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THE HEAT OF SOLUTION OF CURIUM METAL AND THE HEATS OF FORMATION OF $Cm^{+3}_{(aq)}$ AND $CmCl_{3(c)}$*

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ABSTRACT

The heat of solution of curium metal in 1 M HCl at 298.4 ± 0.2°K has been measured and found to be -140.2 ± 1 kcal mol^{-1}. Calculated values for the heats of formation of $CmCl_{3(c)}$ and $Cm^{+3}_{(aq)}$ are -226.4 ± 1.2 and -140.9 ± 1.3 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.[1] 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 $HF_{(g)}$, obtained by thermal decomposition of $NaHF_2$ 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 ± 0.003A, c = 11.331 ± 0.005A as reported previously.[1] 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.[2]

Mass analyses of the curium used in the calorimeter measurements showed the isotopic composition to be: 96.6% Cm^{244}; 1.6% Cm^{245}; 1.8% Cm^{246}.

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[3]; a detailed description of the construction and use of the instrument has been given by Burnett.[4]

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 ± 0.2°K.

Sample no.	Weight (μgm)	Micromoles of Cm	Heat (cal)	ΔH Soln* (kcal mol^{-1})
1	265.5	1.088	0.1540	141.5 ± 1
2	605.1	2.480	0.3465	139.7 ± 1
3	118.3	0.4848	0.0677	139.6 ± 0.5
4	192.0	0.7869	0.1101	139.9 ± 0.5
		Average		140.2 ± 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±3] × 10^{-4} cal bulb^{-1}).

The observed heat corresponds to the reaction:

$$Cm_{(c)} + (3000 \text{ to } 16000)\ [HCl \cdot 54.2\ H_2O] \longrightarrow$$

$$\{CmCl_3 \text{ in } (3000\text{-}3 \text{ to } 16000\text{-}3)\ [HCl \cdot 54.2\ H_2O]\} + 3/2\ H_{2(g)}$$

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 HCl · 54.2 H_2O to be -39.6 kcal mol^{-1} and calculate -259.0 ± 1 kcal mol^{-1} for the heat of formation of $CmCl_3$ dissolved in (3000 to 16000) HCl · 54.2 H_2O.

Westrum and Robinson[5] measured the heat of solution of $PuCl_{3(c)}$ in various concentrations of hydrochloric acid, obtaining -22.15 ± 0.1, -29.5 ± 0.1 and -31.76 ± 0.1 kcal mol^{-1} in 6 M, 1.5 M and 0.1 M acid, respectively.

Fuger and Cunningham[3] found -31.60 ± 0.35 kcal mol^{-1} for the heat of solution of $PuCl_{3(c)}$ in 0.001 M $HClO_4$, 0.099 M NH_4ClO_4. They also reported -30.60 ± 0.2 and -33.36 ± 0.25 kcal mol^{-1} for the heat of solution of $AmCl_{3(c)}$ 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 $CmCl_{3(c)}$ and $Cm^{+3}_{(aq)}$.

The heat of solution of $AmCl_{3(c)}$ in 1.5 M HCl is more negative than that of $PuCl_{3(c)}$ in acid of the same concentration by 1.1 ± 0.3 kcal. For (HCl) ≦ 0.1 M to 0.001 M, the corresponding difference is 1.4 ± 0.3 kcal.

By extrapolating the above heat of solution data to $CmCl_{3(c)}$ we predict the heat of solution of $CmCl_{3(c)}$ in dilute HCl of a specified concentration to be more negative by 1.2 ± 0.4 kcal than that of $AmCl_{3(c)}$ in acid of the same concentration.

Thus our predicted heat of solution of $CmCl_{3(c)}$ in 1.5 M HCl is -31.8 ± 0.5 kcal mol^{-1}.

From a plot of the $PuCl_3$ heat-of-solution data of Westrum and Robinson[5] against HCl concentration, the interpolated difference between 1.5 M and 1 M HCl is -0.8 kcal mol^{-1}.

Applying this same correction to $CmCl_{3(c)}$ the heat of solution in 1.0 M HCl is predicted to be -32.6 ± 0.5 kcal mol^{-1}.

Accordingly, the heat of formation of $CmCl_{3(c)}$ = (-259.0 ± 1) - (-32.6 ± 0.5) -226.4 ± 1.2 kcal mol^{-1}.

The estimated heat of solution of $CmCl_{3(c)}$ in infinitely dilute HCl is -34.6 ± 0.4 kcal mol^{-1} whence

$$\Delta H^{o}_{f\,Cm^{+3}_{(aq)}} = -226.4 + 3\,(40.02) - 34.6$$

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

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

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FOOTNOTES AND REFERENCES

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