

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

THE HEAT OF SOLUTION OF CURIUM METAL AND THE HEATS OF FORMATION OF  $\text{Cm}^{+3}(\text{aq})$   
AND  $\text{CmCl}_3(\text{c})$

### Permalink

<https://escholarship.org/uc/item/79w979q4>

### Authors

Wallmann, J.C.  
Fuger, J.  
Haug, Hermann  
et al.

### Publication Date

1965-10-01

University of California  
Ernest O. Lawrence  
Radiation Laboratory

THE HEAT OF SOLUTION OF CURIUM METAL AND THE  
HEATS OF FORMATION OF  $\text{Cm}^{+3}_{(\text{aq})}$  AND  $\text{CmCl}_3_{(\text{c})}$

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545*

Berkeley, California

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory  
Berkeley, California

AEC Contract No. W-7405-eng-48

THE HEAT OF SOLUTION OF CURIUM METAL AND THE  
THE HEATS OF FORMATION OF  $\text{Cm}^{+3}$  (aq) AND  $\text{CmCl}_3^*$  (c)

$\dagger$  J. C. Wallmann,  $\dagger$  J. Fuger,  $\dagger$  Hermann Haug,  $\dagger$   
Sayed A. Marei  $\dagger$  and Brij M. Bansal  $\dagger$

October 1965

THE HEAT OF SOLUTION OF CURIUM METAL AND THE  
HEATS OF FORMATION OF  $\text{Cm}^{+3}(\text{aq})$  AND  $\text{CmCl}_3(\text{c})$ \*

J. C. Wallmann<sup>†</sup>, J. Fuger<sup>\*\*</sup>, Hermann Haug<sup>††</sup>,  
Sayed A. Marei<sup>\*\*\*</sup>, and Brij M. Bansal<sup>†††</sup>

Lawrence Radiation Laboratory  
University of California  
Berkeley, California

October 1965

ABSTRACT

The heat of solution of curium metal in 1 M HCl at  $298.4 \pm 0.2^\circ\text{K}$  has been measured and found to be  $-140.2 \pm 1 \text{ kcal mol}^{-1}$ . Calculated values for the heats of formation of  $\text{CmCl}_3(\text{c})$  and  $\text{Cm}^{+3}(\text{aq})$  are  $-226.4 \pm 1.2$  and  $-140.9 \pm 1.3 \text{ kcal mol}^{-1}$ , respectively.

## INTRODUCTION

Although numerous papers dealing with various aspects of the chemistry of curium have been published, none have reported experimental values for the heat or free energy of formation of any curium species. Thermodynamic data are an essential feature of the description of the chemistry of any element; we report here the first such data for curium.

## EXPERIMENTAL

### A. Curium metal

A number of samples of curium metal were prepared essentially according to the method of Cunningham and Wallmann.<sup>1</sup> The first three samples used for calorimetric measurements were made by the reduction of wet precipitated trifluoride subsequently dried over phosphorous pentoxide. Succeeding samples were prepared from wet precipitated trifluoride which was dried 6-7 hours in a stream of anhydrous  $\text{HF}_{(g)}$ , obtained by thermal decomposition of  $\text{NaHF}_2$  and subsequent distillation after the addition of a small amount of elemental fluorine.

All of the samples of curium metal so prepared exhibited the double hexagonal structure,  $a = 3.496 \pm 0.003\text{A}$ ,  $c = 11.331 \pm 0.005\text{A}$  as reported previously.<sup>1</sup> This structure is believed to be the stable crystalline form at room temperature and hence to represent the standard state for the metal at the temperature of the calorimeter runs.

Spectrographic analyses by copper spark excitation failed to reveal impurities in the metal samples at levels that would alter significantly the heat of solution. A list of impurities and limits for their detection by this method of analysis has been published in a previous paper.<sup>2</sup>

Mass analyses of the curium used in the calorimeter measurements showed the isotopic composition to be: 96.6% Cm<sup>244</sup>; 1.6% Cm<sup>245</sup>; 1.8% Cm<sup>246</sup>.

Pieces of metal weighing from 100 to 600 micrograms were used for the heat measurements; these were dissolved in about 8 ml of standardized 1 M HCl.

#### B. Calorimeter

The basic features of the calorimeter and technique of measurement have been described briefly by Fuger and Cunningham<sup>3</sup>; a detailed description of the construction and use of the instrument has been given by Burnett.<sup>4</sup>

The first three measurements of the heat of solution of curium were carried out prior to improvements in construction, which resulted in marked improvement in instrument stability. During the first measurement in this series the tracking was so erratic that the result was discarded. Instrument performance was acceptable in the two subsequent runs in this series, but was markedly improved before the measurements of the succeeding series.

## RESULTS AND DISCUSSION

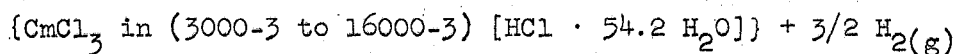
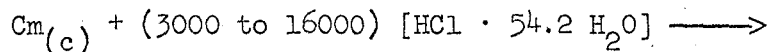
The results of the calorimetric measurements are given in Table 1 below.

TABLE 1. Heat of solution of curium metal in 1 M HCl at  $298.4 \pm 0.2^\circ\text{K}$ .

Sample no.	Weight ( $\mu\text{gm}$ )	Micromoles of Cm	Heat (cal)	$\Delta H_{\text{Soln}}^*$ (kcal mol $^{-1}$ )
1	265.5	1.088	0.1540	$141.5 \pm 1$
2	605.1	2.480	0.3465	$139.7 \pm 1$
3	118.3	0.4848	0.0677	$139.6 \pm 0.5$
4	192.0	0.7869	0.1101	$139.9 \pm 0.5$
		Average		$140.2 \pm 1$

\* Corrected for: a) the heat of vaporization of the water required to saturate the dry nitrogen in the sample bulb, b) the heat of vaporization of water required to saturate the hydrogen evolved, and c) the heat of bulb breakage ( $[6 \pm 3] \times 10^{-4}$  cal bulb $^{-1}$ ).

The observed heat corresponds to the reaction:



We neglect the slight change in composition of the HCl solution resulting from reaction with the metal, take the relative heat content of HCl in  $\text{HCl} \cdot 54.2 \text{ H}_2\text{O}$  to be  $-39.6 \text{ kcal mol}^{-1}$  and calculate  $-259.0 \pm 1 \text{ kcal mol}^{-1}$  for the heat of formation of  $\text{CmCl}_3$  dissolved in  $(3000 \text{ to } 16000) \text{ HCl} \cdot 54.2 \text{ H}_2\text{O}$ .



Westrum and Robinson<sup>5</sup> measured the heat of solution of  $\text{PuCl}_3(c)$  in various concentrations of hydrochloric acid, obtaining  $-22.15 \pm 0.1$ ,  $-29.5 \pm 0.1$  and  $-31.76 \pm 0.1$  kcal mol<sup>-1</sup> in 6 M, 1.5 M and 0.1 M acid, respectively.

Fuger and Cunningham<sup>3</sup> found  $-31.60 \pm 0.35$  kcal mol<sup>-1</sup> for the heat of solution of  $\text{PuCl}_3(c)$  in 0.001 M  $\text{HClO}_4$ , 0.099 M  $\text{NH}_4\text{ClO}_4$ . They also reported  $-30.60 \pm 0.2$  and  $-33.36 \pm 0.25$  kcal mol<sup>-1</sup> for the heat of solution of  $\text{AmCl}_3(c)$  in 1.5 and 0.001 M HCl, respectively.

We may use the data given above to arrive at an estimate for the heat of formation of  $\text{CmCl}_3(c)$  and  $\text{Cm}^{+3}(aq)$ .

The heat of solution of  $\text{AmCl}_3(c)$  in 1.5 M HCl is more negative than that of  $\text{PuCl}_3(c)$  in acid of the same concentration by  $1.1 \pm 0.3$  kcal. For  $(\text{HCl}) \leq 0.1$  M to 0.001 M, the corresponding difference is  $1.4 \pm 0.3$  kcal.

By extrapolating the above heat of solution data to  $\text{CmCl}_3(c)$  we predict the heat of solution of  $\text{CmCl}_3(c)$  in dilute HCl of a specified concentration to be more negative by  $1.2 \pm 0.4$  kcal than that of  $\text{AmCl}_3(c)$  in acid of the same concentration.

Thus our predicted heat of solution of  $\text{CmCl}_3(c)$  in 1.5 M HCl is  $-31.8 \pm 0.5$  kcal mol<sup>-1</sup>.

From a plot of the  $\text{PuCl}_3$  heat-of-solution data of Westrum and Robinson<sup>5</sup> against HCl concentration, the interpolated difference between 1.5 M and 1 M HCl is  $-0.8$  kcal mol<sup>-1</sup>.

Applying this same correction to  $\text{CmCl}_3(c)$  the heat of solution in 1.0 M HCl is predicted to be  $-32.6 \pm 0.5$  kcal mol<sup>-1</sup>.

Accordingly, the heat of formation of  $\text{CmCl}_3(c)$  =  $(-259.0 \pm 1) - (-32.6 \pm 0.5) - 226.4 \pm 1.2$  kcal mol<sup>-1</sup>.

The estimated heat of solution of  $\text{CmCl}_3(\text{c})$  in infinitely dilute HCl is  $-34.6 \pm 0.4 \text{ kcal mol}^{-1}$  whence

$$\Delta_{\text{f}}^{\text{H}^\circ} \text{Cm}^{+3}(\text{aq}) = -226.4 + 3(40.02) - 34.6$$

$$-140.9 \pm 1.3 \text{ kcal mol}^{-1}.$$

Although americium and curium metals have similar crystal structures and similar lattice parameters,<sup>1</sup> the heat of formation of  $\text{Cm}^{+3}(\text{aq})$  is some 20 kcal less negative than that of  $\text{Am}^{+3}(\text{aq})$ .<sup>3</sup> A contributing factor to this difference may be the larger heat of vaporization of curium.

#### ACKNOWLEDGMENTS

The authors wish to thank George Shalimoff and Ralph McLaughlin for spectrographic analyses, Mrs. Gertrude Bolz for radiation protection monitoring and Dr. Maynard Michel for the mass analysis of the curium used in this work.

FOOTNOTES AND REFERENCES

\* This work was performed under the auspices of the U. S. Atomic Energy Commission.

† Deceased.

\*\* Present address: Université de Liège, Laboratoire de Chimie Nucléaire, 2 rue A. Stévant, Liège, Belgium.

†† Present address: Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

\*\*\* Present address: Department of Chemistry, University of Pittsburg, Pittsburg, Pennsylvania.

††† Part of the work described here represents research carried on by Brij Bansal in partial satisfaction of the requirements for the degree of doctor of philosophy.

1. B. B. Cunningham and J. C. Wallmann, *J. Inorg. Nucl. Chem.* 27, 271 (1964).
2. D. B. McWhan, B. B. Cunningham and J. C. Wallmann, *J. Inorg. Nucl. Chem.* 24, 1025 (1962).
3. J. Fuger and B. B. Cunningham, *J. Inorg. Nucl. Chem.* 25, 1423 (1963).
4. John L. Burnett, "The Thermochemistry of Di- and Tri-valent Europium," Ph.D. Thesis, University of California Lawrence Radiation Laboratory report UCRL-11850, December 18, 1964.
5. E. F. Westrum, Jr., and H. P. Robinson, Radiochemical Studies: The Transuranium Elements (Edited by G. T. Seaborg, J. J. Katz and W. M. Manning) Plutonium Project Record NNES, Div. IV, Vol. 14-B, p. 922, (McGraw-Hill Book Co., Inc., New York, 1949).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

