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HEATS OF REACTIONS OF SOME OXIDES OF AMERICIUM AND PRASEO-DYMIUM WITH NITRIC ACID AND AN ESTIMATE OF THE POTENTIALS OF THE Am(III)-Am(IV) AND Pr(III)-Pr(IV) COUPLES

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Chemistry-Transuranic Elements

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L. Eyring, B. B. Cunningham, and H. R. Lohr

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DECLASSIFIED

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PRASEODYMIUM WITH NITRIC ACID AND AN ESTIMATE OF
THE POTENTIALS OF THE Am(III)-Am(IV) AND
Pr(III)-Pr(IV) COUPLES

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Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

July 7, 1950

It has been shown previously¹ that the potential of the Am(III)-Am(IV) couple

(1) 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, 1949).

in acid solution is more negative than -2.0v. The work described in this paper was undertaken for the purpose of evaluating the magnitude of the potential more precisely. It seems scarcely necessary to remark that an extensive correlation of the chemical properties of an element is possible when its oxidation potentials are known. The chemistry of americium possesses 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 that a less costly and less hazardous material be employed as a "stand-in" in perfecting the techniques which were intended ultimately to be applied to americium. Praseodymium was chosen for this purpose, primarily because existing information indicated that the Pr(III)-Pr(IV) potential probably would not differ greatly from that of the corresponding americium couple. The work reported here permits a reasonably accurate evaluation of the potential of the (III)-(IV) couple of praseodymium as well as that of americium.

*Now at the Department of Chemistry, 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.

**Present address: Argonne National Laboratories, Chicago, Illinois.

Since it was known that the potential of the americium couple was so negative as to make the tetrapositive state highly unstable in 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 direct and somewhat 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, and values of ΔH and ΔS are given only to the nearest 0.1 kcal. or 0.1 e.u., consistent with the accuracy of the experimental measurements.

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

Our results are not corrected to unit activities, since the activity coefficients of the +3 ions in our solutions are not known. Consequently, our derived values are not designated as ΔH_f° values.

Such corrections probably are negligible compared with our experimental errors of several tenths of a kilocalorie.

EXPERIMENTAL

Preparation of $\text{Pr}_2\text{O}_3(\text{c})$ and Measurements of Its Heat of Reaction

With 6M Nitric Acid

Bichowski and Rossini² record data obtained by Prandtl and Huttner³ in 1925

(2) Bichowski and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York (1936).

(3) Prandtl and Huttner, Z. anorg. allgem. Chem. 149, 235 (1925).

on the heats of reaction of $\text{Pr}_2\text{O}_3(\text{c})$, $\text{Pr}_6\text{O}_{11}(\text{c})$, and $\text{PrO}_2(\text{c})$ with $\text{HNO}_3(6)$.

Because of the difficulty of obtaining pure samples of the rare earths prior to the development of modern ion exchange methods⁴ there is reason to question much

(4) Harris and Tompkins, J. Am. Chem. Soc. 69, 2792 (1947); Ketelle and Boyd, ibid., 2800; Spedding, Voigt, Gladrow, Sleight, Powell, Wright, Butler, and Figard, ibid., 2786.

of the early work on the chemistry of these elements. Our measurements on praseodymium were therefore made as accurately as possible with the equipment available to us.

The praseodymium used in the experiments described herein was obtained as "spectrographically pure Pr_2O_3 " from Johnson, Matthey and Co., Ltd., of London. This material was found to contain about four percent of sodium and potassium, and one-half of one percent of other rare earths, principally neodymium. This 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. No impurities were detected by spectrographic analysis of a 50 μg sample. Elements analyzed for, and their limits of detection in micrograms, were as follows: Al, 0.01; Ba, 0.1; Be, 0.005; Ca, 0.01; 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.

The praseodymium from the column runs was precipitated as oxalate from 0.1M HCl-0.25M NH_4Cl -0.25M H_3Cit solution by the addition of oxalic acid to 0.1M. The praseodymium oxalate was ignited in air to the black oxide usually called " Pr_6O_{11} ." The ignition was carried out in a platinum container at about 650°C. This oxide constituted the stock material from which the succeeding praseodymium calorimeter samples were prepared.

The oxide was placed in the hydrogen reduction apparatus shown in Fig. 1 and pumped down to remove all adsorbed moisture. The molybdenum radiation shield used to heat the oxide sample in the reduction apparatus was found to resist the action of hydrogen at these high temperatures to a much greater degree than

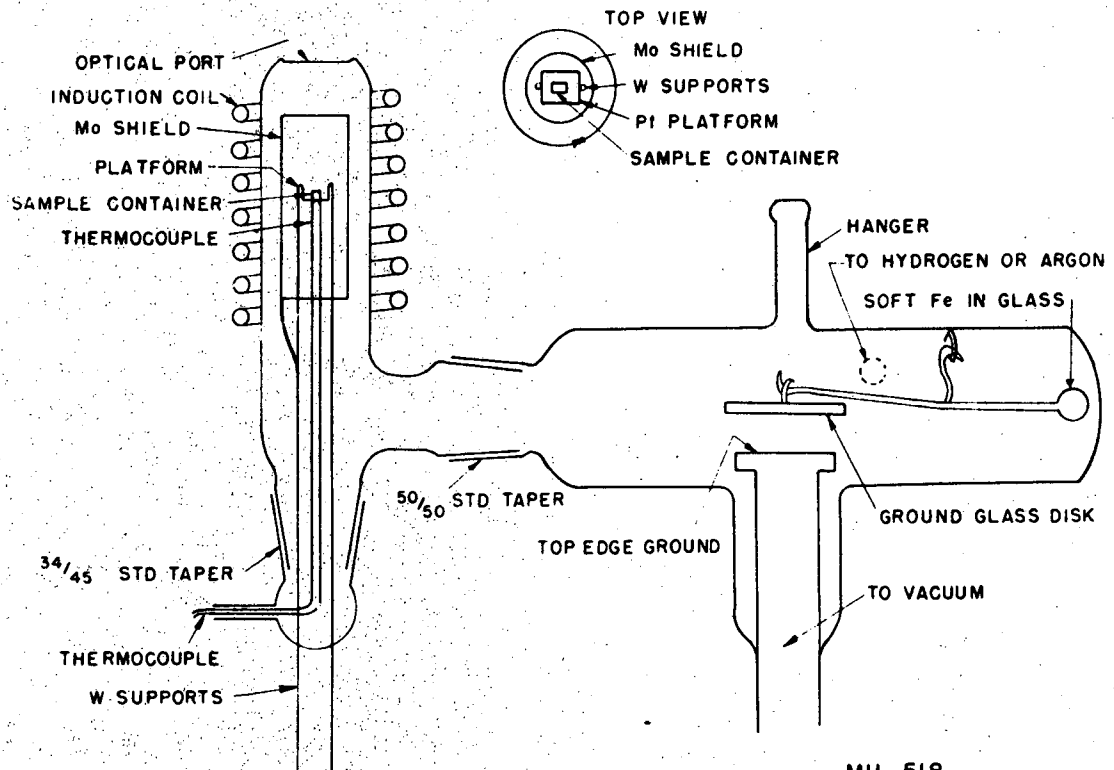
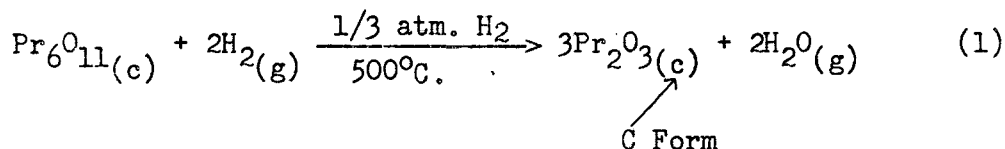


FIG. 1
HYDROGEN REDUCTION APPARATUS

MU 518

tungsten, tantalum, cold rolled steel or stainless steel. The chromel vs. alumel thermocouple was spot welded to the bottom of the platinum sample holder. About one-third atmosphere of pure hydrogen was admitted from a tube of uranium hydride maintained at 360°C.

The oxide charge was heated to 500°C. and maintained at that temperature throughout the reduction. After two or three minutes the black oxide began to change to yellow-green Pr₂O₃. 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 adequate time of one and one-half hours was adopted for the reduction to Pr₂O₃. X-ray diffraction results on this material consistently 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°C. 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 Pr₆O₁₁ was reduced at 1000°C., the A form was produced directly. The reaction at lower temperature may be represented as:



Praseodymium sesquioxide prepared as described above was removed immediately into the dry atmosphere of a nitrogen "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 a quartz fiber torsion balance similar to that described by Kirk, Craig, Gullberg, and Boyer.⁵ The

(5) Kirk, Craig, Gullberg, and Boyer, Anal. Chem. 19, 427 (1947).

instrument had a sensibility of ± 0.01 μg and an accuracy of calibration of ± 0.1%.

The microcalorimeter used for the heat measurements was that described by Westrum.⁶ It was not suited to the measurement of heats developed over a time

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

longer than a very few minutes. It was essential, therefore, that the oxides be prepared in readily soluble form.* Preliminary experiments mentioned below showed that AmO₂ could not be prepared in any form which would dissolve rapidly in nitric acid more dilute than 6M. Praseodymium sesquioxide prepared as described above was found to dissolve in 6.02M nitric acid in about two minutes. The first heat measurements were made, therefore, in 6.02M nitric acid.

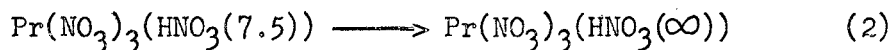
The results of the determination of the heat of solution of praseodymium sesquioxide in 6.02M HNO₃ at 25°C. are given in Table I.

Table I

Heat of Reaction of Pr₂O₃ (C form) with 6.02M HNO₃ at 25°C.

Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal./mole
1	7.312	2.355	-106.2
2	4.109	1.324	-106.3
3	4.539	1.459	<u>-106.0</u>
			-106.2 ± 0.2

In order to estimate the heat for the reaction:



additional measurements were made of the heat of reaction of Pr₂O₃(c) with 1.0M nitric acid. These measurements are summarized in Table II below:

*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 (Giauque, J. Am. Chem. Soc., 71, 3192 (1949)).

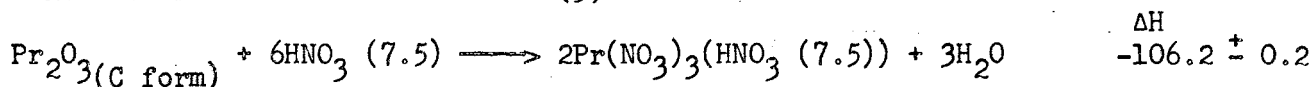
Table II

Heat of Reaction of $\text{Pr}_2\text{O}_3(\text{C form})$ with 1.0M HNO_3 at 25°C.

Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal./mole
1	3.825	1.136	-97.9
2	10.769	3.180	-97.4
3	3.081	0.897	<u>-96.0</u>
			-97.1 ± 0.7

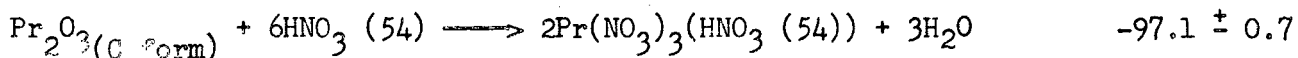
Hence we write:

(3)

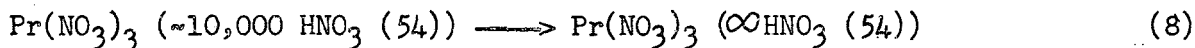
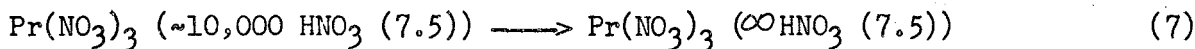
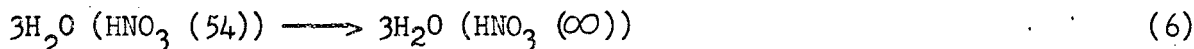
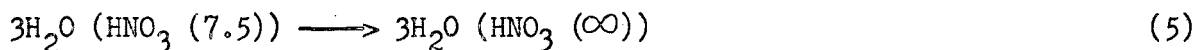


and

(4)



We neglect the heats for the following reactions:



From equation (3) we calculate the heat of formation of $\text{Pr}(\text{NO}_3)_3(\text{HNO}_3 (7.5))$ as:

$$1/2 (-106.2 + 3 \times 68.3 - 6 \times 48.8 - 444.5) = -319.3 \text{ kcal./mole}$$

and from equation (4) the heat of formation of $\text{Pr}(\text{NO}_3)_3(\text{HNO}_3 (54))$ as:

$$1/2 (-97.1 + 3 \times 68.3 - 6 \times 49.2 - 444.5) = -316.0 \text{ kcal./mole,}$$

based on values for the heats of formation of $\text{H}_2\text{O}(l)$, $\text{Pr}_2\text{O}_3(c)$, $\text{HNO}_3 (7.5)$

and $\text{HNO}_3 (54)$ taken from SVCTP. We estimate the heat of formation of $\text{Pr}(\text{NO}_3)_3(\text{aq})$

to be -315.5 kcal./mole at 298°K, and the heat of formation of $\text{Pr}^{+3}(\text{aq})$ to

be $-315.5 + 3 \times 49.4 = -167.3 \text{ kcal./mole.}$

Preparation of PrO₂ and Measurement of Its Heat of
Reaction with 6M Nitric Acid

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. OD and 2-3 mm. ID with a rounded bottom and a constricted portion at the other end. The constriction insured a thick wall when the end was sealed.

The Pr₂O₃ was loaded into the bomb and the open end attached to a system which was alternately evacuated and flushed with oxygen from which water and carbon dioxide were removed previously by passing the gas through a copper coil kept at -100°C. by an alcohol-liquid nitrogen mixture. Finally, with oxygen in the bomb, the end was immersed in liquid nitrogen and oxygen was liquified in an amount previously calculated to produce 100 atmospheres pressure in the tube at 500°C. 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 against a possible explosion. The complete assembly was put into a muffle furnace and heated at 500°C. for 8-12 hours. The resulting product was a reddish-black mono-phasic substance having a fluorite type structure, with $a = 5.395 \pm 0.005 \text{ \AA}$.

The oxide was transferred to a small phosphorus pentoxide desiccator inside a "dry box" ready for loading into calorimeter bulbs.

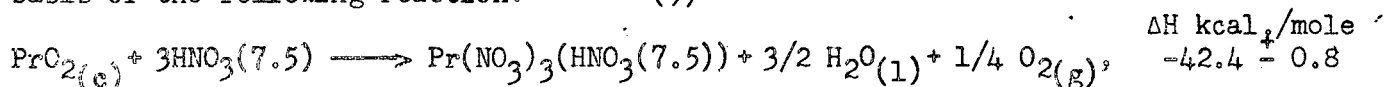
The results of calorimetric measurements on this material are given in Table III.

Table III
Heat of Reaction of PrO₂ with 6.02M HNO₃ at 25°C.

Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal/mole
1	1.0042	0.2381	-41.0
2	0.5712	0.1412	-42.8
3	0.4722	0.1186	-43.4
4	0.8412	0.2071	-42.6
			-42.4 \pm 0.8

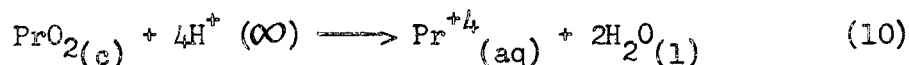
The solution time for these samples was from fifteen to twenty minutes and the drift correction amounted to some ten to twenty-five percent of the observed heat. This fact leads to a greater uncertainty than that indicated by the mean deviation given above.

From the above data we calculate the heat of formation of $\text{PrO}_2(\text{c})^*$ on the basis of the following reaction:** (9)



$$\Delta\text{Hf} = -319.3 - 102.4 + 146.4 + 42.4 = -232.9 \text{ kcal./mole}$$

We estimate ΔH_{298} for the reaction:



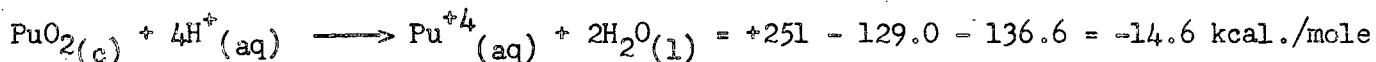
by analogy with the corresponding plutonium reaction, as follows.

Brewer, Bromley, Gilles, and Lofgren⁷ give for the heat of formation of

(7) Brewer, Bromley, Gilles, and Lofgren, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 6.40 (McGraw-Hill Book Co., Inc., New York, 1949).

$\text{Pu}^{+4}(\text{aq})$ and $\text{PuO}_2(\text{c})$ at 298°K , -129.0 and -251 kcal./mole, respectively, whence

ΔH_{298} for the reaction: (11)

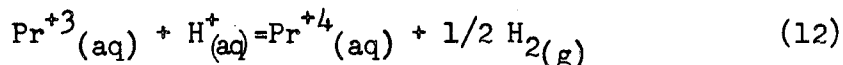


Since PuO_2 and PrO_2 have identical crystal structures and very nearly the same lattice dimensions, we believe that the difference between the lattice energy of PuO_2 and the energy of hydration of Pu^{+4} on the one hand and of PrO_2 and Pr^{+4} on the other will be nearly the same and that, therefore, the heat of reaction (10) will not differ from that of reaction (11) by more than a kilocalorie.

*X-ray diffraction measurements showed the lattice constant of the oxide produced by heating with high pressures of oxygen to be $5.394 \pm 0.002 \text{ \AA}$ as compared with $5.468 \pm 0.001 \text{ \AA}$ for " Pr_6O_{11} ." The decrease in lattice constant is that expected for complete oxidation to PrO_2 , within the experimental error of the measurements.

**It has been shown by Prandtl and Huttner¹ that the only products of the reaction between $\text{PrO}_2(\text{c})$ and $\text{HNO}_3(6)$ are $\text{Pr}(\text{NO}_3)_3$, H_2O and O_2 .

We therefore take the heat of reaction (10) to be -14.6 kcal./mole whence, from our calculated value of the heat of formation of $\text{PrO}_2(\text{c})$, we calculate the heat of formation of $\text{Pr}^{+4}(\text{aq})$ to be $-232.9 - 14.6 + 136.6 = -110.9$ kcal./mole. For the reaction:



$$\Delta H_{298} = -110.9 + 167.3 = +56.4 \text{ kcal.}$$

Estimation of ΔS for the Reaction $\text{Pr}^{+3}(\text{aq}) + \text{H}^+(\text{aq}) = \text{Pr}^{+4}(\text{aq}) + 1/2 \text{H}_2(\text{g})$

Our estimate of ΔS for reaction (12) is based on analogy with the corresponding plutonium reaction, which has been investigated by Evans.⁸ Evans reports

(8) Evans, ibid., Paper No. 3.30.

$$S_{\text{Pu}^{+4}} - S_{\text{Pu}^{+3}} = -48.0 \text{ cal./degree}$$

The work of Howland and Calvin⁹ on the magnetic susceptibilities of the

and
(9) Howland Calvin, J. Phys. Chem., in press.

plutonium ions indicates that about 0.3 e.u. of the ΔS value given above is due to a magnetic contribution. Correcting $S_{\text{Pr}^{+4}} - S_{\text{Pr}^{+3}}$ for the magnetic contributions, we estimate:

$$S_{\text{Pr}^{+4}} - S_{\text{Pr}^{+3}} = -48.3 - 0.8 = -49.1 \text{ cal./degree.}$$

Although the absolute entropies of Pr^{+3} and Pu^{+3} , of Pr^{+4} and Pu^{+4} will be somewhat different, we believe that ΔS for the two reactions will differ significantly only in the magnetic terms since the ionic radii of the corresponding ions are nearly the same, and the mass correction cancels. Hence we now write:

$\text{Pr}^{+3}(\text{aq}) + \text{H}^+(\text{aq}) = \text{Pr}^{+4}(\text{aq}) + 1/2 \text{H}_2(\text{g})$	ΔH_{298}	ΔS_{298}	ΔF_{298}
	kcal.	e.u.	kcal.
	+56.4	-49.1	+66.4
		+15.6	
		-33.5	

and $E = -\frac{\Delta F}{nF} = \frac{-66.4}{23.07} = -2.88\text{v}$

In the above calculations we have made no attempt to correct for activity coefficients since there are no satisfactory experimental data on which to base such a correction.

Preparation of AmO₂ and Measurement of its Heat of Reaction

The americium used in these experiments was obtained from β^- -decay of Pu²⁴¹ produced by successive (n, γ) reactions on Pu²³⁹ irradiated with pile neutrons.¹⁰

(10) Seaborg, Phys. Rev. 78, 472 (1950).

The separation, concentration, and purification of americium from a source of this kind has been described elsewhere.¹ The results of a spectrographic analysis of our americium stock solution are given in Table IV.

Table IV

Spectrographic Analysis
Micrograms per 50 microgram sample

Al <0.01	Fe <0.1
Be <0.005	K <0.1
Ca 0.02	Mn <0.01
Ce <0.1	Na <0.01
Cr <0.01	Ni < 0.01
	Pb <0.1

The americium was precipitated with a small excess of pure oxalic acid and the dried oxalate decomposed in air at a temperature of 650°C. This treatment produced a black dioxide which was very slowly soluble under all conditions tried. The black AmO₂ was reduced with hydrogen at 600°C. in the apparatus previously described, forming Am₂O₃ (identified by x-ray diffraction analysis). The sesquioxide is a bright persimmon (bright red-orange) colored compound.

No evidence for the formation of AmO , reported by Fried,¹¹ was obtained in these

(11) Fried, private communication (1948).

experiments.

The sesquioxide was heated in air at about 250°C . for one hour producing AmO_2 in a form soluble in 6M HNO_3 0.1M HBF_4 (but not in 6M HNO_3 alone) in a sufficiently short time to be satisfactory for calorimetric measurements. The dioxide possessed the same fluorite type structure as PrO_2 with $a = 5.393 \pm 0.005 \text{ \AA}$. It has been shown by Asprey and Cunningham¹² that the composition of the oxide obtained

(12) Asprey and Cunningham, to be published.

under these conditions is $\text{AmO}_{1.98 \pm 0.02}$.

Four runs were made in the calorimeter on AmO_2 yielding the values of ΔH indicated in Table V.

Table V

Heat of Reaction of AmO_2 with 6.0M HNO_3 , 0.1M HBF_4
at 25°C .

Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal./mole
1	0.834	0.09062	-29.7
2	0.672	0.07466	-30.3
3	1.177	0.1326	-30.8
4	1.449	0.1636	-30.8
			<u>-30.4</u> \pm 0.4

In order to investigate the possible heat effect of the fluoboric acid on the reaction we measured the heat of reaction of PrO_2 with HNO_3 (7.5), HBF_4 (550). The results are summarized in Table VI below.

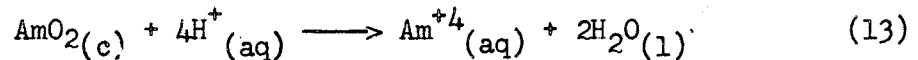
Table VI

Heat of Reaction of PrO_2 with 6.0M Nitric Acid,
0.1M Fluoboric Acid at 25°C.

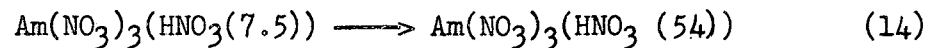
Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal./mole
1	0.827	0.2002	-41.9
2	1.430	0.3471	-42.0
3	1.229	0.3031	-42.7
4	1.177	0.2818	-41.4
			42.0 \pm 0.4

Within experimental error the mean value of the heat is the same as that found in HNO_3 (7.5) alone. We therefore assume that the heat of reaction of AmO_2 or PrO_2 with HNO_3 (7.5), HBF_4 (550) is not significantly different from that with HNO_3 (7.5) alone.

We take the heat for the reaction:



to be -14.6 kcal./mole, the same as that for the corresponding plutonium reaction, and the heat for the reaction



to be the same as that for the corresponding praseodymium reaction, namely +3.3 kcal./mole.

As in the case of praseodymium we neglect the heats corresponding to those reactions listed as (5), (6), (7), and (8) appearing in the section describing the measurement of the heat of reaction of $\text{Pr}_2\text{O}_3(\text{c})$ with six molar nitric acid.

Our estimate of the heat of the reaction: $\text{Am}^{+3}(\text{aq}) + \text{H}^+(\text{aq}) = \text{Am}^{+4}(\text{aq}) + 1/2 \text{H}_2(\text{g})$ (15) will therefore differ from that estimated for the corresponding praseodymium reaction only by the difference in the heats of reaction of PrO_2 and AmO_2 with

six molar nitric acid. This difference amounts to $+30.4 - 42.4 = 12.0$ kcals.

We therefore estimate ΔH_{298} for reaction (15) to be:

$$+56.4 - 12.0 = 44.4 \text{ kcal./mole}$$

Our estimate of ΔS_{298} for reaction (15) again is based on that for the corresponding plutonium reaction, after making a correction for magnetic entropy based on the work of Howland and Calvin.

Whence we estimate ΔS_{298} for reaction (15) to be:

$$-48.3 + 1.4 + 15.6 = -31.3 \text{ e.u.}$$

ΔF_{298} for reaction (15) is therefore :

$$44.4 + \frac{298}{1000} 31.3 = 53.7 \text{ kcal./mole,}$$

$$\text{and } E = \frac{-53.7}{23.1} = -2.32\text{v.}$$

DISCUSSION

Our calculations of the heats of formation of $\text{Pr}(\text{NO}_3)_3(\text{HNO}_3 (7.5))$, $\text{Pr}(\text{NO}_3)_3(\text{HNO}_3 (54))$ and of $\text{Pr}^{+4}(\text{aq})$ are all based on an accepted value of -444.5 kcal. for the heat of formation of $\text{Pr}_2\text{O}_3(\text{c})$. Any revision of this value will require a corresponding revision of our calculated values. Our justification for several estimations of ΔH and ΔS values by analogy between praseodymium, plutonium and americium is based on the fact that the ionic radii, structures and types of bonding in analogous compounds and ions of these elements are known to be closely similar.

It is evident that the potentials of the $\text{Pr}^{+3}-\text{Pr}^{+4}$ and $\text{Am}^{+3}-\text{Am}^{+4}$ couples are so negative as to make it difficult, if not impossible, to obtain observable concentrations of these ions in aqueous solution. This conclusion is consistent with the failure of numerous attempts¹ to obtain substantial concentrations of the $+4$ ion by oxidation in aqueous solution. Presumably such attempts could succeed only in the presence of complexing or precipitating agents capable of

forming very stable complexes or very insoluble compounds of the tetrapositive ion.

There is some evidence that oxidation of americium from the plus three to the plus four state can occur in the presence of peroxide in alkaline solution. This is not inconsistent with the potential of the peroxide-water couple and the estimated solubility products of $\text{Am}(\text{OH})_3$ and $\text{Am}(\text{OH})_4$, which would not be expected to be very greatly different than those listed by Latimer¹³ for $\text{La}(\text{OH})_3$ and $\text{Th}(\text{OH})_4$.

(13) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N.Y., 1938.

It is of some interest to compare the oxidation potential of the Am^{+3} - Am^{+4} couple with that of preceding elements of the actinide series. The data are summarized in Table VI below.

Table VI

Oxidation Potentials of the III-IV Couples
of Various Actinide Elements¹⁴

Couple	Potential (volts)
U(III)-U(IV)	+0.64
Np(III)-Np(IV)	-0.14
Pu(III)-Pu(IV)	-0.97
Am(III)-Am(IV)	-2.3

(14) Seaborg, *Nucleonics* 5, No. 5, 17 (1949).

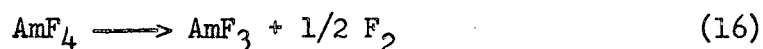
The potential of the Np(III)-Np(IV) couple is almost exactly midway between that of the U(III)-U(IV) and Pu(III)-Pu(IV) couples. It has been suggested by Brewer¹⁵ that this is due to a regular increase in the ionization potential of

(15) Brewer, U. S. Atomic Energy Commission Declassified Document AECD-1899 (1948).

the fourth electron in succeeding members of the actinide series. The pronounced deviation of americium from this regularity indicates that this suggestion may not be correct. However, the magnitude of the potential in each case depends upon a relatively small difference between large energy terms (the heats of sublimation and hydration of the ions and the ionization potentials) and small irregularities in the trends in any of these terms would suffice to obscure regularities in the other terms.

The value of the potential of the Am^{+3} - Am^{+4} couple may be used to estimate the free energies of other reactions involving the tri and tetrapositive states.

For example, if we assume that the difference between the free energies of $\text{Pu}^{+3}(\text{aq})$ and $\text{Pu}^{+4}(\text{aq})$ on the one hand and of $\text{Am}^{+3}(\text{aq})$ and $\text{Am}^{+4}(\text{aq})$ also extend to their fluorides we calculate from the data of Brewer, Bromley, Gilles and Lofgren⁷ on the free energies of formation of PuF_3 and PuF_4 that ΔF_{298} for the reaction:



is equal to +11.8 kcals. Taking the entropy for the reaction to be the same as that for the corresponding plutonium reaction, 16 e.u., we estimate ΔF_{1000} to be +0.6 kcal. It should be possible to prepare stable AmF_4 by treatment of the trifluoride with fluorine and also to investigate the equilibrium experimentally.

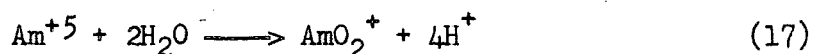
No other solid halides of tetrapositive americium will be stable.

Finally it is emphasized that our considerations apply only to the tetrapositive state of americium. Solid compounds of Am(V) and Am(VI) are known.^{16,17}

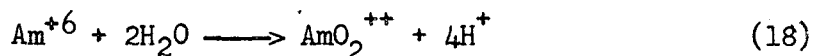
(16) Werner and Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 22.5 (McGraw-Hill Book Co., Inc., New York, 1949).

(17) Asprey, Stephanou, and Penneman, J. Am. Chem. Soc. 72, 1425 (1950).

The stability of the ions of these higher oxidation states is undoubtedly due to the large negative free energy values for the reactions:



and



SUMMARY

The heats of reaction at 25°C. of $\text{Pr}_2\text{O}_3(\text{C form})$ with 6.02M nitric acid and with 1.0M nitric acid were found to be -106.2 ± 0.2 and -97.1 ± 0.7 kcal./mole, respectively. From these measurements and an accepted value of -444.5 kcal. for the heat of formation of $\text{Pr}_2\text{O}_3(\text{c})$ the heats of formation of $\text{Pr}(\text{NO}_3)_3(\text{HNO}_3(7.5))$ and $\text{Pr}(\text{NO}_3)_3(\text{HNO}_3(54))$ are calculated to be -319.3 ± 0.3 and -316.0 ± 0.8 kcal., respectively. A value of -315.5 ± 1 kcal. is estimated for the heat of formation of $\text{Pr}(\text{NO}_3)_3(\text{HNO}_3(\infty))$ and from this -167.3 ± 1 kcal. for the heat of formation of $\text{Pr}^{+3}(\text{aq})$.

The heats of reaction of $\text{PrO}_2(\text{c})$ with 6.02M nitric acid and with 6.0M nitric acid - 0.1M fluoboric acid were measured as -42.4 ± 0.8 and -42.0 ± 0.4 kcal., respectively. The heat of formation of $\text{PrO}_2(\text{c})$ is calculated to be -232.9 ± 1.0 kcal.

The heat of the reaction: $\text{PrO}_2(\text{c}) + 4\text{H}^+(\text{aq}) \longrightarrow \text{Pr}^{+4}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ is estimated to be -14.6 ± 1 kcal., by analogy with the corresponding plutonium reaction, and the heat of formation of $\text{Pr}^{+4}(\text{aq})$ to be -110.9 ± 1.5 kcal.

The heat of the reaction: $\text{Pr}^{+3}(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow \text{Pr}^{+4}(\text{aq}) + 1/2 \text{H}_2(\text{g})$ is estimated to be $+56.4 \pm 1.7$ kcal. and the entropy -33.5 ± 1 e.u. Hence ΔF_{298} is equal to $+66.4 \pm 2$ kilocalories and $E = -2.88 \pm 0.1\text{v}$.

The heat of reaction of AmO_2 with 6.0M nitric acid - 0.1M fluoboric acid was measured as -30.4 ± 0.4 kcal.

The heat of the reaction: $\text{Am}^{+3}(\text{aq}) + \text{H}^{+}(\text{aq}) \longrightarrow \text{Am}^{+4}(\text{aq}) + 1/2 \text{H}_2(\text{g})$
is estimated to be $+44.4 \pm 2$ kcals. and ΔS as -31.3 cal./degree. Hence, for
this reaction, $\Delta F_{298} = +53.7 \pm 2$ kcals. and $E = -2.32 \pm 0.1\text{v}$.

ΔF_{298} for the reaction: $\text{AmF}_4 \longrightarrow \text{AmF}_3 + 1/2 \text{F}_2$ is estimated to be $+11.8$
kcals. and ΔF_{1000} to be $+0.6$ kcal.

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