[Contribution from the Department of Chemistry and Radiation Laboratory, University of California]

The Vapor Phase Hydrolysis of the Actinide Halides.[1] I. Heat and Free Energy of the Reaction $AmCl_3(s) + H_2O(g) = AmOCl(s) + 2HCl(g)$

By C. W. Koch[2] and B. B. Cunningham

Received November 21, 1953

Equilibrium constants for the reaction $AmCl_3(s) + H_2O(g) = AmOCl(s) + 2HCl(g)$, have been measured at various temperatures between 682 and 800°K. These data have been combined with an estimated ΔC_p function of $-2.8 - 0.36 \times 10^{-3}T + 0.44 \times 10^5T^{-2}$ to give the free energy function: ΔF^0 (kcal.) $= 22.38 + (6.4T \log T/1000) + 1.8 \times 10^{-7}T^2 - (22/T) - (52.31T/1000)$, which agrees with the experimental data within an average deviation of ±40 cal. per mole. Extension of the free energy function to temperatures well outside of the experimental range, however, involves a greater uncertainty because of possible error in the ΔC_p function. Calculated thermodynamic constants for the reaction are:

$$\Delta F^0_{785} = -4.06 \text{ kcal.};\ \Delta H^0_{785} = 20.01 \text{ kcal.};\ \Delta S^0_{785} = 30.6 \text{ e.u.}$$
$$\Delta F^0_{298} = +11.45 \text{ kcal.};\ \Delta H^0_{298} = 21.38 \text{ kcal.};\ \Delta S^0_{298} = 33.3 \text{ e.u.}$$

The thermodynamic properties of this reaction are similar to those of corresponding reactions of the rare earth trichlorides. The heat and free energy of the trichloride hydrolysis reaction appear to be determined rather exactly by the ionic radius of the cation, with evidence for only a slight difference between an actinide and lanthanide element of the same radius.

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.[3] 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.

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 α-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.

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

$$\Delta F^0 \text{ (kcal.)} = 22.38 + \frac{6.4T \log T}{1000} + 1.8 \times 10^{-7}T^2 - \frac{22}{T} - \frac{52.31T}{1000}$$

Table I

Equilibrium Constants for the Reaction $AmCl_3(s) + H_2O(g) = AmOCl(s) + 2HCl(g)$

Run no.	T, °K.	P_{HCl}, mm.	P_{H_2O}, mm.	K_{max} K_{min}	K_{mean}	ΔF^0, kcal. exp.	calcd.	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	− .01
		306	4.07	30.3				
2	807	198	2.43	21.2	19.4 ± 1.8	−4.76	−4.73	− .03
		179	2.40	17.6				
5	789	225	4.91	13.6	13.4 ± 0.2	−4.07	−4.18	+ .11
		212	4.46	13.3				
4	780	178	3.31	12.6	12.3 ± 0.4	−3.89	−3.90	+ .01
		169	3.15	11.9				
6	739	153.6	4.89	6.27	5.83 ± 0.44	−2.59	−2.66	+ .07
		139.8	4.76	5.40				
7	700	94.9	4.04	2.93	2.85 ± 0.08	−1.46	−1.43	− .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 dev.	+ .11
							Av. dev.	± .04

The free energy equation assumes the same ΔC_p relation for this reaction as that estimated for the corresponding reaction of lanthanum, namely, $\Delta C_p = -2.8 - 0.36 \times 10^{-3}T + 0.44 \times 10^5T^{-2}$. The constants ΔH_0 (= 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.

---

[1] This work was performed under the auspices of the A.E.C.

[2] The data reported here were included in a dissertation submitted by C. W. Koch to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] C. W. Koch, A. Broido and B. B. Cunningham, This Journal, **74**, 2349 (1952).

The calculated thermodynamic constants of the reaction are

$\Delta F^0_{785} = -4.06$ kcal.; $\Delta H^0_{785} = 20.01$ kcal.; $\Delta S^0_{785} = 30.6$ e.u.

$\Delta F^0_{298} = +11.45$ kcal.; $\Delta H^0_{298} = 21.38$ kcal.; $\Delta S^0_{298} = 33.3$ e.u.

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 ΔC_p relation is substantially in error.

It is of interest to compare the free energy values for the corresponding reactions of some rare earth and actinide elements. In an accompanying paper[4] the ΔH^0 values for the rare earth hydrolysis reactions at 785°K. have been plotted as a function of the reciprocal of the ionic radii[5] of the metal cation corrected to coördination number 9.

The ΔH^0_{785} values for the rare earths may be fitted to a single smooth curve. The heats for the $AmCl_3(s)$ and $PuCl_3(s)$ hydrolysis reactions appear to lie on a parallel curve, shifted along the abscissa by about −0.01 reciprocal ångströms. The difference is qualitatively consistent with a somewhat greater polarizability of O^{--} than Cl^-, and of an actinide element as compared with a lanthanide element of the same radius. (The heat values are from the following sources: lanthanum,[3] samarium and gadolinium,[6] praseodymium and neodymium[4] and plutonium.[7])

In view of the fact that polarization forces must contribute something of the order of 60 kcal. to the stability of the solids, it seems somewhat surprising that the heat of the reaction should be defined within a kilocalorie by the ionic radius of the cation, independently of the atomic number. Larger differences between actinide and lanthanide elements may appear in the hydrolysis reactions of the tribromides or triiodides, and it is hoped that this point can be investigated experimentally in the near future.

Acknowledgments.—Mrs. Carol Dauben and Mrs. Helena Ruben of Professor D. H. Templeton's X-ray diffraction group obtained the X-ray data on AmOCl reported in this paper.

The design and construction of the radiation protection equipment used in this work was carried out by Mr. Bill Ruehle and Mr. A. F. Azzalini of the Health Chemistry group of the Radiation Laboratory.

BERKELEY, CALIFORNIA

---

[4] C. W. Koch and B. B. Cunningham, THIS JOURNAL, **76**, 1471 (1954).

[5] W. H. Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).

[6] C. W. Koch and B. B. Cunningham, THIS JOURNAL, **75**, 796 (1953).

[7] 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.

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

The Vapor Phase Hydrolysis of the Rare Earth Halides.[1] III. Heat and Free Energy of the Reactions $PrCl_3(s) + H_2O(g) = PrOCl(s) + 2HCl(g)$ and $NdCl_3(s) + H_2O(g) = NdOCl(s) + 2HCl(g)$

BY C. W. KOCH[2] AND B. B. CUNNINGHAM

RECEIVED NOVEMBER 21, 1953

Equilibrium constants for the hydrolysis of $PrCl_3(s)$ and $NdCl_3(s)$ by water vapor have been determined at various temperatures between 700 and 900°K. Free energy functions based on the experimental data and an estimated ΔC_p relation agree with experiment within an average deviation of ±30 cal. $mole^{-1}$ for the praseodymium reaction and ±10 cal. $mole^{-1}$ for neodymium. Calculated thermodynamic constants for the reactions are

$PrCl_3(s)$: $\Delta F^0_{785} = -2.07$ kcal.; $\Delta H^0_{785} = 21.53$ kcal.; $\Delta S^0_{785} = 30.07$ e.u.

$\Delta F^0_{298} = 13.22$ kcal.; $\Delta H^0_{298} = 22.98$ kcal.; $\Delta S^0_{298} = 32.75$ e.u.

$NdCl_3(s)$: $\Delta F^0_{785} = -2.88$ kcal.; $\Delta H^0_{785} = 20.91$ kcal.; $\Delta S^0_{785} = 30.31$ e.u.

$\Delta F^0_{298} = 12.41$ kcal.; $\Delta H^0_{298} = 22.24$ kcal.; $\Delta S^0_{298} = 32.99$ e.u.

It is pointed out that for the rare earth trichlorides of lanthanum through gadolinium the heats of hydrolysis show an approximately linear dependence upon the reciprocal of the cation radius.

An experimental method for determining equilibrium constants for reactions of the type specified in the title of this paper has been described previously.[3] Results have already been reported for the hydrolysis of the trichlorides of lanthanum, samarium and gadolinium.[3,4] The investigations have now been extended to neodymium and praseodymium. In the case of these elements a significant improvement in the precision of the measurements has been realized by certain refinements of the apparatus and experimental technique, as described below.

Experimental

Apparatus.—The apparatus used for the work with praseodymium and neodymium was modified from that described previously[3] in the following ways.

(1) Temperature regulation of the thermostat containing aqueous hydrochloric acid solutions was improved from ±0.1 to ±0.005° by installing a toluene–mercury regulator and new stirring system.

---

[1] This work was performed under the auspices of the A.E.C.

[2] The data reported here were included in a dissertation submitted by C. W. Koch to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] C. W. Koch, A. Broido and B. B. Cunningham, THIS JOURNAL, **74**, 2349 (1952).

[4] C. W. Koch and B. B. Cunningham, *ibid.*, **75**, 796 (1953).