num chloride as shown in Curve 1, Fig. 3, are much the same as those obtained with solutions of aluminum bromide.[5] The lack of a marked change in slope or an inflection point in the curve near a molar ratio of 1.0 and the fact that the yellow color of the salt–solvent complex does not vanish until the molar ratio approaches a value of 2.0 indicates that effective competition occurs between reactions forming the complexes C_6H_5CN:$AlCl_3$ and $C_6H_5NO_2{\cdot}AlCl_3{\cdot}C_6H_5CN$.

3. **Trimethylamine.**—On addition of trimethylamine to solutions of aluminum chloride a curve similar to that obtained for pyridine is observed (Curve 4, Fig. 3). The only significant difference is that the initial rise in conductance on addition of amine is much less than was observed on addition of pyridine. Again a significant difference in the form of the curve is obtained as between nitrobenzene solutions of aluminum chloride and bromide.[3] It was found impossible to continue this study much beyond a molar ratio of unity due to apparent decomposition involving the solvent molecule. This situation has been observed with aluminum bromide solutions also.[3]

Ammonia.—A typical curve for ammonia as complexing agent in aluminum chloride solutions is shown in Curve 2, Fig. 3. The curve for ammonia is much the same as that obtained on addition of pyridine for molar ratios as high as 1.0. This is clearly shown by comparing Curves 2 and 3 of Fig. 3. Beyond the ratio of 1.0 the conductance on addition of ammonia increases much more rapidly than is the case with pyridine. At a ratio value in the neighborhood of 1.3 precipitation of the ammonia complex occurs. It seems clear that the reactions of ammonia with aluminum chloride in nitrobenzene are much the same as those with pyridine and trimethylamine. Curves 2, 3 and 4 of Fig. 3 for these three complexing agents are remarkably similar in form in contrast to the curves obtained with the same complexing agents and aluminum bromide solutions in which each of the three curves is significantly different.[3,4]

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

The Heat of Reaction of Americium Metal with 1.5 *M* Hydrochloric Acid and a Note on the Heats of Formation of La^{+3}(aq.) and Pr^{+3}(aq.)

BY H. R. LOHR[1] AND B. B. CUNNINGHAM

The measurements described in the content of this paper were made for the purpose of securing basic thermodynamic information concerning americium and some of its compounds. Such information is of twofold interest: as a part of the data required for the systematic comprehension of the chemistry of americium and as a basis for correlating the chemistry of americium with that of other actinide elements for which similar data are available. The heat of reaction of americium metal with 1.5 *M* HCl was found to be −162.3 ± 2.7 kcal. per mole at 25°. 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, −240.3 ± 3 and −251.3 ± 2.7 kcal. mole^{-1}, respectively. The *E* value for the couple Am(c) = Am^{+3}(aq.) + $3e^-$, at unit concentration uncorrected for the activity coefficient of Am^{+3} is estimated to be 2.36 ± 0.04 v. The heats of formation of Am^{+3}(aq.) and $AmCl_3$(c) given above are about 21 kcal. more negative than those for the corresponding plutonium compounds, while the heat of formation of AmO_2(c) is about 11 kcal. more positive than that of PuO_2(c). The potential of the Am(c) = Am^{+3}(aq.) + $3e^-$ couple is 0.30 v. more positive than that of the corresponding plutonium couple. Americium metal is substantially more electropositive than plutonium metal, and is closely similar to lanthanum or praseodymium in this respect. Preliminary measurements, carried out as an incidental part of the measurements on americium, suggest that the heats of formation of La^{+3}(aq.) and Pr^{+3}(aq.) are −167.0 ± 1.4 and −165.3 ± 0.9 kcal. mole^{-1}, respectively.

Introduction

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

$$Am^{+3}(aq.) + H^{+}(aq.) = Am^{+4}(aq.) + {}^{1}/_{2}H_2(g) \quad (1)$$

at 298°K. have been reported elsewhere.[1a]

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. Strictly speaking, we are not justified in designating our calculated heats of formation as ΔH° values, and we have not done so.

Experimental

The americium for 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, purification, and isolation of americium produced in this way have been dis-

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[1] 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.

[1a] L. Eyring, B. B. Cunningham and H. R. Lohr, reported at the Symposium on the Chemistry of the Actinide Elements, 118th National Meeting, American Chemical Society, Chicago, September 5, 1950.

[2] G. T. Seaborg, *Phys. Rev.*, **78**, 472 (1950).

cussed by Cunningham.[3] An analysis of a typical stock solution of americium nitrate and a typical sample of americium metal used in this work are given in Table I.

TABLE I

SPECTROGRAPHIC ANALYSIS[a] OF 50 MICROGRAMS OF AMERICIUM AS I, AMERICIUM NITRATE AND II, AMERICIUM METAL

Element analyzed for	Found (μg) I	Found (μg) II	Limit of detection (μg)
Al	0.04	0.03	0.01
Be	< .005	.02	.005
Ca	.07	.06	.01
Ce	< .01	< .01	.01
Co	< .05	< .05	.05
Cr	< .01	< .01	.01
Eu	< .01	< .01	.01
Fe	< .02	.05	.02
Gd	< .1	< .1	.1
Ho	< .1	< .1	.1
Lu	< .1	< .1	.1
Tb	< .1	< .1	.1
Zn	< .1	< .1	.1
Mg	.02	< .01	.01
Mn	< .05	< .05	.05
Ni	< .05	< .05	.05
Pt	< .1	< .1	.1
Sc	< .01	< .01	.01
Yb	< .01	< .01	.01
Y	.08	< .01	.01
Ba		< .1	.1

[a] Analysis based on spark spectrum, using copper electrodes.

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

A method of preparation of americium metal has been described by Westrum.[4] Americium metal was prepared by us as follows: Americium trifluoride was precipitated from an aqueous solution ~0.01 M in Am^{+3} and 0.5 M 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. 0.5 atm.), H_2 (g. 0.5 atm.) at 550° for 30 minutes. The anhydrous trifluoride was pelleted in 100 to 500 μg pellets in a stainless steel pellet press.

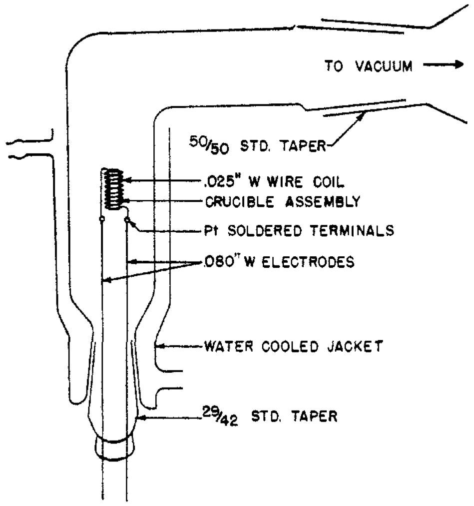

Fig. 1.—Tungsten coil furnace assembly.

The fluoride pellets were reduced with barium metal vapor in a vacuum furnace[5] 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°. When barium metal began to distill from the outer crucible, the temperature was lowered to 1125° 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.

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 and an accuracy of calibration of ±0.1%.

Calorimetry.—The heat of reaction of the metal with 1.5 M 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 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 1.0 M HCl at 25°. 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 II. This value may be compared with that of −111.32 ± 0.04 kcal./mole found by Shomate and Huffman[8] for the same reaction.

TABLE II

CHEMICAL CALIBRATION WITH MAGNESIUM METAL 1.0 M HCl AT 25°

Run	Weight milligrams	Heat evolved, cal.	ΔH, kcal./mole
1	0.2032	0.932	−111.9
2	.1583	0.734	−113.0
3	.5280	2.410	−111.3
4	.2706	1.210	−109.0
5	.5866	2.673	−111.1
6	.2861	1.309	−111.6
		Mean, ± σ	−111.3 ± 1.2

Corrections for heat leakage were determined by graphical integration.

Of eight measurements of the heat of reaction of americium metal with 1.5 M hydrochloric acid, six were satisfactory and the results are tabulated in Table III. 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.

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 deviations between different measurements are quite consistent with those observed in many previous heat measurements with

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(3) B. B. 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).

(4) E. F. Westrum, Jr., "The Preparation and Some Properties of Americium Metal," reported at the 118th National Meeting of the American Chemical Society, Chicago, September 5, 1950.

(5) S. Fried and N. R. Davidson, THIS JOURNAL, **70**, 3539 (1948).

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

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

(8) C. H. Shomate and E. H. Huffman, THIS JOURNAL, **65**, 1625 (1943).

TABLE III

HEAT OF REACTION OF AMERICIUM METAL WITH 1.50 M HCl AT 25°

Sample	Weight, mg.	Heat evolved, cal.	ΔH, kcal./mole
2	0.3531	0.2347	−160.9
4	.1449	.0961	−160.7
5	.3425	.2245	−158.7
6	.7806	.5248	−162.6
7	.4028	.2721	−163.4
8	.3604	.2492	−167.4
		Mean, ± σ	−162.3 ± 2.7

this instrument, 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. We therefore take the heat of the reaction

$$Am(s) + 3HCl\ (36) = AmCl_3\ (HCl\ (36)) + 3/2H_2(g) \qquad (2)$$

to be −162.3 ± 2.7 kcal., and calculate the heat of formation of $AmCl_3(HCl\ (36))$ to be −162.3 ± 2.7 + (−39.5 × 3) = −280.8 ± 2.7 kcal./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 per cent.

A few measurements of the heats of reaction of these metals with 1.5 M 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 IV.

TABLE IV

HEATS OF REACTION OF LANTHANUM METAL AND PRASEODYMIUM METAL WITH 1.50 M HCl AT 25°

Sample	Weight, mg.	Source of metal	Purity of metal, %	$+\Delta H$, kcal./mole
La-1	0.2428	Iowa State	>99.0	−163.5
La-2	.8658	Iowa State	>99.0	−165.9
La-3	.5486	Berkeley	>99.5	−167.8
La-4	.6396	Berkeley	>99.5	−167.3
				−166.1 ± 1.4
Pr-1	.2252	Berkeley	>99.5	−165.4
Pr-2	.1933	Berkeley	>99.5	−167.3
Pr-3	.1809	Berkeley	>99.5	−159.9
Pr-4	.6174	Berkeley	>99.5	−165.1
				−164.4 ± 2.3

We correct the mean values to −167.0 and −165.3 kcal, respectively, 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 kcal.

Discussion

Taking −280.8 ± 2.7 kcal. 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 concentrations of hydrochloric acid. These authors found −29.5 ± 0.1 kcal./mole for the heat in 1.5 M hydrochloric acid and from this and other measurements in more dilute acid 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 kcal., whence the heat of formation of $AmCl_3$ (HCl (∞)) = −283.2 ± 2.7 kcal.

Taking the heat of formation of 3 Cl^-(aq.) to be −120.0 kcal., the heat of formation of Am^{+3}(aq.) = −163.2 ± 2.7 kcal.

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

$$AmO_2(c) + 3HNO_3\ (\infty) = Am(NO_3)_3(HNO_3\ (\infty)) + 3/2H_2O(l) + 1/4O_2(g) \qquad (4)$$

ΔH_{298} = −25.3 ± 1.0 kcal.

Using our value of −163.2 ± 2.7 kcal. for the heat of formation of Am^{+3}(aq.), we estimate ΔH_f for $AmO_2(c)$ = −240.3 ± 3 kcal.

If the heat of solution of $AmCl_3(c)$ is taken to be the same as that of $PuCl_3(c)$, as given by Robinson and Westrum,[10] we calculate ΔH_f of $AmCl_3(c)$ to be

$$-283.1 \pm 2.7 - 31.9 = -251.3 \pm 2.7 \text{ kcal./mole}$$

In order to estimate the free energy of the reaction

$$Am(s) + 3H^+(aq.) = Am^{+3}(aq.) + 3/2H_2(g) \qquad (5)$$

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 ΔS_{298} = 3 e.u. These authors estimate 13 e.u. for the 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. Low energy states for various actinide ions have been suggested by Howland and Calvin.[12] However, recent work on the magnetic susceptibilities of compounds of plutonium (III)[13] and americium (III)[14] at various temperatures has shown that these substances exhibit very pronounced deviations from the theoretical susceptibilities expected from the ground state assignments suggested by Howland and Calvin.

We feel, therefore, that corrections for the mag-

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[9] H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **248**, 357–396 (1941).

[10] H. Robinson and E. F. Westrum, Jr., 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, N. Y., 1949).

[11] L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, *ibid.*, Paper No. 6.40.

[12] J. J. Howland, Jr., and M. Calvin, *J. Chem. Phys.*, **18**, 239 (1950).

[13] N. Elliott and W. B. Lewis, "Magnetic Susceptibilities of Some Uranium and Plutonium Salts," reported at the 118th National Meeting of the American Chemical Society, September 6, 1950.

[14] W. W. T. Crane, J. C. Wallmann and B. B. Cunningham, "Magnetic Susceptibilities of Some Compounds of Americium and Curium," *ibid.*

netic entropies of these ions cannot be made with confidence on the basis of the evidence now available.

Accordingly, we shall ignore such corrections and take the entropy of Am^{+3}(aq.) to be the same as that of Pu^{+3}(aq.), except for a correction of −0.8 e.u. because of the smaller ionic radius of the tripositive ion of americium.[11] Whence

$$S[Am^{+3}(aq.)] = -30 - 0.8 = -30.8 \text{ e.u.}$$

The entropy of metallic americium probably is substantially different from that of plutonium since the two metals differ greatly in density,[4] and melting point.[4] The melting point of americium metal is closer to that of lanthanum or cerium 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 (La or Ce, for example), multiplied by the ratio of the atomic weight of americium to that of the rare earths. The metallic radii and bonding in these metals are probably quite similar.

We estimate the entropy of Am(s) from the entropy of Ce(s), given by Latimer,[15] using his formula for the mass correction

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

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

$$S[Am^{+3}(aq.)] + S[3/2H_2(g)] - S[Am(s)] = -30.8 + 46.8 - 15.4 = 0.6 \text{ e.u.},$$

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

$$-163.2 \pm 2.7 - \frac{0.6 \times 298}{1000} = -163.4 \pm 2.7 \text{ kcal.}$$

and E for the substances at unit concentration, = $(163.4 \pm 2.7)/23.07 \times 3 = 2.36 \pm 0.04$ 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 (formal) 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.

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.

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[15] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, 1938.

[16] D. M. Yost, H. Russell, Jr., and C. S. Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, 1947.

BERKELEY, CALIFORNIA RECEIVED OCTOBER 10, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Reaction between Oxygen and Thorium

BY PASCAL LEVESQUE AND DANIEL CUBICCIOTTI

A study of the oxidation of thorium has been made in order to make comparisons with the oxidations of other metals of group IVB of the Periodic table.

The reaction was studied in the range 250 to 700°. Above 450°, the temperature of the sample was found to rise considerably above the temperature of the furnace; below 450°, the oxidations were found to be essentially isothermal. From 350 to 450°, the oxidation curves were linear in time. The rate constants for the linear oxidation were measured and the energy of activation calculated to be 22 kcal. per mole. From 250 to 350°, the oxidation proceeded according to the parabolic law and the energy of activation for the reaction was calculated to have a value of 31 kcal. per mole.

The oxidation of a metal at high temperatures will follow a linear law if the oxide formed scales off.[1] If the ratio of molal volume of oxide to metal is greater than unity and the oxide is strongly adherent, the metal oxidizes according to the parabolic law.[2] The rate-determining step of the parabolic reaction is assumed to be diffusion through the growing coating of oxide on the metal surface.[3,4] Titanium[5] and zirconium[6] have been found to follow the parabolic law over a wide range of temperatures.

The present study was made to compare the behavior of thorium with other metals of group IVb. The reaction was found to follow the parabolic and the linear laws in different temperature ranges.

Experimental

Method. Above 350°.—The apparatus used was a modification of the one used in this Laboratory for studies of zirconium.[6] The oxidation was followed by observing the drop in pressure of oxygen gas in a closed system containing a sample of metal. Two silica glass bulbs were connected to a manometer containing amyl sebacate, a low vapor pressure oil, and through suitable stopcocks to a vacuum line and oxygen supply. The bulbs were heated in an electric muffle furnace whose temperature was maintained con-

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[2] N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, **29**, 579 (1923).

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[6] D. Cubicciotti, THIS JOURNAL, **72**, 4138 (1950); E. A. Gulbransen and K. F. Andrew, *A. I. M. E.*, *J. of Metals*, **185**, 515 (1949).