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The Vapor Phase Hydrolysis of the Rare Earth Halides. II. Heat and Free Energy of the Reactions: $SmCl_3(s) + H_2O(g) = SmOCl(s) + 2HCl(g)$ and $GdCl_3(s) + H_2O(g) = GdOCl(s) + 2HCl(g)$

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Measurements of equilibrium constants for the reactions: $SmCl_3(s) + H_2O(g) = SmOCl(s) + 2HCl(g)$ and $GdCl_3(s) + H_2O(g) = GdOCl(s) + 2HCl(g)$ at various temperatures give the free energy functions $\Delta F°(\text{kcal.}) = 21.56 + (6.4T \log T/1000) + 1.8 \times 10^{-7} T^2 - (22/T) - (53.01\ T/1000)$, and $\Delta F°(\text{kcal.}) = 19.96 + (6.4T \log T/1000) + 1.8 \times 10^{-7} T^2 - (22/T) - (51.88\ T/1000)$, respectively, using an estimated ΔC_p function of $-2.8 - 0.36 \times 10^{-3}\ T + 0.44 \times 10^6\ T^{-2}$ for both reactions. Within the experimental temperature range of about 700–900°K. these functions are consistent with the experimental measurements within an average deviation of about ±0.07 kcal. Because of the possible error in the estimated ΔC_p function, however, extrapolation to 298°K. involves a much larger uncertainty.

Introduction

An experimental method of measuring equilibrium constants for the reaction: $LaCl_3(s) + H_2O(g) = LaOCl(s) + 2HCl(g)$ at various temperatures has been described in a previous paper.[1] The method has now been applied to an investigation of the corresponding reactions of samarium and gadolinium. The results are of interest because they furnish thermodynamic data not previously available for the rare earth oxychlorides and also because they provide information for a consideration of the influence of crystal geometry on the thermodynamic properties of compounds of close structural similarity. This latter subject will be considered in a subsequent paper.

Experimental

Apparatus and Technique.—A detailed description of the apparatus and experimental technique used for the hydrolysis measurements on lanthanum trichloride has been given previously.[1] No modifications of apparatus or technique were necessary for the measurements reported here. However, a platinum foil radiation shield some four inches in length has now been placed around the central portion of the reaction chamber, although it was found that the apparent temperature of the sample was not affected significantly by this change in the experimental set-up.

Materials.—Samarium was obtained as the sesquioxide from Dr. Frank Spedding of Iowa State College. Spectrographic analysis by Mr. John Conway of the Radiation Laboratory gave the following results: europium, 0.01–0.1%; calcium, 0.01–0.1%; lanthanum, 0.01–0.1%.

Gadolinium sesquioxide was purchased from Adam Hilger and Sons, London, England. The results of a spectrographic analysis of a sample of this material were as follows: iron, 0.01–0.1%; magnesium, 0.01–0.1%; and no other rare earth detected.

X-Ray Diffraction Data.—Powder patterns of rare earth trichlorides and oxychlorides prepared by the methods described in this paper were obtained by Mrs. Carol Dauben and Mrs. Helena Rubin of the X-ray diffraction group. Estimates of the crystallite size of some of our preparations were made by Professor D. H. Templeton from measurements of the line broadening of the diffraction patterns.

Results

The results of the hydrolysis measurements on solid $SmCl_3$ and $GdCl_3$ are summarized in Tables I and II. Calculated free energy values based on the function

$$\Delta F^0_T = \Delta H_0 + \frac{6.4T \log T}{1000} + 1.8 \times 10^{-6}\ T^2 - \frac{22}{T} + IT$$

are given for comparison. This function assumes the same ΔC_p equation as that estimated for lanthanum[1]

$$\Delta C_p = -2.8 - 0.36 \times 10^{-3}\ T + 0.44 \times 10^5 T^{-2}$$

The constants ΔH_0 and I were evaluated for the samarium and gadolinium reactions by taking the mean of individual values calculated from various pairs of free energy values derived from experimentally observed equilibrium constants.

The right hand columns of Tables I and II give the deviations of the experimental ΔF^0 values from the ΔF^0 values calculated from the free energy functions. Within the experimental temperature range the agreement is reasonably satisfactory.

It should be emphasized, however, that heat capacity data for the rare earth chlorides and oxychlorides are not available and the uncertainty in our estimated ΔC_p equation therefore is considerable. This leads to an uncertainty of perhaps 1.5 kcal. and 2–3 entropy units in the extrapolation of our data to room temperature.

The thermodynamic constants for the hydrolysis of the solid trichlorides of lanthanum, samarium and gadolinium by water vapor are summarized in Table III.

ΔS_{785} for the reactions has a mean value of 30.8 ± 0.6 cal. mole^{-1} deg.$^{-1}$, and may be regarded as constant within the experimental error of the measurements.

The most noticeable feature of the hydrolysis reactions is that their heats and free energies become progressively more negative with increasing atomic number. A consideration of this effect in terms of the crystal energies of the trichlorides and oxychlorides of lanthanum, samarium and gadolinium will be presented in a subsequent paper.

In a previous paper[1] on the reaction of lanthanum trichloride with water vapor, we combined our thermochemical data with data given in the Bureau of Standard's "Selected Values of Chemical Thermodynamic Properties" (Series I, Table 76-1, December 31, 1949) to calculate a heat and free energy of formation of LaOCl. It now appears[2,3] that the heats of formation of the rare earth trichlorides given in "S.V.C.T.P." are substantially in error. It does not seem worthwhile therefore to attempt

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

[2] H. R. Lohr and B. B. Cunningham, *ibid.*, **73**, 2025 (1951).

[3] F H. Spedding and C. F. Miller, Iowa State College, Ames Laboratory Report ISC-167 (July 25, 1951).

TABLE I

EQUILIBRIUM CONSTANTS FOR THE REACTION: $SmCl_3(s) + H_2O(g) = SmOCl(s) + 2HCl(g)$

Run No.	T, °K.	P_{HCl}, mm.	P_{H_2O}, mm.	K_{max} K_{min}	K_{mean}	$\Delta F^0_{expt.}$ kcal.	$\Delta F^0_{calcd.}$ kcal.	Δ, kcal.
7	893	418.8	1.60	144	140 ± 4	−8.77	−8.83	+0.06
		406.3	1.60	136				
8	885	423.7	1.77	133	124.5 ± 8.5	−8.48	−8.55	+0.07
		390.8	1.74	116				
9	867	454.9	2.54	107	104.5 ± 2.5	−8.01	−8.00	+0.01
		442.5	2.52	102				
10	848	441.9	2.99	85.9	80.8 ± 5.1	−7.40	−7.40	0.00
		407.8	2.89	75.7				
11	830	363.7	2.70	64.4	62.9 ± 1.6	−6.83	−6.84	+0.01
		347.3	2.59	61.3				
1	816	387.8	3.45	57.3	55.5 ± 1.8	−6.51	−6.40	−0.11
		329.6	2.66	53.7				
12	811	326.1	2.65	52.8	51.4 ± 1.5	−6.35	−6.24	−0.09
		309.8	2.53	49.9				
2	797	273.6	2.43	40.5	39.5 ± 1.0	−5.82	−5.81	−0.01
		262.7	2.36	38.5				
13	774	298.2	4.14	28.3	27.5 ± 0.8	−5.10	−5.08	−0.02
		272.1	3.64	26.8				
4	755	258.3	4.26	20.6	19.3 ± 1.3	−4.44	−4.48	+0.04
		231.9	3.90	18.1				
5	727	205.3	4.37	12.7	12.2 ± 0.5	−3.61	−3.70	+0.09
		193.6	4.22	11.7				
14	703	152.7	3.81	8.05	7.53 ± 0.52	−2.82	−2.84	+0.02
		133.6	3.35	7.01				
							Average deviation	±0.05
							Net deviation	+0.05

TABLE II

EQUILIBRIUM CONSTANTS FOR THE REACTION: $GdCl_3(s) + H_2O(g) = GdOCl(s) + 2HCl(g)$

Run No.	T, °K.	P_{HCl}, mm.	P_{H_2O}, mm.	K_{max} K_{min}	K_{mean}	$\Delta F^0_{expt.}$, kcal.	$\Delta F^0_{calcd.}$, kcal.	Δ, kcal.
1	895	610	2.46	199	192 ± 7	−9.35	−9.45	+0.10
		636	2.87	185				
8	880	472	1.80	163	156 ± 8	−9.19	−9.00	−0.19
		397	1.40	148				
3	870	620	3.17	159	155 ± 4	−8.72	−8.70	−0.02
		605	3.18	151				
9	858	453	1.97	137	134 ± 3	−8.35	−8.34	−0.01
		415	1.72	132				
10	840	344	1.55	101	100 ± 2	−7.69	−7.80	+0.11
		318	1.36	98				
11	821	346	1.84	86	84 ± 2	−7.23	−7.23	0.00
		300	1.42	83				
5	800	478	4.36	69	65 ± 5	−6.64	−6.60	−0.04
		387	3.22	60				
12	751	322	4.16	32.8	31.5 ± 1.4	−5.15	−5.11	−0.04
		303	4.01	30.1				
7	701	212	4.08	14.4	14.0 ± 0.5	−3.68	−3.58	−0.10
		218	4.66	13.5				
							Average deviation	±0.07
							Net deviation	−0.19

TABLE III

SUMMARY OF THERMODYNAMIC CONSTANTS FOR THE TRICHLORIDE HYDROLYSIS REACTIONS

Values are ΔH in kcal. per mole and ΔS in cal. per degree per mole

	ΔF^0_{785}	ΔH^0_{785}	ΔS^0_{785}	ΔF^0_{298}	ΔH^0_{298}	ΔS^0_{298}	ΔH_0	I
La	+1.4	25.6	30.8	17.0	27.0	33.5	27.9	−52.4
Sm	−5.4	19.2	31.4	10.4	20.6	34.0	21.6	−53.0
Gd	−6.2	17.6	30.2	9.2	19.0	32.9	20.0	−51.9

to calculate heats and free energies of formation of SmOCl and GdOCl from our data until reliable thermochemical values are available for the trichlorides.

Crystallite size estimates of some of our preparations indicated a particle size in excess of 500 Å. Therefore the departure from macrocrystalline behavior probably was unimportant in comparison with the experimental error.

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