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THE HEAT OF REACTION OF AMERICIUM METAL WITH 1.5M HYDROCHLORIC ACID AND A NOTE ON THE HEATS OF FORMATION OF $La^{+3}_{(aq.)}$ AND $Pr^{+3}_{(aq.)}$

H. R. Lohr and B. B. Cunningham

July 18, 1950

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THE HEAT OF REACTION OF AMERICIUM METAL WITH 1.5M HYDROCHLORIC ACID AND A NOTE ON THE HEATS OF FORMATION OF $La^{+3}_{(aq.)}$ AND $Pr^{+3}_{(aq.)}$

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ABSTRACT

The heat of reaction of americium metal with 1.5M HCl was measured to be -162.3 ± 2.7 kcals. per mole at 25°C. The heats of formation at the same temperature of $Am^{+3}_{(aq.)}$, $AmO_{2(c)}$ and $AmCl_{3(c)}$ are calculated to be -163.2 ± 2.7, -244.4 ± 3 and -251.3 ± 2.7 kcals. $mole^{-1}$, respectively.

The E value for the couple

$$Am_{(c)} = Am^{+3}_{(aq.)} + 3\ e^{-}$$

uncorrected for the activity coefficient of Am^{+3} is estimated to be 2.36 ± 0.04 v.

Preliminary measurements suggest that the heats of formation of $La^{+3}_{(aq.)}$ and $Pr^{+3}_{(aq.)}$ are -167.0 ± 1.4 and -165.3 ± 0.9 kcals. $mole^{-1}$, respectively.

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H. R. Lohr* and B. B. Cunningham
Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

July 18, 1950

The work described here represents a continuation of a systematic investigation of the basic thermodynamic properties of americium and its compounds. Estimates of the heat and free energy of the reaction:

$$Am^{+3}_{(aq.)} + H^{+}_{(aq.)} = Am^{+4}_{(aq.)} + 1/2\ H_{2(g)} \qquad (1)$$

at 298°K. have been reported previously.[1]

(1) Eyring, Cunningham, and Lohr, to be published.

The objective of the present investigation was to determine the heat of formation of $Am^{+3}_{(aq.)}$.

Throughout this paper all heats of reaction, formation, etc. and all entropies are values at 298°K., unless designated otherwise, and all accepted values for heats of formation, vaporization, etc. used in our calculations are those given by the National Bureau of Standards "Selected Values of Chemical Thermodynamic Properties" unless some other source is credited. All values are expressed only to the nearest 0.1 kcal., consistent with our experimental accuracy. The activity coefficients of the aqueous tripositive and tetrapositive ions dealt with in this work are not known. Our calculated thermodynamic values involving such ions do not therefore include this customary correction.

*Present address: Argonne National Laboratory, Chicago, Illinois. Part of the work described here was included in a dissertation submitted to the Graduate Division of the University of California by H.R. Lohr in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

EXPERIMENTAL

Preparation of Americium Metal

The americium used in this work was prepared by the sequence of nuclear reactions:[2] $Pu^{239}(n,\gamma)Pu^{240}(n,\gamma)Pu^{241} \xrightarrow{\beta^-} Am^{241}$. Methods of concentration,

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

purification, and isolation of americium produced in this way have been discussed by Cunningham.[3] An analysis of a typical stock solution of americium nitrate

(3) Cunningham, to be published.

(~0.01M, dissolved in 0.5M nitric acid) used in this work is given in Table I.

Table I

Spectrographic Analysis of 50 Micrograms of Americium as Americium Nitrate

Element Analyzed For	Found (μg)	Limit of Detection (μg)
Al	0.04	0.01
Be	<0.005	0.005
Ca	0.07	0.01
Ce	<0.01	0.01
Co	<0.05	0.05
Cr	<0.01	0.01
Eu	<0.01	0.01
Fe	<0.02	0.02
Gd	<0.1	0.1
Ho	<0.1	0.1
Lu	<0.1	0.1
Tb	<0.1	0.1
Zn	<0.1	0.1
Mg	0.02	0.01
Mn	<0.05	0.05
Ni	<0.05	0.05
Pt	<0.1	0.1
Sc	<0.01	0.01
Yb	<0.01	0.01
Y	0.08	0.01

Additional chemical procedures used in the metal production resulted in further purification from all impurities detected in the stock solution, except yttrium.

A method of preparation of americium metal has been described by Westrum.[4]

(4) Westrum, to be published.

Americium metal was prepared by us as follows: Americium trifluoride was precipitated from an aqueous solution ~0.01M in Am^{+3} and 0.5M in nitric acid by the addition of excess hydrofluoric acid. The trifluoride was washed with dilute hydrofluoric acid solution and transferred to a platinum hydrofluorination line where it was treated with a mixture of HF (g, 1/2 atm.), H_2 (g, 1/2 atm.) at 550°C for 30 minutes. The anhydrous trifluoride was pelleted in 100 to 500 μg pellets in a stainless steel pellet press.

The fluoride pellets were reduced with barium metal vapor in a vacuum furnace[5]

(5) Fried and Davidson, J. Am. Chem. Soc., 70, 3539 (1948).

using the assembly shown in Fig. 1. The inner crucibles used were made of sintered beryllia. The crucible system containing the trifluoride and barium metal was heated initially to 1300°C. When barium metal began to distill from the outer crucible, the temperature was lowered to 1125°C. and held at this level for one and one-half minutes.

This method produced single pellets of americium metal which were quite malleable and which possessed a grayish luster.

The metal pellets were cleaned under xylene in an atmosphere of dry nitrogen by scraping the outer surface until it was shiny and free of beryllia or slag.

Attempts to determine the structure of the metal by x-ray diffraction methods were not successful, probably because of insufficient annealing.

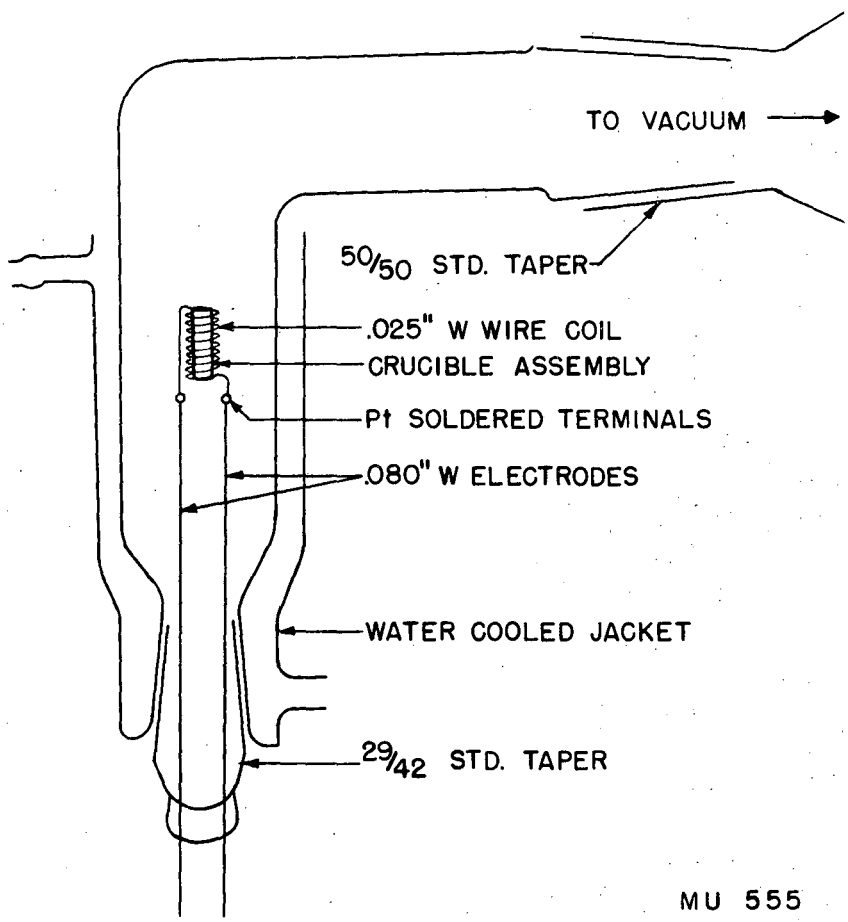

FIG. 1

TUNGSTEN COIL FURNACE ASSEMBLY

A spectrographic analysis of a typical sample of americium metal prepared as described above is given in Table II.

Table II

Spectrographic Analysis* of 50 Micrograms of Americium Metal

Element Analyzed For	Found (μg)	Limit of Detection (μg)
Al	0.03	0.01
Be	0.02	0.005
Ca	0.06	0.01
Ce	<0.01	0.01
Co	<0.05	0.05
Cr	<0.01	0.01
Eu	<0.01	0.01
Fe	0.05	0.02
Gd	<0.1	0.1
Ho	<0.1	0.1
Lu	<0.1	0.1
Tb	<0.1	0.1
Zn	<0.1	0.1
Mg	<0.01	0.01
Mn	<0.05	0.05
Ni	<0.05	0.05
Pt	<0.1	0.1
Sc	<0.01	0.01
Yb	<0.01	0.01
Y	<0.01	0.01
Ba	<0.1	0.1

*Analysis based on spark spectrum, using copper electrodes.

The clean pellets of americium metal were weighed by difference into calorimeter bulbs which had a mass of less than twenty milligrams. The weighings were done on a quartz fiber torsion balance similar to that described by Kirk, Craig,

Gullberg, and Boyer.[6] The instrument used by us had a sensibility of 0.01 μg

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

and an accuracy of calibration of ±0.1%.

Calorimetry

The heat of reaction of the metal with 1.5M hydrochloric acid (previously saturated with hydrogen gas) was measured in the microcalorimeter described by Westrum.[7] It is perhaps worth mentioning that several measurements of the thermal

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

leakage modulus of this instrument showed it to be 0.025, rather than 0.001 degree per degree minute, as reported by Westrum.

Before the instrument was used to determine the heat of reaction of americium metal, several measurements were made of the heat of reaction of magnesium metal with 1.0M HCl at 25°C. The values obtained, corrected by -0.3 kcal./mole for the heat of vaporization of the water necessary to saturate the evolved hydrogen, are listed in Table III.

Table III

Chemical Calibration With Magnesium Metal
1.0M HCl at 25°C.

Run No.	Weight Mg.	Heat Evolved Calories	ΔH (kcal./mole)
1	0.2032	0.932	-111.9
2	0.1583	0.734	-113.0
3	0.5280	2.410	-111.3
4	0.2706	1.210	-109.0
5	0.5866	2.673	-111.1
6	0.2861	1.309	-111.6
		Mean, ± σ	-111.3 ± 1.2

This value may be compared with that of -111.32 ± 0.04 kcal./mole found by Shomate and Huffman[8] for the same reaction.

(8) Shomate and Huffman, J. Am. Chem. Soc., 65, 1625 (1943).

Corrections for heat leakage were determined by graphical integration.

Of eight measurements of the heat of reaction of americium metal with 1.5M hydrochloric acid, six were satisfactory and the results are tabulated in Table IV. Of the two results omitted, one (Number 1) was unsatisfactory because of the small size of the sample (50 μg), and the second (Number 3) because the sample failed to dissolve properly, perhaps because of entrapment in a bubble of hydrogen gas.

Table IV

Heat of Reaction of Americium Metal With 1.50M HCl at 25°C.

Sample No.	Weight Mg.	Heat Evolved Calories	ΔH (kcal./mole)
2	0.3531	0.2347	-160.9
4	0.1449	0.0961	-160.7
5	0.3425	0.2245	-158.7
6	0.7806	0.5248	-162.6
7	0.4028	0.2721	-163.4
8	0.3604	0.2492	-167.4
		Mean, ± σ	-162.3 ± 2.7

Although omission of the result on sample 8 may be justified on statistical grounds, we prefer to include it on computing our final result. Except for sample 8, the standard deviation is quite consistent with that observed in many previous heat measurements, if account is taken of the quantity of heat measured.

The values of ΔH have been corrected for the heat of vaporization of that quantity of water required to saturate the one and one-half moles of hydrogen evolved per mole of metal dissolved and for the vaporization of water into the air contained in the glass calorimeter bulbs, assuming a volume of 0.02 milliliter for each bulb.

We therefore take the heat of the reaction:

$$Am_{(s)} + 3HCl\ (36) = AmCl_3\ (HCl\ (36)) + 3/2\ H_{2(g)} \qquad (2)$$

to be -162.3 ± 2.7 kcals., and calculate the heat of formation of $AmCl_3$ (HCl (36)) to be $-162.3 \pm 2.7 + (-39.5 \times 3) = -280.8 \pm 2.7$ kcals./mole.

The Heats of Formation of $La^{+3}_{(aq.)}$ and $Pr^{+3}_{(aq.)}$

In developing procedures suited to the preparation of americium metal and measurement of its heat of reaction with dilute hydrochloric acid, we made limited use of two rare earths - lanthanum and praseodymium - as "stand-in" elements more readily obtainable than americium, which is, of course, of extremely limited availability.

Lanthanum metal and praseodymium metal were prepared by the same technique as that described for the preparation of americium metal. The resulting metal was shown by spectrographic analysis to be >99.5% pure. Volumes of hydrogen liberated by known weights of metal dissolved in acid were equal to theoretical volumes for pure metal within a few tenths of one percent.

A few measurements of the heats of reaction of these metals with 1.5M hydrochloric acid were made. As a further check, heats were also run on samples of lanthanum metal made outside this laboratory. The results are tabulated in Table V.

Table V

Heats of Reaction of Lanthanum Metal and Praseodymium Metal With 1.50M HCl at 25°C.

Sample No.	Weight Mg.	Source of Metal	Purity of Metal	+ΔH (kcal./mole)
La - 1	0.2428	Iowa State	>99.0%	-163.5
La - 2	0.8658	Iowa State	>99.0%	-165.9
La - 3	0.5486	Berkeley	>99.5%	-167.8
La - 4	0.6396	Berkeley	>99.5%	-167.3
				-166.1 ± 1.4
Pr - 1	0.2252	Berkeley	>99.5%	-165.4
Pr - 2	0.1933	Berkeley	>99.5%	-167.3
Pr - 3	0.1809	Berkeley	>99.5%	-159.9
Pr - 4	0.6174	Berkeley	>99.5%	-165.1
				-164.4 ± 2.3

We correct these values to -167.0 and -165.3 kcals. for the heat in infinitely dilute acid, as explained subsequently in our treatment of the heat of solution of americium metal.

Although we do not claim high precision for our measurements, the results are so different from those reported by Bommer and Hohmann[9] that we believe the Bommer and Hohmann values to be in error by the order of ten kcals.

(9) Bommer and Hohmann, Z. anorg. allgem. Chem., 248, 357-396 (1941).

DISCUSSION

Taking -280.8 ± 2.7 kcals. for the heat of formation of $AmCl_3$ (HCl (36)), we estimate the heat of formation of $AmCl_3$ (HCl (∞)) on the basis of measurements by Robinson and Westrum[10] of the heat of solution of $PuCl_{3(c)}$ in various

(10) Robinson and Westrum, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 6.54 (McGraw-Hill Book Co., Inc., New York, 1949).

concentrations of hydrochloric acid. These authors found -29.5 ± 0.1 kcal./mole for the heat in 1.5M hydrochloric acid and from this and other measurements estimated the heat in HCl (∞) to be -31.9 kcal./mole. We take the heat for the reaction:

$$AmCl_3\ (HCl\ (36)) = AmCl_3\ (HCl\ (\infty)) \qquad (3)$$

to be the same as that for the corresponding plutonium reaction, namely, -2.4 kcals., whence the heat of formation of $AmCl_3$ (HCl (∞)) = -283.2 ± 2.7 kcals.

Taking the heat of formation of 3 $Cl^-_{(aq.)}$ to be -120.0 kcals., the heat of formation of $Am^{+3}_{(aq.)} = -163.2 \pm 2.7$ kcals.

From data supplied by Eyring, Cunningham and Lohr,[1] we estimate for the reaction:

$$AmO_{2(c)} + 3HNO_3\ (\infty) = Am(NO_3)_3(HNO_3\ (\infty)) + 3/2\ H_2O_{(l)} + 1/4\ O_{2(g)} \qquad (4)$$

$\Delta H_{298} = -21.3 \pm 1.0$ kcals.

Using our value of -163.2 ± 2.7 kcals. for the heat of formation of $Am^{+3}_{(aq.)}$, we estimate ΔH_f for $AmO_{2(c)} = -244.4 \pm 3$ kcals.

If the heat of solution of $AmCl_{3(c)}$ is taken to be the same as that of $PuCl_{3(c)}$, as given by Westrum,[10] we calculate ΔH_f of $AmCl_{3(c)}$ to be:

$$-283.2 \pm 2.7 - 31.9 = -251.3 \pm 2.7 \text{ kcals./mole.}$$

In order to estimate the free energy of the reaction:

$$Am_{(s)} + 3H^+_{(aq.)} = Am^{+3}_{(aq.)} + 3/2\ H_{2(g)} \qquad (5)$$

we take the heat to be equal to that for the formation of $Am^{+3}_{(aq.)}$.

To a first approximation the entropy of the reaction may be taken as equal to that of the corresponding plutonium reaction, for which Brewer, Bromley,

Gilles and Lofgren[11] give $\Delta S_{298} = 3$ e.u. These authors estimate 13 e.u. for the

(11) Bromley, Brewer, Gilles, and Lofgren, ibid., Paper No. 6.40.

entropy of Pu metal and -30 e.u. (including an estimated magnetic contribution of 0.9 e.u.) for $Pu^{+3}_{(aq.)}$. Sufficient data are not available for an accurate calculation of the magnetic entropies of the ions, but we shall use for this purpose the ground state assignments suggested by Howland and Calvin.[12] Thus,

(12) Howland and Calvin, Phys. Rev., in press.

they suggest $^6H_{5/2}$ for the ground state of $Pu^{+3}_{(aq.)}$ and hence the magnetic entropy = R ln 6 = 3.6 e.u., 2.7 e.u. more than the correction applied by Brewer, et al. The case of $Am^{+3}_{(aq.)}$ is more complicated, since there are two low lying states separated by an energy difference comparable to kT. We estimate from the measured $X_M = 721 \times 10^{-6}$ c.g.s. units and the calculated X_M's of 1900×10^{-6} and 0 for the states $^7F_1$ and $^7F_0$, respectively.

$$S_{mag} = -2/3\ R \ln 2/3 - 1/9\ R \ln 1/9 - 1/9\ R \ln 1/9 - 1/9\ R \ln 1/9 = 2 \text{ e.u.}$$

Hence, $S_{mag}\left[Am^{+3}_{(aq.)}\right] = S_{mag}\left[Pu^{+3}_{(aq.)}\right] - 1.6$ e.u.

We also subtract 0.8 e.u. from the entropy of Pu^{+3} for the 0.01 Å decrease in radius of $Am^{+3}_{(aq.)}$ as compared to $Pu^{+3}_{(aq.)}$.[11] Whence:

$$S\left[Am^{+3}_{(aq.)}\right] = -30 + 2.7 - 1.6 - 0.8 = -30.3 \text{ e.u.}$$

The entropy of metallic americium probably is substantially different from that of plutonium since the two metals differ greatly in density,[4] melting point,[4] and heat of vaporization.[13,14] The melting point of americium metal is closer

(13) Phipps, Seifert, and Simpson, Manhattan Project Metallurgical Laboratory Report CN-3223 (September, 1945).
(14) Erway and Simpson, Manhattan Project Metallurgical Laboratory Report CC-3721 (April, 1947).

to that of the rare earth metals than to plutonium. We also regard it as significant that the density of americium metal is about equal to that of the lighter rare earths (Nd, for example), multiplied by the ratio of the atomic weight of americium to that of the rare earths. The metallic radii and bonding in the two metals are probably quite similar.

We estimate the entropy of $Am_{(s)}$ from the entropy of $Ce_{(s)}$, given by Latimer,[15]

(15) Latimer, "Oxidation Potentials," (Prentice-Hall, Inc., New York, 1938).

using his formula for the mass correction:

$$S(Am) = S(Ce) + 3/2\ R \ln \frac{241}{140} = 13.8 + 1.6 = 15.4 \text{ e.u.}$$

There are no data on which to base a correction for magnetic entropy. We take:

$$S\left[Am^{+3}{}_{(aq.)}\right] + S\left[3/2\ H_{2(g)}\right] - S\left[Am_{(s)}\right] = -30.3 + 46.8 - 15.4 = 1.1 \text{ e.u.},$$

whence ΔF_{298} for reaction (5) is equal to:

$$-163.2 \pm 2.7 - \frac{1.1 \times 298}{1000} = -163.5 \pm 2.7 \text{ kcals. and E,}$$

for the substances at unit concentration, $= \frac{163.5 \pm 2.7}{23.07 \times 3} = 2.36 \pm 0.04$ v.

Even if the estimated entropies are in error by several entropy units, the result will be affected by only a few hundredths of a volt.

The E value for the corresponding plutonium reaction is given by Brewer, et al.[11] as 2.06 v.

Americium metal is thus substantially more electropositive than plutonium and is about as electropositive as the lighter rare earths, if we take the electrode potentials quoted by Yost, Russell, and Garner[16] to be correct.

(16) Yost, Russell, and Garner, "The Rare Earth Elements and Their Compounds," (John Wiley and Sons, Inc., New York, 1947).

It seems to us that in many respects americium may be regarded as the first of the transuranium elements which is rare-earth-like in the metallic state. It is also the first in which the stability of the tripositive state is comparable to that of the rare earths.

ACKNOWLEDGMENT

We wish to express our thanks to Mrs. Winifred Heppler and Mr. Herman Robinson, who provided technical assistance in making our calorimetric measurements, and to members of the Health Chemistry Group of the Radiation Laboratory for their efforts in providing adequate safeguards against the hazards of handling high levels of radioactivity. We also wish to thank Mr. John Conway and Mr. Milton Moore, who carried out all spectrographic analyses reported in this paper.

The work described here was carried out under the auspices of the Atomic Energy Commission.

SUMMARY

The heat of reaction of americium metal with 1.5M HCl was found to be -162.3 ± 2.7 kcals. per mole at 25°C. The heats of formation of $Am^{+3}_{(aq.)}$, $AmO_{2(c)}$ and $AmCl_{3(c)}$ are calculated to be -163.2 ± 2.7, -244.4 ± 3 and -251.3 ± 2.7 kcals., respectively.

The E value for the couple

$$Am_{(c)} = Am^{+3}_{(aq.)} + 3\ e^-$$

uncorrected for the activity coefficient of Am^{+3} is estimated to be 2.36 ± 0.04 v.

It is suggested that americium is the first of the transuranium elements to be rare-earth-like in the metallic state.

Preliminary measurements suggest that the heats of formation of $La^{+3}_{(aq.)}$ and $Pr^{+3}_{(aq.)}$ are -167.0 ± 1.4 and -165.3 ± 0.9 kcals., respectively, rather than -176.5 and -172.9 kcals., as reported by Bommer and Hohmann.

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