt in each case.

It has been shown previously[3] that the potential of the Am(III)–Am(IV) couple in acid solution is more negative than −2.0 volts. The work described in this paper was undertaken to evaluate the magnitude of the potential more precisely. The chemistry of americium is of special interest in that it is the first of the transuranium elements in which the stability of the tripositive state is comparable to that observed for some of the lanthanide elements.

In the course of development of this work it was necessary to use a substitute material as a "stand-in" in perfecting the techniques which were intended ultimately to be applied to americium, which is available in very limited quantities. Praseodymium was chosen for this purpose because of a convenient similarity in the chemical properties of its dioxide to that of americium. The work reported here thus permits an approximate evaluation of the potential of the (III)–(IV) couple of praseodymium as well as that of americium.

Since it was known that the potential of the americium couple was so negative as to make the tetrapositive state unstable in acidic aqueous solution, it did not appear feasible to measure the potential in the conventional manner by incorporating the couple in a reversible chemical cell.

We chose, therefore, to evaluate the free energy of this reaction by the less accurate method of evaluating its heat and estimating the entropy change.

Unless otherwise noted, our ΔH and ΔS values refer to a temperature of 298° K. Results are expressed in kcal./mole for the reaction as written.

Accepted values for entropies, heats of formation, etc., are those given in "Selected Values of Chemical Thermodynamic Properties" (hereafter abbreviated SVCTP), issued by the National Bureau of Standards.

Our results are not corrected to unit activities, since the activity coefficients of the +3 and +4

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[1] Presented at the 118th Meeting of the American Chemical Society at Chicago, Illinois, September, 1950.

[2] Now at the Department of Chemistry and Chemical Engineering, State University of Iowa, Iowa City, Iowa. Part of the data reported here was included in a dissertation submitted by L. Eyring to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Cunningham, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 19.2 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

ions in our solutions are not known. Such corrections probably are negligible compared with our experimental errors.

Experimental Method

Preparation of Compounds. A. $Pr_2O_3(c)$.—The praseodymium used in the experiments described herein was obtained as "Pr_6O_{11}" from Johnson, Matthey and Co., Ltd., of London. This material was found to contain about 4% of sodium and potassium, and one-half of one per cent. of other rare earths, principally neodymium. The relatively pure oxide was further purified by D. C. Stewart and R. C. Lilly of this Laboratory by a cation-exchange column separation procedure using Dowex-50 resin.

The praseodymium from the column runs was precipitated as oxalate from 0.1 *M* HCl—0.25 *M* NH_4Cl—0.25 *M* citric acid solution by the addition of oxalic acid to give a concentration of 0.1 *M*. The praseodymium oxalate in a platinum container was ignited in air at 650° to produce the black oxide, "Pr_6O_{11}." This oxide constituted the stock material from which the succeeding praseodymium calorimeter samples were prepared. No impurities were detected by spectrographic analysis of a 50-μg. sample of this material. Elements analyzed for, and their limits of detection in micrograms, were as follows: Al, 0.01; Ba, 0.1; Be, 0.005; Ca, 0.1; Ce, 0.1; Dy, 0.1; Er, 0.1; Eu, 0.01; Fe, 0.05; Gd, 0.1; Ho, 0.1; K, 0.1; La, 0.01; Lu, 0.01; Na, 0.1; Nd, 0.05; Sm, 0.1; Sr, 0.01; Ta, 0.5; Tb, 0.1; Yb, 0.01; Y, 0.01.

A sample of oxide in a platinum container was placed in a vacuum system and pumped down to remove adsorbed moisture and gases. Pure hydrogen ($^1/_3$ atm. pressure) was then admitted from a tube of uranium hydride maintained at 360°.

The oxide charge was heated to 500° and maintained at that temperature throughout the reduction. After two or three minutes the black oxide began to change to yellow-green Pr_2O_3. From time to time the sample container was removed from the reduction apparatus, capped and weighed on an Ainsworth FDJ microbalance. No further decrease in weight was observed after one hour of heating with hydrogen. Therefore, an apparently adequate time of one and one-half hours was adopted for the reduction to Pr_2O_3 for calorimetric measurements. X-Ray diffraction results on this material showed it to be the cubic "C" form with a = 11.14 ± 0.01 Å. When the temperature of this product was increased to 1000° in vacuum it changed over to the pale green hexagonal "A" form with a = 3.859 ± 0.003 Å., c = 6.008 ± 0.003 Å. If the Pr_6O_{11} was reduced at 1000°, the "A" form was produced directly. Praseodymium sesquioxide ("C" form) prepared as described above was removed immediately into the dry atmosphere of a nitrogen-filled "dry box." There it was quickly loaded into weighed sample bulbs and sealed off with Apiezon "W" wax ready for reweighing and calorimetric runs. The weighings were carried out on an Ainsworth FDJ Microbalance.

B. $PrO_{2(c)}$.—Praseodymium dioxide was prepared from the sesquioxide by heating the latter in a quartz bomb in a high pressure of oxygen gas.

The bomb consisted of a thick-walled quartz tube of about 8 mm. o.d. and 2–3 mm. i.d. with a rounded bottom and a constricted portion at the other end. The constriction ensured a thick wall when the end was sealed.

After the bomb was loaded with Pr_2O_3 the open end was attached to a system which was alternately evacuated and flushed with oxygen gas previously purified by passage through a copper coil immersed in an alcohol–liquid nitrogen mixture. Finally, with oxygen in the system, the end of the bomb was dipped in liquid nitrogen and oxygen was liquefied in an amount previously calculated to produce 100 atmospheres pressure in the tube at 500°. At this point the bomb was sealed off with a gas–oxygen flame. The quartz bomb was then placed in a stainless steel jacket which served as protection in case of an explosion. The complete assembly was put into a muffle furnace and heated at 500° for 8–12 hours. The resulting product was a reddish-black monophasic substance having a fluorite type structure, with a = 5.395 ± 0.005 Å.

The oxide was transferred to a small phosphorus pentoxide desiccator inside a "dry box" ready for loading into weighed calorimeter bulbs. Bulbs and samples were weighed on a quartz fiber balance similar to that described by Kirk, Craig, Gullberg and Boyer.[4]

C. Am_2O_3 and AmO_2.—The americium used in these experiments was obtained from β^--decay of Pu^{241} produced by successive (n, γ) reactions on Pu^{239} irradiated with pile neutrons.[5]

The separation, concentration and purification of americium from a source of this kind has been described elsewhere.[3] The results of a spectrographic analysis of our americium stock solution are given in Table I. The symbol "<" signifies that the element was below the indicated limit of detection.

TABLE I

SPECTROGRAPHIC ANALYSES OF AMERICIUM STOCK SOLUTION MICROGRAMS PER 50 MICROGRAMS OF AMERICIUM

Al	<0.01	Ce	<0.1	K	<0.1	Ni	<0.01
Be	< .005	Cr	< .01	Mn	< .01	Pb	< .1
Ca	.02	Fe	< .1	Na	< .01		

The americium was precipitated with a small excess of pure oxalic acid and the dried oxalate decomposed in air at a temperature of 650°. This treatment produced a black dioxide which was very slowly soluble under all conditions tried. The black AmO_2 was reduced with hydrogen at 600°, in the apparatus previously described, forming a persimmon-colored (red-orange) compound which was identified as Am_2O_3 by X-ray diffraction analysis. The compound possessed the cubic "C" form rare earth sesquioxide structure, with a = 11.03 ± 0.01 Å. No evidence for the formation of AmO was obtained in these experiments.

The sesquioxide was heated in air at about 250° for one hour producing AmO_2 in a form which dissolved in 6 *M* HNO_3–0.1 *M* HBF_4 (but not in 6 *M* HNO_3 alone) in a sufficiently short time to be satisfactory for calorimetric measurements. The dioxide was identified by its X-ray diffraction pattern and was shown to be isostructural with PrO_2, PuO_2 and NpO_2, with a = 5.393 ± 0.005 Å. It has been shown by Asprey and Cunningham[6] that the composition of the oxide obtained under these conditions is $AmO_{1.98 \pm 0.02}$. The americium dioxide was loaded into calorimeter bulbs inside a protective dust box.

Bulbs and samples were weighed on a simple quartz fiber cantilever balance, similar to that described by Cunningham.[7]

Calorimeter Measurements.—The microcalorimeter used for the heat measurements was that described by Westrum,[8] and Westrum and Eyring.[9] It was not suited to the measurement of heats developed over a time longer than a few minutes. It was essential, therefore, that the calorimeter reactions occur rapidly, and consequently solvents and methods of preparing the compounds were chosen to meet this requirement.[10]

The results of the determination of the heats of reaction of the several oxides with various solvents are given in Table II.

Calculations

A. **The Heat of Formation of $Pr^{+3}_{(aq)}$.**—From our measurements of the heat of reaction of $Pr_2O_{3(c)}$ with 6.02 *M* and 1.00 *M* nitric acid, and the value −109.5 kcal./mole re-

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(4) P. L. Kirk, R. E. Craig, J. E. Gullberg and R. Q. Boyer, *Anal. Chem.*, **19**, 427 (1947).

(5) A. Ghiorso, R. A. James, L. O. Morgan and G. T. Seaborg, *Phys. Rev.*, **78**, 472 (1950).

(6) L. B. Asprey and B. B. Cunningham, to be published.

(7) B. B. Cunningham, *Nucleonics*, **5**, 62 (1949).

(8) E. F. Westrum, U. S. Atomic Energy Commission Declassified Document AECD-1903, 1948.

(9) E. F. Westrum, Jr., and L. Eyring, "The Heat of Solution of Neptunium Metal and the Heats of Formation of the Neptunium Chlorides. A Microcalorimeter for Heat of Solution Measurements." Presented at the 118th Meeting of the American Chemical Society, September, 1950.

(10) In general, oxides prepared at low temperatures dissolve much more rapidly than those prepared at higher temperatures, probably because of smaller particle size. It is recognized that the heat content of such finely divided material may be appreciably different (perhaps of the order of a kilocalorie) from that of oxide prepared at higher temperatures (W. F. Giauque, THIS JOURNAL, **71**, 3192 (1949)).

TABLE II

HEAT OF REACTION OF SOME OXIDES OF PRASEODYMIUM AND AMERICIUM WITH NITRIC ACID SOLUTIONS, AT 25°

Oxide	Solvent	Approx. weight of sample, mg.	Number of runs made	ΔH(kcal./mole) (mean ± mean dev.)
Pr_2O_3(c, C form)	1.00 M HNO_3	5	3	−97.1 ± 0.7
Pr_2O_3(c, C form)	6.02 M HNO_3	5	3	−106.0 ± .1
PrO_2(c)	6.02 M HNO_3	1	4	−42.4 ± .8[a]
PrO_2(c)	6.02 M HNO_3–0.1 M HBF_4	1	4	−42.0 ± .4[a]
AmO_2(c)	6.02 M HNO_3–0.1 M HBF_4	1	4	−30.4 ± .4[a]

[a] Uncorrected for the heat of vaporization of water into the O_2 liberated.

ported by Prandtl and Huttner[11] for this reaction in 7.16 M nitric acid we extrapolate to obtain −95.6 kcal./mole for the heat in infinitely dilute acid, with an estimated probable error of ±1.5 kcal./mole. This value is less negative by about 10 kcal./mole than that calculated for the reaction, using SVCTP data on Pr_2O_3 and $Pr^{+3}_{(aq)}$. Preliminary measurements[12] on the heats of reaction of lanthanum and praseodymium metals with 1.5 M HCl indicate that SVCTP data for the heats of formation of the aqueous tripositive ions of the lighter rare earths are too negative by several kilocalories. The SVCTP figure of −444.5 kcal./mole for the heat of formation of $Pr_2O_{3(c)}$, combined with our extrapolated heat of reaction with infinitely dilute nitric acid gives −167.6 kcal./mole for ΔH_f (heat of formation) of $Pr^{+3}_{(aq)}$, in satisfactory agreement with our data on the heat of solution of the metal. It should be pointed out that this value of ΔH_f for $Pr^{+3}_{(aq)}$ involves possible error in the ΔH_f of Pr_2O_3.

B. **The Heats of Formation of $Pr(NO_3)_{3(aq)}$, $Pr(NO_3)_{3(aq,\ in\ HNO_3\cdot 54H_2O)}$ and $Pr(NO_3)_{3(aq,\ in\ HNO_3\cdot 7.5H_2O)}$.**—From "A" above, the data of Table II and SVCTP for $Pr_2O_{3(c)}$, $H_2O_{(l)}$ and various dilutions of nitric acid.

ΔH_f of $Pr(NO_3)_{3(aq)} = -167.5–3(49.4) = -315.7$ kcal./mole

ΔH_f of $Pr(NO_3)_{3(aq,\ in\ HNO_3\cdot 54H_2O)} = -{}^1/_2(444.5 + 295.2 + 97.1 - 204.9) = -316.0$ kcal./mole

ΔH_f of $Pr(NO_3)_{3(aq,\ in\ HNO_3\cdot 7.5H_2O)} = -{}^1/_2(444.5 + 292.5 + 106.0 - 204.9) = -319.1$ kcal./mole

In these calculations we have neglected heat effects due to dilution of the 0.001 to 0.005 M solutions of praseodymium nitrate to infinite dilution in the solvents employed and to dilution of the solvents with water formed in the reaction, since they are smaller effects than the uncertainties of the measurements themselves.

C. **The Heat of Formation of $Pr(NO_3)_{3(aq,\ in\ HNO_3\cdot 0.017HBF_4\cdot 7.5H_2O)}$.**—From "B" above and the data of Table II, the heat of formation of $Pr(NO_3)_{3(aq,\ in\ HNO_3\cdot 0.017HBF_4\cdot 7.5H_2O)}$ is taken to be $-319.0 + 0.4 = -318.7$ kcal./mole.

D. **The Heat of Formation of $PrO_{2(c)}$.**—From $PrO_{2(c)} + 3HNO_{3(HNO_3\cdot 7.5H_2O)} = Pr(NO_3)_{3(aq.\ in\ HNO_3\cdot 7.5H_2O)} + 3/2H_2O_{(l)} + {}^1/_4O_{2(g)}$, $\Delta H = -42.4$ kcal./mole.[13] Using −319.1 kcal./mole for the heat of formation of $Pr(NO_3)_{3(aq.\ in\ HNO_3\cdot 7.5H_2O)}$, ΔH_f of $PrO_{2(c)} = -(319.1 + 102.5 - 42.4 - 146.3) = -232.9$ kcal./mole. The value is in reasonable agreement with −234.0 kcal./mole given in SVCTP.

E. **The Heat of Formation of $Pr^{+4}_{(aq)}$.**—The heat of the reaction: $PrO_{2(c)} + 4H^+_{(aq)} = Pr^{+4}_{(aq)} + 2H_2O_{(l)}$, cannot be measured directly, because Pr^{+4} is reduced instantly in acidic aqueous solutions. However, we believe that the heat will not differ by more than a few kilocalories/mole from that of the corresponding plutonium reaction. For the latter reaction, a calculated heat of −12.6 kcal./mole is obtained from SVCTP. That the corresponding praseodymium reaction should have a similar heat seems probable, since PuO_2 and PrO_2 are isostructural, typically ionic compounds having nearly the same lattice parameters. We wish to point out that the estimate of −12.6 kcal./mole for the heat of solution of PrO_2 is in very poor agreement with the heat of solution of CeO_2 calculated from the heat of formation of CeO_2 and $Ce^{+4}_{(aq)}$ given in SVCTP. However, the value given for the heat of formation of $Ce^{+4}_{(aq)}$ probably is derived from that for $Ce^{+3}_{(aq)}$, which may be considerably in error. From "D" above and the estimated heat of −12.6 kcal./mole for the solution of PrO_2, ΔH_f of $Pr^{+4}_{(aq)} = -(232.4 + 12.6 - 136.6) = -108.9$ kcal./mole.

F. **Oxidation Potential of the Pr(III)–Pr(IV) Couple.**—Combination of the values calculated in "A" and "E" gives $Pr^{+3}_{(aq)} + H^+_{(aq)} = Pr^{+4}_{(aq)} + {}^1/_2H_{2(g)}$, $\Delta H = +58.7$ kcal./mole.

An accurate value for the entropy of the reaction cannot be given, since the entropies of the praseodymium ions are not known. As a rough approximation it may be assumed that the difference in entropy between $Pr^{+3}_{(aq)}$ and $Pr^{+4}_{(aq)}$ is the same as the difference in entropy between $Pu^{+3}_{(aq)}$ and $Pu^{+4}_{(aq)}$, for which Connick and McVey give −46 e.u.[14] Since the ionic radii of Pr^{+3} and Pu^{+3} and of Pr^{+4} and Pu^{+4} are nearly the same, this approximation is not likely to be greatly in error, although the uncertainty is increased somewhat because magnetic contributions to the entropies of $Pu^{+3}_{(aq)}$ and $Pu^{+4}_{(aq)}$ cannot be calculated with certainty from available data. Within a few entropy units, however: $\Delta S = -46 + 15.6 = -30.4$ e.u. for the reaction of $Pr^{+4}_{(aq)}$ with hydrogen. The free energy of the reaction at 298°K. is therefore $58.7 + (298 \times 30.4)/1000 = 67.8$ kcal./mole, and the corresponding potential $-67.8/23.07 = -2.94$ volts.

In view of the many uncertainties in the thermodynamic data this value is approximate, with an estimated probable error of the order of ±0.2 volt.

G. **The Heat of Formation of $AmO_{2(c)}$.**—From Table II: $AmO_{2(c)} + 3HNO_{3(in\ HNO_3\cdot 0.017HBF_4\cdot 7.5H_2O)} = Am(NO_3)_{3(aq,\ in\ HNO_3\cdot 0.017HBF_4\cdot 7.5H_2O)} + {}^3/_2H_2O_{(l)} + {}^1/_4O_{2(g)}$, $\Delta H = -30.4$ kcal./mole.

Taking the difference between the heat of formation of $Am(NO_3)_{3(aq,\ in\ HNO_3\cdot 0.017HBF_4\cdot 7.5H_2O)}$ and $Am(NO_3)_{3(aq,\ in\ HNO_3\ \infty\ H_2O)}$ to be the same as the difference in the heats of formation of praseodymium nitrate in the corresponding solutions: $AmO_{2(c)} + 3HNO_{3(in\ HNO_3\cdot\infty H_2O)} = Am(NO_3)_{3(aq,\ in\ HNO_3\cdot\infty H_2O)} + {}^3/_2H_2O_{(l)} + {}^1/_4O_{2(g)}$; $\Delta H = -30.4 + 318.7 - 315.7 + 3(49.4 - 48.8) = -25.6$ kcal./mole. Using −163.0 kcal./mole for ΔH_f of $Am^{+3}_{(aq)}$, as found by Lohr and Cunningham,[12] ΔH_f of $AmO_2 = -239.9$ kcal./mole.

H. **The Heat of Formation of $Am^{+4}_{(aq)}$.**—The heat of the reaction: $AmO_{2(c)} + 4H^+_{(aq)} = Am^{+4}_{(aq)} + 2H_2O_{(l)}$, is taken to be −12.6 kcal./mole the same as that for the corresponding plutonium reaction considered in "E" above.

Using −239.9 kcal./mole for the heat of formation of AmO_2, ΔH_f of $Am^{+4}_{(aq)} = -(240.1 + 12.6 - 136.6) = -115.9$ kcal./mole.

J. **The Oxidation Potential of the Am(III)–Am(IV) Couple.**—From "H" above, and the value −163.0 kcal./mole for the heat of formation of $Am^{+3}_{(aq)}$: $Am^{+3}_{(aq)} + H^+_{(aq)} = Am^{+4}_{(aq)} + {}^1/_2H_{2(g)}$, $\Delta H = -115.9 + 163.0 = 47.1$ kcal./mole. The entropy of the reaction is taken to be −30.4 e.u. the same as that for the corresponding plutonium reaction $\Delta F = 47.1 + \dfrac{30.4 \times 298}{1000} = 56.2$ kcal./mole, and $E = \dfrac{-56.2}{23.07} = -2.44$ volts with an estimated uncertainty of about ±0.2 volt.

Discussion

Unfortunately the estimates of the potentials of the Pr(III)–Pr(IV) and Am (III)–Am(IV) couples carried out by the methods outlined above are far from precise. To a large extent this lack of precision arises because of the uncertainty in the estimates of the heats of solution of PrO_2 and AmO_2 to form the tetrapositive ions and water. Because of the rapidity of reduction of Pr(IV) and Am(IV) in acidic aqueous solution these heats are experi-

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(11) Prandtl and Huttner, *Anorg. allgem. Chem.*, [2] **149**, 235 (1925).

(12) H. Lohr and B. B. Cunningham, USAEC, AECD 2902, July 18, 1950, and H. Lohr and B. B. Cunningham, THIS JOURNAL, **73**, 2025 (1951).

(13) It has been shown by Prandtl and Huttner[10] that the only products of the reaction between PrO_2(c) and HNO_3(6) are $Pr(NO_3)_3$, H_2O and O_2.

(14) R. E. Connick and W. H. McVey, THIS JOURNAL, **73**, 1798 (1951).

mentally inaccessible and must be arrived at by indirect methods.

If accurate and extensive data on the heats of solution of other dioxides isostructural with AmO_2 and PrO_2 were available, the heats for these compounds probably could be estimated with considerable confidence. However, of the available data on the dioxides which have the fluorite-type structure only those on UO_2 and PuO_2 seem to be of acceptable accuracy. These data have been carefully reviewed by Brewer, Bromley, Gilles and Lofgren.[15]

The heats of solution of UO_2 and PuO_2 calculated from SVCTP are −13.3 and −12.6 kcal./mole, respectively. It seems probable that the heat for the corresponding americium reaction should be the same within a kilocalorie; it is more doubtful that this is the case for praseodymium.

Nevertheless, after making allowances for uncertainties of this kind, it is evident that the potentials of the Pr(III)-Pr(IV) and Am(III)-Am(IV) couples are negative as to make it difficult, if not impossible, to obtain observable concentrations of the uncomplexed tetrapositive ions in aqueous solution. This conclusion is consistent with the failure of numerous attempts. Presumably tetrapositive ions could be observed only in the presence of substances capable of forming very stable complex ions or very insoluble compounds with them.

In basic solution the exceedingly small solubility[16] of $Am(OH)_4$ would favor oxidation to the tetrapositive state, and presumably in 1 *M* OH^- such oxidation could be effected by moderately powerful oxidizing agents.

It is of interest to note that the potential of the Am(III)-Am(IV) couple is substantially more negative than that predicted by simple extrapolation from the corresponding uranium, neptunium and plutonium couples, which, among themselves, show a remarkably regular decrease of −0.81 ± 0.03 volt per unit increase in atomic number. This degree of regularity probably is fortuitous. Neither the ionization energy to form the tetrapositive from the tripositive ion nor the difference in energy of hydration of the tri- and tetrapositive ions would be expected to be linear functions of atomic number. For example in the sequence Sc, Ti, V, the first ionization potential initially changes but slightly and then drops by one volt. Or, in the sequence Al, Si, P, the first ionization potential increases initially by 2.2 volts and then increases by 2.8 volts. Although greater regularity might be expected for "f" electrons, especially in the middle region between the unfilled and half-filled shells, there is no reason to expect a linear variation. The irregularity in Sc, Ti and V probably arises from the closeness of the 4s and 3d levels, but the separation between the 5f and 6d levels in U and Pu is small also.

That the difference in hydration energies of the tri- and tetrapositive ions would not be a linear function of atomic number may be shown by a consideration of their atomic radii. For this purpose, in Fig. 1, we have plotted Zachariasen's[17] data on the crystal radii of the tri- and tetrapositive ions of the actinide elements. Since we are interested in the radii only as they apply to a series of isostructural hydrated ions, we have drawn smooth curves through the points. This is consistent with the fact that the lattice parameters of isostructural tripositive compounds of the rare earth elements, when plotted as a function of atomic number, fall on a smooth curve up to the point of the half-filled subshell. A second smooth curve extends from the half-filled to the completed subshell.

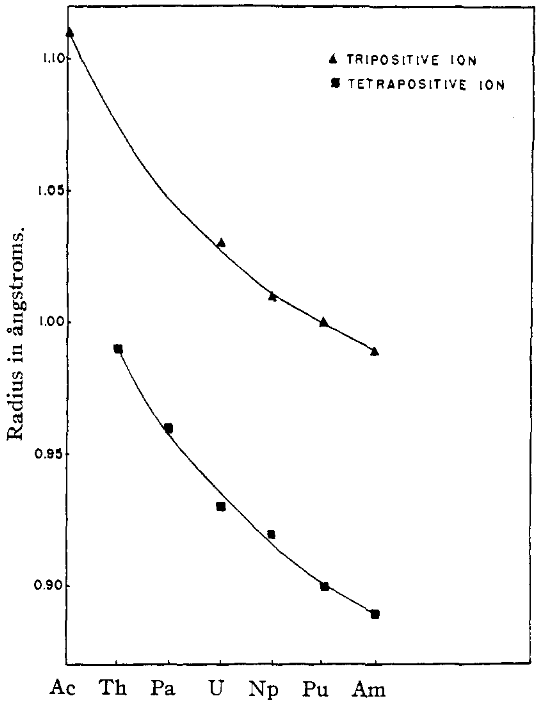

Fig. 1.—Ionic crystal radii of some actinide ions.

In the case of the actinide elements, considered as a "5f" series, their tripositive radii likewise should fall on a smooth curve up to and including curium. From similar reasoning the tetrapositive radii would be expected to lie on a smooth curve up to and including berkelium.

Thus, in Fig. 1, the radii are represented by two smooth curves, which, as is evident by inspection, show increasing divergence with increasing atomic number. This divergence is to be expected for the following reason. For any particular element the difference between the tri- and the tetrapositive radius represents the contraction resulting from the removal of an "f" electron from the tripositive ion. Since the screening effect of a single "f" electron for the outer electrons increases as the available "f" orbitals become more fully occupied (up to the $5f^7$ configuration), removal of an "f" electron produces a greater contraction as the atomic number increases.

It is of interest to compare the radii in another

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[15] L. Brewer, L. Bromley, P. Gilles and N. L. Lofgren, NNES 14B Paper 6.40, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

[16] W. M. Latimer, "Oxidation Potentials," Prentice-Hill, Inc., New York, N. Y., 1938, gives 10^{-50} for K_{sp} of $Th(OH)_4$ and 10^{-20} for K_{sp} of $La(OH)_3$. The solubility products of $Am(OH)_4$ and $Am(OH)_3$ would be expected to be less, respectively, although of a comparable order of magnitude.

[17] W. H. Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).

way by shifting the curve for the tetrapositive ions one atomic number to the left. The differences in ordinate values for the two curves now represent the contraction in radius produced by a unit increase in nuclear charge for pairs of isoelectronic ions having from zero to five electrons in the "5f" subshell. For the heavy elements, this contraction would be expected to be nearly uniform for the various ion pairs. The comparison thus represents a test of the validity of the curves shown in Fig. 1. It is found that the contraction is nearly uniform for pairs of isoelectronic ions.

Approximate values for the hydration energies may be obtained from the radii of Fig. 1 and the Born equation[18]

$$E_{\text{hyd}} = \frac{e^2}{2R}(1 - 1/D)$$

where E_{hyd} is the hydration energy, e the charge on the ion, R the distance from the center of charge to the center of the surrounding water dipoles, and D is the dielectric constant in the immediate neighborhood of the ion. For D we have used the somewhat arbitrary value of 3, and for R we have taken the crystal radii from the smooth curves of Fig. 1, plus 0.6 Å. for the water dipole. Coördination number corrections to the radii have been ignored. The values of the hydration energies calculated in this way are given in Table III. It is observed that the differences in hydration energies of the tri and tetrapositive ions diminish in a non-linear fashion with increasing atomic number.

TABLE III

DIFFERENCE IN HYDRATION ENERGY OF TETRAPOSITIVE AND TRIPOSITIVE IONS OF SOME ACTINIDE ELEMENTS

Element	$E_{\text{hyd}}^{+4} - E_{\text{hyd}}^{+3}$ (kcal./mole)	Change in $E_{\text{hyd}}^{+4} - E_{\text{hyd}}^{+3}$ for unit increase in atomic number (kcal./mole)
Pa	−532.0	
U	−542.0	−10.0
Np	−550.5	− 8.5
Pu	−557.5	− 7.0
Am	−562.7	− 5.2

Thus it seems unlikely that the oxidation potentials of the (III)–(IV) couples of the actinide elements should vary linearly with atomic number, even should the ionization potentials do so. The divergence of the Am(III)–Am(IV) potential therefore is scarcely surprising.

It is of interest to compare the oxidation potentials of the (III)–(IV) couples of cerium, praseodymium, plutonium and americium. The cerium–praseodymium pair show nearly the same difference in their (III)–(IV) potentials as do plutonium and americium. Since in this group of elements, ions of the same charge have nearly the same ionic radii, it might be concluded that the increase in ionization potential of the fourth electron between atomic numbers 58 and 59 is nearly the same as that between atomic numbers 94 and 95.

The value of the potential of the Am(III)–Am(IV) couple may be used to estimate the free energies of other reactions involving the tripositive and tetrapositive states.

For example, if we assume a constant difference between the heats of formation of the solid fluorides and the corresponding aqueous cations, we calculate from SVCTP data on neptunium that ΔHf of AmF_4 − ΔHf of AmF_3 = ΔH of $Am^{+4}{}_{(aq)}$ + ΔH of $NpF_{4(c)}$ − ΔHf of $Np^{+4}{}_{(aq)}$ = ΔH of $Am^{+3}{}_{(aq)}$ + ΔH of $NpF_{3(c)}$ − ΔHf of $Np^{+3}{}_{(aq)}$ = $-115.9 - 428 + 133.2 - (-163 - 360 + 127.3) = -15$ kcal./mole whence

$$AmF_{4(c)} \longrightarrow AmF_{3(c)} + {}^1/{}_2F_{2(g)},\ \Delta H_{298} = 15 \text{ kcal./mole}$$

The free energy functions for AmF_4 and AmF_3 are taken to be the same as those for the corresponding plutonium compounds[15] so that ΔS for the above reaction is equal to +15 e.u. and ΔF_{298} is equal to +10.5 kcal./mole.

It should be possible to prepare stable AmF_4 by treatment of the trifluoride with fluorine at moderately elevated temperatures, and to investigate the equilibrium experimentally.

Finally, it is emphasized that the data presented in this paper are concerned only with the tri- and tetrapositive states of americium and praseodymium, and hence restrict our considerations to these states alone.

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[18] M. Born, *Z. Physik*, 1, 45 (1920).