Thermochimica Acta, 116 (1987) 235–240
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE ENTHALPY OF SOLUTION OF ^{243}Am METAL AND THE STANDARD ENTHALPY OF FORMATION OF Am^{3+}(aq)

J.U. MONDAL *, D.L. RASCHELLA **, R.G. HAIRE and J.R. PETERSON

Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 (U.S.A.) and Transuranium Research Laboratory (Chemistry Division), Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375 (U.S.A.)

(Received 4 December 1986)

ABSTRACT

The enthalpy of solution of americium metal (double hexagonal close packed) in 1 M HCl has been measured at 298.15 ± 0.05 K giving a value of -620.6 ± 1.3 kJ mol^{-1}. From this value, the standard enthalpy of formation of Am^{3+}(aq), ΔH_f^0 (Am^{3+}, aq), is derived as -621.2 ± 2.0 kJ mol^{-1}, and using reasonable entropy estimates, the standard potential of the Am^{3+}/Am^0 couple is calculated to be -2.08 ± 0.01 V.

INTRODUCTION

The measurement of heat evolved from the dissolution of an actinide metal in an acid solution is a fundamental step in determining the enthalpies of formation of compounds of that actinide metal. Limited access to sufficient quantities of reasonably pure actinide metals has resulted in often repeated measurements to obtain more reliable enthalpies of solution for the actinide metals. From these dissolution data and separate entropy estimates, one can derive the related thermodynamic quantities ΔH_f^0 (M^{n+}, aq), ΔG_f^0 (M^{n+}, aq), and E^0 ($M^{n+} \rightarrow M$).

The enthalpy of solution of americium (Am) metal in aqueous hydrochloric acid was first determined in 1950. The ΔH_{soln} values reported for this ^{241}Am metal of unreported structure were -679.1 ± 11.3 kJ mol^{-1} [1] and -670 ± 17 kJ mol^{-1} [2]. Years later, from dissolution experiments with americium metal containing a considerable amount of impurities, a value of -626.9 kJ mol^{-1} was suggested [3]. In 1972 Fuger et al. obtained

---

* Present address: Department of Chemistry, Florida Atlantic University, P.O. Box 3091, Boca Raton, FL 33431-0991, U.S.A.

** Present address: Westvāco, Kraft Division, P.O. Box 5207, N. Charleston, SC 29406, U.S.A.

thermodynamic data for americium from heat of solution measurements of ^{241}Am metal of known purity and crystalline structure (double hexagonal close packed) in hydrochloric acid solution [4]. Their reported value for the ΔH_{soln} in 1 M HCl, -616.1 ± 0.8 kJ mol^{-1}, was less exothermic than all the previously reported values [1–3]. The enthalpy of solution of americium metal has been found to be less exothermic with each series of measurements over time, presumably due to improvements in the preparative techniques involving larger samples and more complete analysis by spark-source mass spectrometry [5].

Each of these previous studies of the thermodynamic properties of americium metal used the most common isotope of americium, i.e., mass number 241 (α emitter, $t_{\frac{1}{2}} = 432$ y). For the first time we report here data from solution microcalorimetric studies of well-characterized ^{243}Am metal (α emitter, $t_{\frac{1}{2}} = 7.38 \times 10^3$ y). Moreover it was felt necessary to verify the heat of solution data obtained several years ago in our laboratory on well-characterized samples of ^{243}Am metal [6].

EXPERIMENTAL

Materials

The two ^{243}Am metal samples (preparations I and II) prepared several years apart were obtained by lanthanum metal reduction of AmO_2 in a tantalum vessel and distillation of the metal onto a tantalum condenser. Portions of the metal samples from both preparations were analyzed by spark-source mass spectrometry in the ORNL Analytical Chemistry Division. The magnesium metal (> 99.99%) was obtained from the Research Organic/Inorganic Chemical Corporation. Fisher certified 1 M HCl, degassed and saturated by prolonged bubbling of H_2 gas, was used as the dissolving medium.

Procedure

The samples for calorimetry were cut from a larger piece of americium metal in a gloved box in which the atmosphere of argon contained less than 10 p.p.m. of water and oxygen. Each sample (200–800 μg) was examined under a microscope for cleanliness, placed into either a flat and thin-bottom Pyrex bulb (~ 40 μl) made in a glass shop at the University of Liège, Belgium or a barrel-shaped container (~ 25 μl) designed in our laboratory [7], and weighed in situ. Then the sample container was sealed with a Pyrex bead coated with Apiezon-W wax with the aid of a resistively heated wire. A Perkin-Elmer AD-2Z electrobalance with a nominal sensitivity of 0.1 μg was used for all weighings and was calibrated with NBS class M weights.

Calorimeter

Our solution microcalorimeter has a capacity of 5 cm^3 and has been described in detail elsewhere [8]. Release of the metal sample to the solution was initiated by remotely pressing the sample container against a fixed wire anvil at the base of the calorimeter cup. The dissolution of each sample was preceded and followed by a set of at least two electrical heat input calibrations. The resulting $Am^{3+}(aq)$ solution and the broken sample container were checked under a microscope and found in each case to be free of undissolved particles. All calorimetric measurements are reported at 298.15 ± 0.05 K. The performance of the calorimeter was checked just prior to the Am experiments by measuring the enthalpy of solution of magnesium metal in 1 M HCl. In the earlier study [6] six magnesium samples (14–578 μg) were dissolved, and the average value of its enthalpy of solution (2σ) in 1 M HCl was determined to be -465.7 ± 1.7 kJ mol^{-1}. In the more recent set of experiments, six magnesium samples between 140 and 330 μg were dissolved in 1 M HCl. The average value of the enthalpy of solution (2σ) was -466.6 ± 2.6 kJ mol^{-1}. Both of these values compare favorably to the literature value, -465.5 ± 0.2 kJ mol^{-1} [9], obtained from the dissolution of much larger samples of magnesium metal, and confirm the performance of our solution microcalorimeter.

Units, error limits and auxiliary data

The literature data reported in calories have been converted to joules using the conversion factor 1 cal (thermochemical) = 4.184 J. The atomic weight of americium was taken as 243.06 based on the ^{12}C scale of atomic masses. Uncertainty limits based on the mean of several measurements represent the Student t 95% (2σ) confidence level. The reported standard reduction potential follows the sign convention recommended by IUPAC [10], i.e., the greater the positive potential, the more stable is the reduced form.

RESULTS AND DISCUSSION

X-ray powder diffraction analysis confirmed that the americium metal exhibited the double hexagonal close packed (dhcp) structure. The spark-source mass spectrometric analyses showed that preparation I of the ^{243}Am metal had a higher level of impurities for each element reported than did Am metal preparation II, so only the results of the former analysis are given in Table 1. An isotopic mass analysis showed that the total of all other (non-243) isotopes of americium was less than 150 p.p.m.

TABLE 1

Spark-source mass spectrometric analysis of americium metal (preparation I)

Impurity	Amount (wt. p.p.m.)	Impurity	Amount (wt. p.p.m.)
Al	5	Na	1
B	0.2	Ni	2
Ba	2	P	0.3
Ca	20	Pb	10
Co	0.2	Si	10
Cr	20	Sr	2
Cu	10	Ta	$\leqslant 20$
Fe	50	Te	10
K	0.5	Ti	$\leqslant 0.5$
La	–	V	$\leqslant 0.3$
Mg	1	Zn	0.8
Mn	10		

Total: $\leqslant$175.8 p.p.m.

TABLE 2

Enthalpy of solution of dhcp americium metal in 1 M HCl at 298.15 ± 0.05 K

Am metal preparation	Weight of sample (μg) [a]	$10^4 \times$ molarity of Am^{3+} in solution	Heat effect (J) [b]	$-\Delta H_{soln}$ (kJ mol^{-1})
I	296.2	2.44	0.7556	620.0
	734.0	6.04	1.8775	621.7
	661.2	5.44	1.6864	619.9
	206.6	1.70	0.5268	619.8
	624.8	5.14	1.5997	622.3
	838.5	6.90	2.1457	622.0
	517.4	4.26	1.3301	624.8
	802.4	6.60	2.0437	619.1
II	416.0	3.42	1.0697	625.0
	465.1	3.83	1.1785	615.9
	296.7	2.44	0.7594	622.1
	556.0	4.58	1.4166	619.3
	435.2	3.58	1.1053	617.3
	647.3	5.33	1.6493	619.3
	425.9	3.50	1.0860	619.8
	281.6	2.32	0.7195	621.0
Mean value (2σ)				620.6 ± 1.3

[a] Corrected for buoyancy and known impurities.

[b] Corrected for vaporization of the solvent into the evolved hydrogen gas and into the argon space in the sample container, known impurities, and heat of reaction initiation. Details of these corrections to the observed heat effects may be found elsewhere [11].

The enthalpies of solution, ΔH_{soln}, of the individual samples of americium metal are given in Table 2. The reaction representing the dissolution of dhcp americium metal in an excess of hydrochloric acid is

$$\mathrm{Am(c,}\ \alpha) + [a\mathrm{HCl},\ b\mathrm{H_2O}] \rightarrow [\mathrm{AmCl_3},\ (a-3)\mathrm{HCl},\ b\mathrm{H_2O}] + 3/2\mathrm{H_2(g)}$$

where $a =$ ca. 4000 and $b/a = 54.41$. Owing to the fact that in all measurements the resulting trivalent americium ion concentration was below 6.9×10^{-4} M (see Table 2), we take the results as measured to be valid for an infinitely dilute solution of trivalent americium in 1 M HCl. A variance ratio test (F-test) of the data in Table 2 indicates that there is no significant statistical difference between the two sets of data obtained from the two, independently prepared samples of americium metal. Therefore, we have combined the enthalpy of solution data from the two sets of experiments in 1 M HCl to obtain $\Delta H_{\mathrm{soln}} = -620.6 \pm 1.3$ kJ mol^{-1}. Although our value is a little more exothermic, it still compares favorably to the last reported ΔH_{soln} of -616.1 ± 0.8 kJ mol^{-1} [4].

It has been recognized that enthalpies of solution of actinide metals have a small dependence on the hydrochloric acid concentration [8,12,13]. Assuming the same variation used by others [4] for americium metal when extrapolating to zero acid concentration, we obtain ΔH_f^0 (Am^{3+}, aq) $= -621.2 \pm 2.0$ kJ mol^{-1}, with the error limits set empirically to account for unknown impurities in the samples and uncertainty in the correction to infinite dilution. The entropy of americium metal at 298.15 K, S^0 (Am, c), has been determined to be 55.4 ± 2.0 J mol^{-1} K^{-1} [14], compared to the calculated value of 55.2 J mol^{-1} K^{-1} [15]. Using our ΔH_f^0 (Am^{3+}, aq) $= -621.2$ kJ mol^{-1} with S^0 (Am^{3+}, aq) $= -201 \pm 12.5$ J mol^{-1} K^{-1} [16], S^0 (Am, c) $= 55.4$ J mol^{-1} K^{-1} [14], S^0 (H$_2$, g) $= 130.570$ J mol^{-1}K^{-1} [17], and S^0 (H$^+$, aq) $= 0$ J mol^{-1} K^{-1} [17], we obtain

$$\Delta G_f^0(\mathrm{Am^{3+}, aq}) = -603 \pm 4\ \mathrm{kJ\ mol^{-1}}$$

and

$$E^0(\mathrm{Am^{3+}/Am^0}) = -2.08 \pm 0.01\ \mathrm{V}$$

which are in excellent agreement with the IAEA-recommended values [18] of -599.1 ± 4 kJ mol^{-1} and -2.07 ± 0.01 V, respectively.

ACKNOWLEDGMENTS

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contracts DE-AS05-76ER04447 with the University of Tennessee, Knoxville and DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc. The services of the ORNL Analytical Chemistry Division in performing the spark-source mass spectrometric analysis of americium metal and helpful discussions with Dr. R.L. Fellows (ORNL Chemical Technology Division) are gratefully acknowledged.

REFERENCES

1 H.R. Lohr and B.B. Cunningham, J. Am. Chem. Soc., 73 (1951) 2025.
2 E.F. Westrum, Jr. and LeRoy Eyring, J. Am. Chem. Soc., 73 (1951) 3396.
3 L.R. Morss, University of California, Lawrence Radiation Lab. Rep. UCRL 18951, 1969.
4 J. Fuger, J.C. Spirlet and W. Müller, Inorg. Nucl. Chem. Lett., 8 (1972) 709.
5 J. Fuger, in N.M. Edelstein (Ed.), Actinides in Perspective, Pergamon Press, New York, 1982, p. 409.
6 D.L. Raschella, R.G. Haire and J.R. Peterson, University of Tennessee, Knoxville and Oak Ridge National Laboratory, unpublished results.
7 D.L. Raschella, R.L. Fellows and J.R. Peterson, Rev. Sci. Instrum., 50 (1979) 1481.
8 D.L. Raschella, R.L. Fellows and J.R. Peterson, J. Chem. Thermodyn., 13 (1981) 303.
9 C.H. Shomate and E.H. Huffman, J. Am. Chem. Soc., 65 (1943) 1625.
10 M.L. McGlashan, Pure Appl. Chem., 21 (1970) 1.
11 D.L. Raschella, Ph.D. Dissertation, University of Tennesee, Knoxville, U.S. Department of Energy Document ORO-4447-081, 1978.
12 J. Fuger, R.G. Haire and J.R. Peterson, J. Inorg. Nucl. Chem., 43 (1981) 3209.
13 J. Fuger, R.G. Haire and J.R. Peterson, J. Less-Common Met., 98 (1984) 315.
14 R.O.A. Hall, J.A. Lee, M.J. Mortimer, D.L. McElroy, W. Müller and J.C. Spirlet, J. Low. Temp. Phys., 41 (1980) 397.
15 J.W. Ward and H.H. Hill, in W. Müller and H. Blank (Eds.), Heavy Element Properties, Elsevier North-Holland, Amsterdam, 1976, p. 65.
16 J. Fuger and F.L. Oetting, in V. Medvedev, M.H. Rand and E.F. Westrum, Jr. (Eds.), The Chemical Thermodynamics of Actinide Elements and Compounds, Part 2, The Actinide Aqueous Ions, International Atomic Energy Agency, Vienna, 1976, p. 46.
17 CODATA Task Group, J. Chem. Thermodyn., 10 (1978) 903.
18 J. Fuger and F.L. Oetting, in V. Medvedev, M.H. Rand and E.F. Westrum, Jr. (Eds.), The Chemical Thermodynamics of Actinide Elements and Compounds, Part 2, The Actinide Aqueous Ions, International Atomic Energy Agency, Vienna, 1976, p. 47.