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The Vapor Phase Hydrolysis of Rare Earth Halides. I. Heat and Free Energy of the Reaction: $LaCl_3(s) + H_2O(g) = LaOCl(s) + 2HCl(g)$[1]

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The equilibrium constant for the hydrolysis of solid $LaCl_3$ by water vapor has been investigated as a function of temperature in the range 730–895°K. These data, combined with a ΔC_p equation for the reaction of $-2.79 - 0.36 \times 10^{-3}T + 0.44 \times 10^5 T^{-2}$, give the following thermodynamic constants: $\Delta H_0 = 27.9$, $\Delta H_{298} = 27.0$, and $\Delta H_{785} = 25.6$, all in kcal. mole^{-1}; $\Delta S_{298} = 33.5$ cal. mole^{-1} deg.$^{-1}$, and $\Delta S_{785} = 30.8$ cal. mole^{-1} deg.$^{-1}$.

Introduction

Although thermodynamic data are available for many of the rare earth oxides and halides no data of this kind have been published for the oxyhalides. This deficiency imposes a serious handicap in some kinds of work with the rare earths, since the oxyhalides are of quite common occurrence, and in fact they are rarely absent entirely from preparations intended to be the pure trihalides.

We have thought it worthwhile, therefore, to determine some of the thermodynamic properties of the oxyhalides, in order that the conditions of their formation may be more clearly defined. To that end we have made an investigation of the variation with temperature of the equilibrium constant of the reaction

$$LaCl_3(s) + H_2O(g) = LaOCl(s) + 2HCl(g) \quad (1)$$

It is planned to extend this type of investigation to other rare earth trihalides.

The method used by us to obtain heat and free energy data for the $LaCl_3$ hydrolysis was chosen principally because of its experimental convenience and adaptability to small quantities of material; it probably will be satisfactory without modification for the investigation of the hydrolysis of nearly all of the rare earth trichlorides.

Experimental

Method.—A schematic drawing of our apparatus is shown in Fig. 1A, B. An experimental run was initiated by adding about 1 mg. of lanthanum oxide to the shallow platinum foil pan (marked 6 in Fig. 1A) which was supported by a quartz ring in the center of a simple quartz fiber cantilever balance,[2] as shown in the drawing. The loaded balance was placed inside a 31 cm. o.d. diameter quartz tube, and heated to an appropriate temperature by a tube furnace. Anhydrous hydrogen chloride was then passed through the tube to convert the oxide to the trichloride. Following the initial conversion to trichloride a mixture of nitrogen, HCl(g) and $H_2O(g)$ of selected composition—obtained by bubbling nitrogen through aqueous HCl solutions—was passed through the tube.

By subsequent careful adjustment of the gas composition and by making slight changes in the temperature of the furnace it was possible to bracket the equilibrium constant $K = (P^2_{HCl}/P_{H_2O})$ for reaction (1) within a few per cent. at a number of selected temperatures. Gas compositions in which the value of (P^2_{HCl}/P_{H_2O}) exceeded K caused the reaction to proceed to the left, as was evident by an increase in weight of the sample. Conversely, when the value of (P^2_{HCl}/P_{H_2O}) was less than K the sample lost weight. In practice the reactions were seldom carried to completion, but were continued for a sufficient length of time to ascertain whether trichloride or oxychloride was being formed.

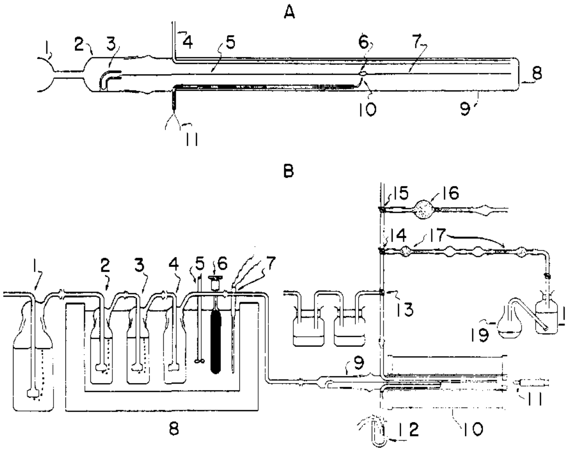

Fig. 1. A.—1, ball joint; 2, standard taper Pyrex male joint, No. 29/42; 3, support for cantilever balance; 4, exit tube for gas mixture; 5, beam of balance; 6, sample in platinum foil pan; 7, balance pointer; 8, optical window; 9, quartz reaction chamber; 10, Pt—87% Pt, 13% Rh thermocouple; 11, thermocouple leads to cold junction and potentiometer.

B.—1, 2, 3, gas bubblers containing aqueous HCl solution; 4, spray trap; 5, stirrer; 6, thermoregulator; 7, knife heater; 8, end of reaction chamber; 9, standard taper joint; 10, tube furnace; 11, low power microscope; 12, cold junction; 13, 14, 15, 3-way stopcocks; 16, absorption tube for purifying nitrogen; 17, absorption tube for water analysis; 18, Mariotte bottle; 19, water collection flask; 20, 21, traps for absorbing HCl.

It was established in early experiments that the lattice constants of the components of the mixture of trichloride and oxychloride produced in this way were the same as those of the pure substances and consequently that these compounds do not form solid solutions.

In order to obtain reliable results by the method just outlined it was necessary to observe certain precautions which are mentioned below.

Composition of the Gas Stream.—The partial pressures of HCl and H_2O were fixed at approximately the desired levels by bubbling tank nitrogen (Linde Air Products, 99.9%) through a series of gas bubblers (1, 2, 3 of Fig. 1B) filled with aqueous solutions of reagent grade HCl, or with this acid fortified by the addition of anhydrous HCl obtained from a cylinder of the compressed gas. Aid in selecting a composition to produce a desired pressure of HCl and H_2O was obtained by reference to the data given in reference 3. Early work[4] indicated that the vapor pressures obtained by bubbling nitrogen through the aqueous solutions were close to the saturation values, but a more careful investigation revealed that they were significantly lower. Consequently, the pressures of HCl(g) and $H_2O(g)$ in the gas stream were determined by analysis, as explained in a subsequent section.

Spray was removed from the gas stream by incorporating a fourth, empty bubbler (of the fritted glass type) in the

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[1] Presented to the Section on Physical and Inorganic Chemistry, XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September 13, 1951.

[2] B. B. Cunningham, *Nucleonics*, **5**, 62 (1949).

[3] "International Critical Tables," McGraw-Hill Book Company, Inc., New York, N. Y., 1926.

[4] A. Broido and B. B. Cunningham, Atomic Energy Declassified Document AECD-2918 (July 14, 1950).

line, as shown in the figure. The second and third bubblers, and the spray trap, were immersed in a thermostatic bath regulated to ± 0.1°.

All gas leads beyond the second bubbler and up to the furnace were wound with nichrome wire through which a current was passed to maintain the leads several degrees above bath temperature. This detail has been omitted from the drawing. Although analysis served to define the composition of the effluent gas stream with satisfactory accuracy, it did not of itself determine the composition of the gas in the interior of the furnace in the neighborhood of the sample. Thermal diffusion effects may produce a substantial separation of the components of a gas mixture in an apparatus of the type used by us, in which large thermal gradients exist.[5] The existence of an experimentally important thermal diffusion effect can be revealed empirically by altering the flow rate and noting the effect on the apparent value of K. This point was investigated at an early stage in our measurements. At 800°K. alteration of the flow rate from 10 ml. per minute to 125 ml. per minute was found to produce a change in the apparent value of K of only 4%; a variation from 15 ml. per minute to 125 ml. per minute produced a change of only 2%. Flow rates used in the subsequent equilibrium constant measurements were in excess of 20 ml. per minute.

Construction and Operation of the Balance.—The quartz fiber cantilever balance used to follow changes in the weight of the sample was constructed from a fiber 20 cm. in length and approximately 200 μ in diameter, bent at one end to form a circular loop of 6-mm. radius, which served to support a shallow platinum pan in which the sample was placed. A quartz fiber pointer 17 cm. in length about 190 μ in diameter was fused to the opposite side of the loop to form a coaxial extension of the beam. In earlier measurements the fixed end of the balance was cemented with silver chloride inside the opening of the L-shaped piece of capillary tubing marked 3 in Fig. 1A. Later the balance was fused to the supports through a graded Pyrex–quartz seal.

The balance pan was made from an 8-mm. diameter disc of 0.2-mil platinum foil, which was placed on several thicknesses of paper and worked into the form of a shallow dish by rubbing the center with the rounded end of a glass rod. The rim of the dish was pierced with several small holes so that it could be "sewn" to the quartz loop of the balance with fine platinum wire.

After the balance was completed it was loaded with a 1.5-mg. weight and the curvature noted. It was then inverted and a compensating curvature imparted by carefully heating along the length of the beam with a relatively cold flame from a microtorch. A little practice made it possible to adjust the initial curvature so that upon reinversion and reloading, the balance assumed a horizontal position over practically its entire length and could be inserted into the reaction chamber without difficulty. The completed balance had a sensitivity of 10 mm./mg. and a sensibility of 0.2 μg.

In use, the balance proved to be remarkably stable and reliable in its operation. No irreversible drifts were noted below 900°K. At constant temperature the rest point was quite constant, and the whole system surprisingly insensitive to vibration. The variation of the rest point with temperature was inconsistent with the value of 1.3×10^{-4} °C.$^{-1}$ reported[6] for the temperature coefficient of Young's modulus for fused silica. Using moderate magnification to observe the movement of the pointer the balance thus behaved as a sensitive and apparently reproducible thermometer, although its behavior in this respect was not investigated in detail.

There was no apparent reaction of the balance or the pan with the gas mixture, even after weeks of use at temperatures above 700°K.

The Reaction Chamber.—The fused quartz reaction chamber, illustrated in Fig. 1A, consisted of 34 cm. of 3.1 cm. o.d. clear quartz tubing, closed with an optical window at one end and fitted with a 29/42 male ground quartz joint at the other. The over-all length, including the joint, was about 38 cm. Two 4-mm. diameter side tubes, also of quartz, were inserted through ring seals at opposite sides of the larger tube, at a distance of 35 cm. from the window. These smaller tubes were bent sharply at right angles, and ran parallel and very close to the inside wall of the chamber. The upper tube extended nearly to the inside wall of the optical window, and served as a velocity exit for the gas mixture.

The lower tube, containing the leads of a platinum:90% platinum–10% rhodium thermocouple, extended about halfway down the chamber and terminated directly beneath the reaction pan. The thermocouple junction extended beyond the quartz tube, which was drawn very thin and sealed around the 5-mil diameter thermocouple wires.

The reaction chamber was closed with a 29/42 Pyrex female joint, having a 5-mm. i.d. inlet for the gas mixture. Just beyond the ground portion of this joint an inverted L shaped piece of 1-mm. i.d. Pyrex capillary was fused at its lower end to the inside wall of the joint. The fixed end of the balance beam was set in the capillary opening and fastened in place, as described previously.

Temperature Measurements.—The temperature of the sample was determined by means of an internal platinum: 87% platinum–13% rhodium thermocouple, constructed of single strands of 5-mil wire. The thermocouple junction was located directly beneath the balance pan and about 3 mm. from it. This working thermocouple was calibrated against a Bureau of Standards platinum:90% platinum–10% rhenium thermocouple. The correction to the working thermocouple varied nearly linearly from 90° at 366° to 12° at 625°.

The leads from the thermocouple were soldered to No. 18 B and S gage copper wire and connected to the binding posts of a Rubicon Precision Potentiometer. The soldered junctions were kept at 0° by immersion in an ice-bath. The potentiometer was used with a Rubicon lamp and scale galvanometer, having a sensitivity of 0.0037 microamp. per mm., and a period of 1.3 seconds. Differences in temperature of 0.3° were readily detected with this arrangement.

The equilibrium measurements were carried out without the interposition of a radiation shield between the reaction tube and the surrounding furnace. It was found, however, that no significant temperature gradient existed between the sample and thermocouple under these conditions. Small samples of $K_2Cr_2O_7$ (m.p. 398°) were observed to melt at the same thermocouple reading, whether the tube was surrounded by a radiation shield or not. Similar results were obtained with potassium chloride (m.p. 776°).

Furnace.—The furnace used to heat the reaction chamber was a Cenco Hevi Duty tube furnace, 33 cm. in outside length, with a central opening 3.2 cm. in diameter. It was operated from power supplied by the house line through a "Sola" constant voltage transformer. Voltage to the furnace was regulated through one 7.5-amp. 115-volt and one 5-amp. 115-volt "Powerstat," connected in series. The temperature of the furnace could easily be adjusted to ± 2° near 800°K. and would stay constant to ± 2° during the course of the day. At night, when there was a substantial rise in the house voltage, the furnace temperature would rise by about 10°.

Gas Analyses.—Gas analyses were carried out on compositions close to the equilibrium values. After preliminary adjustment of the composition, the effluent gas was diverted from passage through the HCl traps, 20 and 21 of Fig. 1B, to the absorption tubes, 17, by manipulating stopcocks 13 and 14. For water analysis the microabsorption tube was filled with anhydrous magnesium perchlorate. The volume of nitrogen passed through the absorber was determined by weighing water displaced from the Mariotte bottle (18) to the collection flask (19) as shown in the figure. The measured volume (usually 500 ml.) was converted to standard conditions by making appropriate corrections for temperature, barometric pressure, the hydrostatic pressure of the Mariotte bottle, and the partial pressure of water. Traces of HCl and H_2O remaining in the line beyond the stopcock numbered "14" were flushed through the absorption tube with dry, carbon dioxide free nitrogen admitted through a tube containing Ascarite and magnesium perchlorate (16 of Fig. 1B).

Water absorbed by the magnesium perchlorate was determined gravimetrically to within ±10 μg. by weighing the absorption tube on an Ainsworth Model FDJ microbalance. It was shown in separate experiments that there was no appreciable absorption of HCl by either anhydrous or partially hydrated magnesium perchlorate.

Analyses for HCl also were done gravimetrically by absorbing the HCl in an absorption tube containing Ascarite.

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(5) L. Brewer and N. L. Lofgren, Atomic Energy Declassified Document AECD-1834 (January 2, 1948).

(6) J. Strong, "Procedures in Experimental Physics," Prentice-Hall Inc., New York, N. Y., 1943.

The last one-fourth of the tube was packed with magnesium perchlorate to prevent loss of water formed in the reaction. To ensure against the loss of CO_2 formed from carbonate previously present in the Ascarite, the tube was replaced when approximately one-half the Ascarite was used up.

Equilibrium Measurements.—In a typical run the furnace was adjusted to the desired temperature and the bubblers were filled with a HCl solution sufficiently concentrated to convert the sample completely to trichloride. The tip of the balance pointer was brought into focus in the field of an externally mounted Spencer SKW binocular microscope in which one ocular was replaced by a filar micrometer. The position of the pointer was noted and the gas mixture was then started flowing through the reaction chamber. The reaction was continued until the change in weight indicated that the sample was converted completely to the trichloride. When starting with fresh oxide this reaction generally required about 5 hours to go to completion at *ca.* 800°K.

The HCl solutions in the bubblers were then changed to less concentrated acid and the reaction was continued for an hour or so to determine if this caused any conversion to oxychloride. This process was continued systematically until a definite loss in weight indicated that oxychloride was being formed. A slight increase in the ratio P^2_{HCl}/P_{H_2O} then caused the sample to gain weight. Further fine adjustments in bracketing the equilibrium constant were made by slight alterations in the temperature of the thermostatic bath. Close approach to equilibrium was indicated by a marked decrease in the rate of the reaction. By careful manipulation, maximum and minimum values of K, differing by only a few per cent., could be obtained. The K value was taken as the mean of these maximum and minimum values.

After a few preliminary measurements which served to give approximate values for the free energy function of the reaction, the adjustment of the gas mixture to the desired composition usually could be carried out rapidly and efficiently.

The reaction rate decreased with decreasing temperature, and below 700°K. became so slow as to make the determination of the equilibrium constant impractical by our method.

On several occasions it was noted that samples of the oxychloride that had been held at a high temperature for 12–15 hours became very unreactive and extremely difficult to convert to the trichloride, even in the presence of anhydrous HCl. It is possible that this behavior may be connected with an actual change in heat content of the solid of the type suggested by Giauque,[7] but X-ray diffraction results on samples of LaOCl taken from our apparatus indicate a crystallite size of *ca.* 1000 Å. and hence a reasonably close approach to the macrocrystalline state.

TABLE I

EQUILIBRIUM CONSTANTS FOR THE REACTION $LaCl_3(s) + H_2O(g) = LaOCl(s) + 2HCl(g)$

Run No.	T°K.	1000/T	v.p. HCl, mm.	v.p. H_2O, mm.	K	ΔF_{exp} kcal.	ΔF_{calc} kcal.	Dev., %
1	892	1.120	80.9	2.92	2.95	−1.82	−1.84	−0.02
			71.6	2.58	2.62			
2	880	1.136	72.6	2.94	2.36	−1.42	−1.46	− .04
			66.8	2.72	2.16			
3	875	1.142	66.8	2.72	2.16	−1.30	−1.32	− .02
			62.9	2.54	2.05			
4	859	1.164	66.2	3.47	1.66	−0.85	−0.81	+ .04
			63.0	3.21	1.63			
5	849	1.178	60.8	3.43	1.42	− .54	− .50	+ .04
			56.2	3.10	1.34			
6	843	1.186	61.0	3.89	1.26	− .34	− .32	+ .02
			55.2	3.37	1.19			
7	820	1.219	55.3	4.66	0.86	.32	.38	+ .06
			49.0	4.05	0.78			
8	804	1.244	48.35	4.75	0.65	.73	.89	+ .16
			44.6	4.21	0.62			
9	787	1.270	36.5	4.34	0.40	1.47	1.39	− .08
			33.54	3.95	0.38			
10	770	1.299	33.4	5.20	0.28	2.00	1.94	− .06
			31.3	4.98	0.26			
11	756	1.322	30.2	5.64	0.21	2.42	2.35	− .07
			27.3	5.26	0.19			
12	733	1.364	23.7	5.70	0.13	3.07	3.07	.00
			21.8	5.42	0.12			
							Av.	0.00

Results

The results of our measurements are plotted graphically on a K *versus* $1/T$ plot in Fig. 2. The value of ΔC_p for the reaction was estimated as follows: Heat capacities of the solids were estimated from the additivity principle discussed by Lewis and Randall.[8] Combining these values with the heat capacity equations given by Kelley[9] for HCl(g) and H_2O(g), ΔC_p for reaction (1) = $-2.79 - 0.36 \times 10^{-3}T + 0.44 \times 10^5 T^{-2}$.

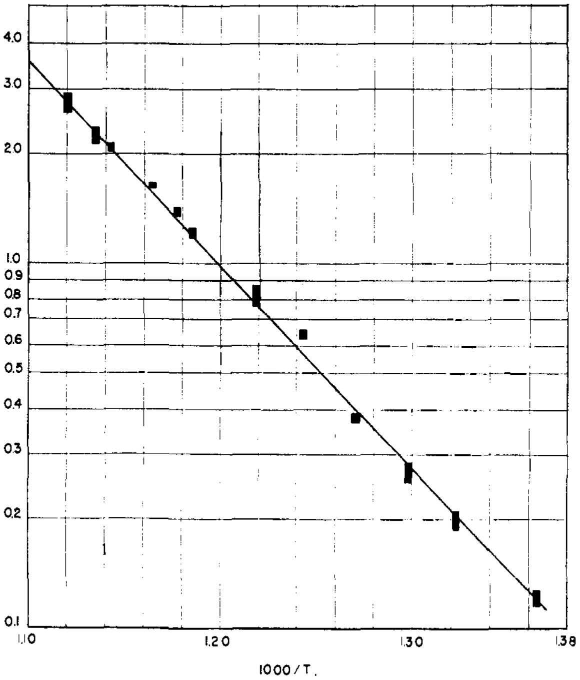

Fig. 2.—log K *versus* $1/T$ plot for the reaction: $LaCl_3(s) + H_2O(g) = LaOCl(s) + 2HCl(g)$.

The line through the experimental points of Fig. 2 has been fitted with reference to this heat capacity function. From our data and the heat capacity equation we calculate for reaction (1)

$\Delta H_0 = 27.9$ kcal. mole^{-1} $\Delta S_{785} = 30.8$ cal. mole^{-1} deg.$^{-1}$
$\Delta H_{298} = 27.0$ kcal. mole^{-1} $\Delta S_{298} = 33.5$ cal. mole^{-1} deg.$^{-1}$
$\Delta H_{785} = 25.6$ kcal. mole^{-1} $K_{785} = 0.389$ cal. mole^{-1} deg.$^{-1}$
$I = -52.4$

Combining ΔH_{298} for the reaction with the heat of formation of $LaCl_3$ given in "Selected Values of Chemical Thermodynamic Properties" we calculate for the heat of formation of LaOCl

$$\Delta H_f°_{298} = -250.2 \text{ kcal. mole}^{-1}$$

Estimating the entropy of formation at 298°K. as −39.3 e.u., then

$$\Delta F_f° \text{ at } 298°\text{K.} = -238.5 \text{ kcal. mole}^{-1}$$

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[7] W. F. Giauque, THIS JOURNAL, **71**, 3192 (1949).

[8] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1926.

[9] K. K. Kelley, "Contributions to the Data of Theoretical Metallurgy," United States Department of the Interior, Bureau of Mines, Bulletin 476 (1949).