HEAT AND FREE ENERGY OF THE REACTION $AmCl_{3(s)} + H_2O_{(g)} = AmOCl_{(s)} + 2HCl_{(g)}$

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C. W. Koch and B. B. Cunningham

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HEAT AND FREE ENERGY OF THE REACTION $AmCl_{3(s)} + H_2O_{(g)} = AmOCl_{(s)} + 2HCl_{(g)}$

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November 10, 1952

ABSTRACT

Equilibrium constants for the reaction

$$AmCl_{3(s)} + H_2O_{(g)} = AmOCl_{(s)} + 2HCl_{(g)}$$

have been measured at various temperatures between 682° and 880° K. These data have been combined with an estimated ΔCp function of $-2.8 - 0.36 \times 10^{-3}T + 0.44 \times 10^{5}T^{-2}$ to give the free energy function

$$\Delta F^{o}\ (\text{kcal.}) = 22.38 + \frac{6.4T \log T}{1000} + 1.8 \times 10^{-7}T^{2} - \frac{22}{T} - \frac{52.31T}{1000}$$

which agrees with the experimental data within an average deviation of $\pm$ 0.04 kcal. Extension of the free energy function to temperatures well outside of the experimental range, however, involves a greater uncertainty (perhaps of the order of a kilocalorie of room temperature) because of possible error in the ΔCp function.

Calculated thermodynamic constants for the reaction are as follows:

$\Delta F^{o}_{785} = -4.06$ kcal.; $\Delta H^{o}_{785} = 20.01$ kcal.; $\Delta S^{o}_{785} \doteq 30.6$ e.u.

$\Delta F^{o}_{298} = +11.45$ kcal.; $\Delta H^{o}_{298} = 21.38$ kcal.; $\Delta S^{o}_{298} = 33.3$ e.u.

The thermodynamic properties of this reaction are similar to those of the corresponding reactions of lanthanum, samarium, gadolinium, and plutonium. The free energy of the hydrolysis reaction appears to be determined with surprising exactitude by the ionic radius of the cation.

HEAT AND FREE ENERGY OF THE REACTION

$$AmCl_{3(s)} + H_2O_{(g)} = AmOCl_{(s)} + 2HCl_{(g)}$$

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November 10, 1952

INTRODUCTION

A method of measuring equilibrium constants at various temperatures for the reaction

$$LaCl_{3(s)} + H_2O_{(g)} = LaOCl_{(s)} + 2HCl_{(g)}$$

has been described in a previous paper.[1] The method has now been applied to an investigation of the corresponding reaction of americium. The work represents a part of a systematic program of investigation of the thermodynamic properties of analogous reactions of the lanthanide and actinide elements.

(1) C. W. Koch, A. Broido and B. B. Cunningham, J. Am. Chem. Soc., 74, 2349 (1952).

EXPERIMENTAL

Apparatus and experimental technique were essentially the same as described for the work with lanthanum, except that the furnace and reaction chamber were enclosed in a ventilated box fitted with glove ports to provide protection from the radioactivity of the americium. Approximately 0.8 mg. of the 475 year alpha particle emitting nuclide $_{95}Am^{241}$ was used for this work. The chemical purity of this material was investigated by spectrographic analysis, using copper

spark excitation, with the following results: lanthanum, 0.5%; plutonium, 0.2%; aluminum, 0.15%; and calcium, 0.1%. No other elements were detected. The reaction product $AmOCl_{(s)}$ was identified by x-ray diffraction methods. The compound is tetragonal, of the PbFCl structure type, and isostructural with PuOCl, LaOCl, SmOCl and GdOCl. The lattice constants are $a_1 = 3.99 \pm 0.01$, $a_3 = 6.77 \pm 0.01$ Å.

Equilibrium constants for the reaction were determined at eight different temperatures. The experimental results are summarized in Table I.

Table I

Equilibrium Constants for the Reaction

$$AmCl_{3(s)} + H_2O_{(g)} = AmOCl_{(s)} + 2HCl_{(g)}$$

Run No.	T^oK	P_{HCl}, mm.	P_{H_2O}, mm.	$K_{max.}$ / $K_{min.}$	K_{mean}	ΔF^o exp., kcal.	ΔF^o calc., kcal.	Δ kcal.
1	880	344	2.85	54.6	52.7 ± 1.9	-6.93	-6.96	+0.03
		304	3.34	50.9				
3	841	323	4.12	33.3	31.8 ± 1.4	-5.78	-5.77	-0.01
		306	4.07	30.3				
2	807	198	2.43	21.2	19.4 ± 1.8	-4.76	-4.73	-0.03
		179	2.40	17.6				
5	789	225	4.91	13.6	13.4 ± 0.2	-4.07	-4.18	+0.11
		212	4.46	13.3				
4	780	178	3.31	12.6	12.3 ± 0.4	-3.89	-3.90	+0.01
		169	3.15	11.9				
6	739	153.6	4.89	6.27	5.83 ± 0.44	-2.59	-2.66	+0.07
		139.8	4.76	5.40				
7	700	94.9	4.04	2.93	2.85 ± 0.08	1.46	-1.43	-0.03
		88.1	3.67	2.78				
8	682	73.3	3.42	2.07	1.96 ± 0.11	-0.91	-0.87	-0.04
		67.4	3.24	1.85				

Net deviation +0.11

Average deviation ±0.04

The right hand column of Table I lists the deviations of the experimental free energy values from those calculated from the equation

$$\Delta F^{o}\ (\text{kcal.}) = 22.38 + \frac{6.4T \log T}{1000} + 1.8 \times 10^{-7}T^{2} - \frac{22}{T} - \frac{52.31T}{1000}\ .$$

The free energy equation assumes the same ΔCp relation for this reaction as that estimated for the corresponding reaction of lanthanum, namely, $\Delta Cp = -2.8 - 0.36 \times 10^{-3}T + 0.44 \times 10^{5}T^{-2}$. The constants ΔH_o (= 22.38 kcal. mole^{-1}) and I (= - 52.31 cal. mole^{-1} deg.$^{-1}$) are the averages of values calculated from various pairs of experimentally observed equilibrium constants.

DISCUSSION

Within the experimental temperature range, agreement between observed and calculated free energy values is quite good. Close agreement would not be expected to be maintained at temperatures much outside this range, if the assumed ΔCp relation is substantially in error. It is possible that the error in the ΔCp equation is sufficient to introduce an error of a kilocalorie in the free energy value calculated for 298° K. Within the experimental temperature range, the calculated free energy values cannot be seriously in error (even if the ΔCp equation is quite incorrect) if the experimental data themselves are reliable.

It is of interest to compare the free energy values for the corresponding reactions of some rare earth and actinide elements. The comparison is presented in graphical form in Fig. 1. The free energies at 785° K. have been plotted as a function of ionic radius of the metal cation, using the radii given by Zachariasen.[2]

(2) W. H. Zachariasen, Phys. Rev., 73, 1104 (1948).

The free energy values are from the following sources: lanthanum,[1] samarium and gadolinium,[3] and plutonium.[4]

(3) C. W. Koch and B. B. Cunningham, University of California Unclassified Report UCRL-1918 (August 1952); J. Am. Chem. Soc., in press.

(4) I. Sheft and N. R. Davidson, "The Transuranium Elements: Research Papers," McGraw-Hill Book Co., Inc., New York, 1949, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, Paper 6.25.

The free energy values may be fitted to a single smooth curve. Although the curve for the rare earths is arbitrary to the extent of perhaps 0.5 kcal. in the neighborhood of the radii for Am^{+3} and Pu^{+3}, it seems somewhat surprising that the free energy of the reaction should be defined within a fraction of a kilocalorie by the ionic radius, independently of the atomic number. The data show no significant difference in polarizing effects between the lanthanides and actinides, although the layer structure of the oxychlorides would permit such a difference to be made evident. Of course it is possible that differences may be revealed by more extensive investigations.

Of perhaps more general interest is the degree of reliability to be expected in the estimation of the thermodynamic properties of reactions of the actinide elements from work with rare earth "stand-ins." The limited data presented in this paper suggest that such

estimations may be made with high accuracy. Of course, reactions involving changes in oxidation state of the cation will not in general be expected to show close correspondence between the lanthanide and actinide elements.

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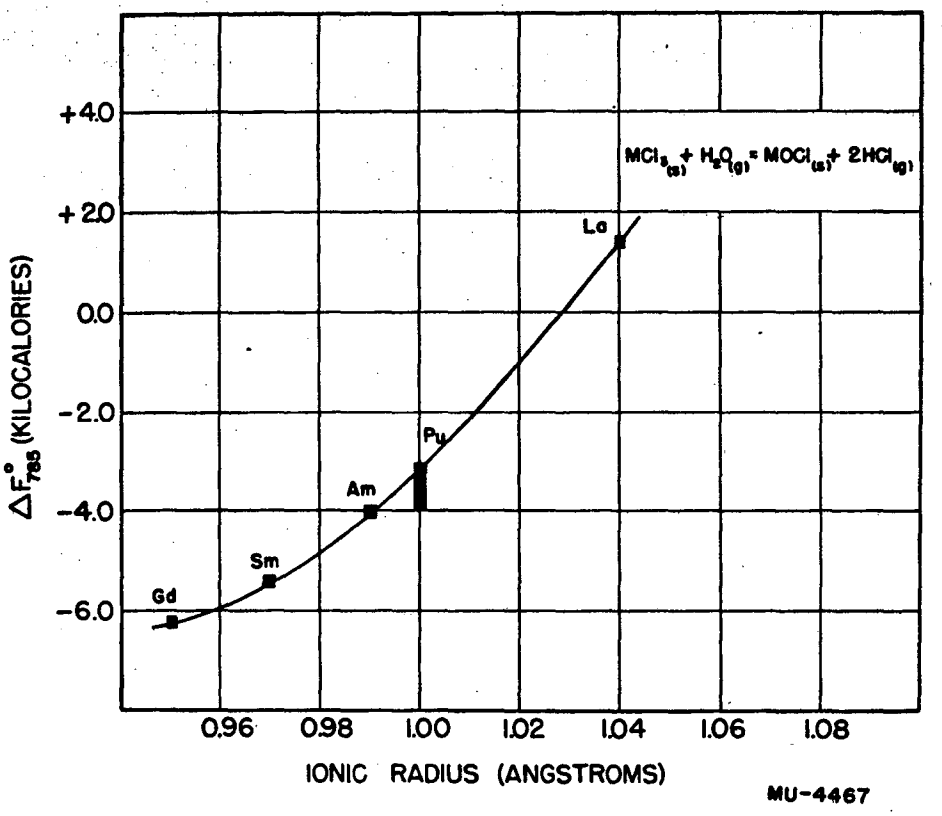

Fig. 1. -- Free energy of the reaction $MCl_{3(s)} + H_2O_{(g)} = MOCl_{(s)} + 2HCl_{(g)}$ as a function of the ionic radius of the cation.

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