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Charles William Koch

(Thesis)

September, 1953

Berkeley, California

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF TABLES (Continued)

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August 1953

ABSTRACT

Equilibrium constants at various temperatures in the range 700°-900° K have been determined for the vapor phase hydrolysis of the trichlorides of lanthanum, praesodymium, neodymium, samarium, gadolinium, terbium and americium. The reactions were studied by a flow method in which mixtures of $HCl_{(g)}$ and $H_2O_{(g)}$ were passed over the solid materials mounted on a cantilever type quartz fiber balance. The progress of the reaction was determined by observing the weight change of the solid.

From the data obtained and an estimate of the ΔC_p of the hydrolysis reactions, values were calculated for the heats and entropies of the reactions.

In addition, the Madelung constants were calculated from x-ray crystallographic data for some of the lanthanide and actinide trichlorides and oxychlorides. Crystal energies were obtained using the appropriate equation for the total Coulombic energy and by considering individual repulsive terms for the touching or overlapping ion pairs. Differences in the calculated crystal energies of the oxychlorides and trichlorides were compared to the experimentally determined heats for the vapor phase hydrolysis of respective lanthanide or actinide trichlorides.

Ionization potentials are estimated for several lanthanide elements as a consequence of the crystal energy calculations. From several of the ionization potentials and from available thermodynamic and crystallographic data an electron affinity is estimated for nitride ion.

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I. INTRODUCTION

The work described in this thesis was undertaken with three objectives in mind:

a. to obtain thermodynamic data on the rare earth and actinide element oxychlorides,

b. to compare the thermodynamic properties of analogous reactions of the lanthanide and actinide elements, and

c. to test the validity of theoretical equations for the calculation of crystal energies by comparing experimentally observed changes in the heat of the reaction:

$$MCl_{3(s)} + H_2O_{(g)} = MOCl_{(s)} + 2HCl_{(g)}$$

with those calculated from the variation in crystal parameters of the solid phases, as the ionic radius of M, the tripositive cation, varies from 1.04 Å for La^{+3} to 0.95 Å for Gd^{+3}. Comparison between calculated and the rather uncertain thermodynamic-cycle energies for the individual solid phases was a matter of secondary interest, but was carried out to get a rough measure of the degree of ionic character in the bonding of the crystals.

The first objective has immediate practical value, since thermodynamic data on the oxychlorides did not exist prior to the work described herein in spite of the fact that the rare earth and actinide oxychlorides are quite stable compounds of common occurrence, frequently found as objectionable contaminants in preparations intended to be the pure trichlorides. Determination of the thermodynamic properties of these substances permits an exact definition of the conditions under which they may be formed. The experimental data reported here, in combination with existing data on the trichlorides, yields the desired information on the oxychlorides.

The second objective has somewhat broader significance, since a considerable body of estimated thermodynamic properties of actinide element compounds rests on an assumed close resemblance to the analogous compounds of the lanthanide series. An accurate test of the quantitative reliability of this assumption seemed highly desirable.

Presumably such data would also be of value in revealing differences of thermodynamic importance due to differences in polarizability between the lanthanide and the actinide ions, or to contributions to bonding through hybridization of the 5f orbitals, in the latter series of elements.[1]

The third objective is of general interest. The calculation of thermodynamic properties of ionic crystals from structural parameters alone is a problem which has interested chemists for some decades. As is well known, relatively simple formulae developed by Born,[2] Haber,[3] Madelung,[4] Ewald,[5] Evjen,[6] and others[7-10] have been applied with moderate success to the calculation of the standard heats of formation of the alkali halides[7] and in some cases to other types of compounds as well.[11,12] To a certain extent the agreement between calculated crystal energies and those derived from thermodynamic cycles is artificial, since the cycles always involve an electron affinity term, for which accurate experimental values are not available. Nevertheless, a value for the electron affinity of a particular anion, chosen to give agreement with the calculated crystal energy for a particular salt, usually appears reasonably valid for other salts of that anion, provided there is no marked change in the degree of ionic character in the bonding in the various salts.

In calculations of this kind the simpler formulae consider only coulombic forces between the ions and a characteristic exponential repulsion ascribed to overlapping of the outer electronic orbitals of the ions.

More elaborate treatments[8,9] include consideration of polarization and van der Waal's forces, but as a rule fail to improve agreement between calculated and thermodynamic-cycle energies to any marked extent.[13]

The test of crystal energy equations possible from the data presented in this thesis is of a different nature from that described above, since its primary objective is the prediction of the change in the difference in crystal energies between a solid trichloride and oxychloride as the radius of the cation common to both undergoes a regular, limited contraction.

The comparison of this function with experimentally determined changes is independent of any unknown or uncertain quantities such as electron affinities, heats of sublimation, ionization potentials, etc., since these quantities cancel in the comparison.

Throughout the series of elements investigated, except for terbium, the trichlorides are isostructural compounds of hexagonal symmetry, exhibiting the UCl_3 structure type. The oxychlorides are also isostructural crystals of tetragonal symmetry of the PbFCl structure type.

In one respect the oxychlorides are unlike any crystals previously subjected to crystal energy considerations. The metal cation is situated in a non-symmetrical anion environment, being surrounded on one side by five chloride nearest neighbors, and on the other by four oxide ions. This condition requires special consideration of the choice of the repulsive exponent, n, applicable to the energy calculations.

Duplication of ionic radii in the lanthanide and actinide series of elements affords a unique opportunity for comparison between crystals of virtually identical structural parameters, differing only in the atomic number of the metal cation.

The crystal energy calculations employed in the comparisons described above have necessitated long and tedious computations of Madelung constants for a number of rare earth and actinide trichlorides and oxychlorides. These constants had not been calculated previously for crystals of these kinds.

II. EXPERIMENTAL

The general method used to obtain heat and free energy data on the compounds of interest was the determination of the temperature coefficient of the equilibrium constant for the reaction:

$$MCl_{3(s)} + H_2O_{(g)} = MOCl_{(s)} + 2HCl_{(g)}$$

where M symbolizes a rare earth or actinide trivalent cation.

The experimental technique evolved permitted the investigation to be carried out with small (milligram) quantities of material--an absolute necessity in the case of americium because of the very limited availability of this synthetic element.

A sample of the oxide of the element to be investigated was mounted on a cantilever type quartz fiber microbalance contained inside a quartz reaction tube maintained at a selected temperature by an electrically heated tube furnace. Conversion of the oxide to the trichloride was achieved by passing anhydrous HCl gas through the reaction tube. Following this preliminary step fixed concentrations of $HCl_{(g)}$ and $H_2O_{(g)}$, carried by a stream of nitrogen, were passed over the sample. If the value of P^2_{HCl}/P_{H_2O} exceeded the value of the quilibrium constant, no reaction occurred, and the weight of the solid phase remained constant. When P^2_{HCl}/P_{H_2O} fell below the value of K, conversion of the trichloride to oxychloride occurred with a change in weight of the solid phase, which was evident in the movement of the balance pointer. Similarly oxychloride could be converted to trichloride again by adjusting the composition of the gas stream until P^2_{HCl}/P_{H_2O} again exceeded K. In this way it was possible to bracket the equilibrium constant quite closely.

A detailed description of these operations, as well as a consideration of possible errors in the measurements, and an estimate of the accuracy of the various values will be found in appropriate places in subsequent sections of the thesis.

A. Apparatus

1. General.--A schematic drawing of the apparatus used for following the progress of the hydrolysis reaction is shown in Fig. 1A,B. Figure 1B indicates the relative positions of the reaction vessel, the optical system used to measure the deflection of the balance pointer, the gas bubblers, thermostat and finally the absorption tubes together with a Mariotte bottle used in determining the composition of the gas stream. Additional apparatus not shown in the figure includes the potentiometer system to which the thermocouple is attached. For the various measurements two galvanometers and two potentiometers were used. The first system had a furnace temperature sensitivity of approximately 0.5° and the second one a sensitivity of 0.1° or better.

2. 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 and 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 support through a graded Pyrex-quartz seal.

In the earlier work 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 stirring 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. There was no apparent reaction of the pan with the gas mixture after weeks of use in the temperature range 350° to 600° C. However, there was rapid corrosion of the pan in the gas stream if the temperature was permitted to fall to 200° C or lower. For this reason, in later work a thin quartz cup was fused to the loop on the balance provided for the pan and the sample placed in this quartz cup rather than on the platinum surface.

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 horizonatal 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 not consistent with the value of $1.3 \times 10^{-4} {}^{\circ}C^{-1}$ reported[14] for the temperature coefficient of Young's modulus for fused silica. Using moderate magnification to observe the movement of the pointer, the balance behaved as a sensitive and apparently reproducible thermometer, although its behavior in this respect was not investigated in detail. The balance was inert to the gas mixture throughout the time required for making the experimental measurements.

3. The reaction chamber.--The fused quartz reaction chamber, illustrated in Fig. 1A, consisted of 34 cm of 3.1 cm outer diameter quartz tubing closed with an optical window at one end and fitted with a 29/42 male ground joint at the other. The overall length, including the joint, was about 38 cm. For some time experiments were carried out in a chamber in which two 4 mm diamter side tubes 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 high velocity exit for the gas mixture.

The lower tube containing the leads of a platinum (90 percent platinum-10 percent rhodium) thermocouple extended about half way down the chamber and terminated directly beneath the reaction pan. The

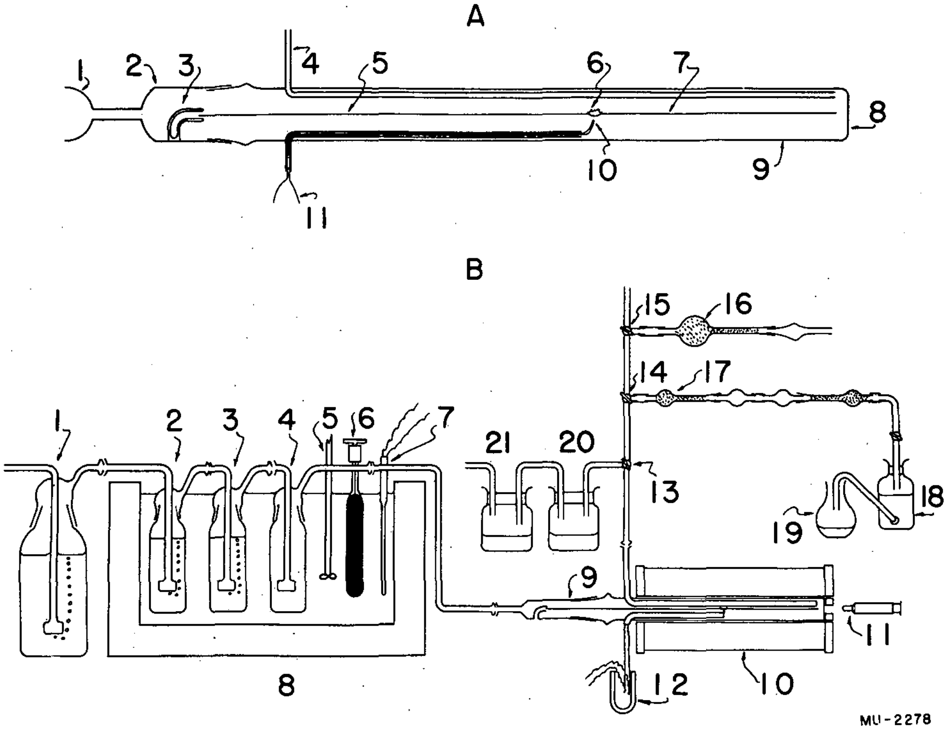
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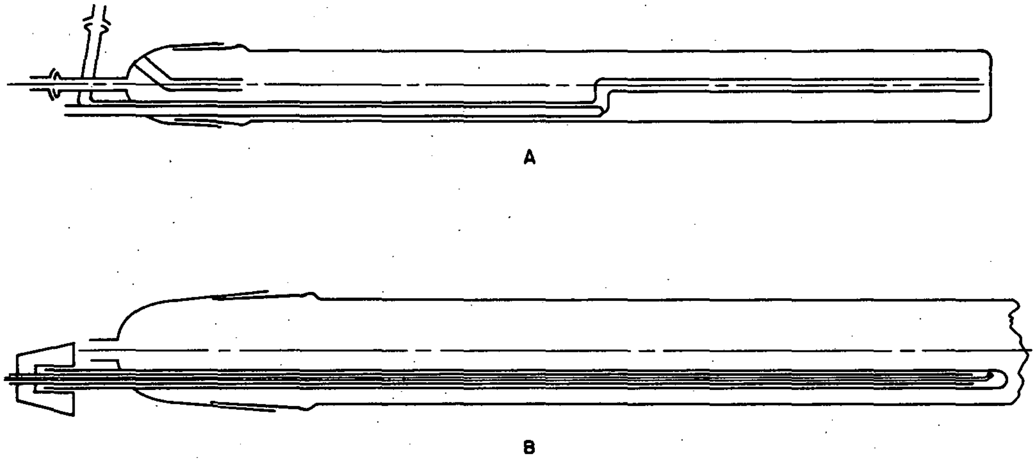
Fig. 1 A and B

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 with a 5 mm inner diameter inlet for the gas mixture. Just beyond the ground portion of this joint an inverted L-shaped piece of 1 mm inner diameter 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. When this chamber was accidentally broken the design was altered somewhat to improve the convenience of the apparatus. In the new design the two 4 mm diameter quartz tubes were inserted into the reaction chamber by means of ring seals through a 29/42 quartz joint. Both tubes ran parallel and very close to the inside wall of the chamber. The tube containing the thermocouple leads terminated with a very thin quartz bubble. The position of the thermocouple junction was adjusted in the tube so that it was approximately 1 mm from the end of the quartz bubble wall. The thermocouple was prevented from moving in the tube by a stopper as shown in Fig. 2. This system permitted the thermocouple to be detached from the apparatus if necessary without cutting the leads. As in the original reaction chamber the balance was so designed that the thermocouple was immediately beneath the sample. The quartz gas exit tube was constructed to parallel the reaction chamber wall approximately half way up the side of the tube to permit maximum freedom for balance displacement. The gas mixture inlet and the capillary tube for attaching the balance were identical with the first type of reaction chamber.



REACTION CHAMBER WITH REMOVABLE THERMOCOUPLE AND VELOCITY EXIT TUBE

FIG.2

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The second type of chamber has three distinct advantages over the previous one. First, the balance can be more easily adjusted so that the quartz fiber is centered in the chamber. Second, all possibility of chemical reaction between the gas mixture and the platinum-rhodium thermocouple is removed. Third, repairs on the reaction chamber are greatly simplified when the parts are readily exposed.

4. 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 thought 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 would remain 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 about 10°.

B. Experimental Procedure

An experimental determination was initiated by adding approximately one milligram of rare earth oxide to the balance pan. The loaded balance was then placed inside the quartz reaction chamber which was heated to an appropriate temperature by the tube furnace. Anhydrous hydrogen chloride was passed through the tube at 350°-400° C until the oxide was completely converted to trichloride as shown by displacement of the balance pointer. If the balance was swinging freely at this temperature the furnace temperature was increased to approximately 600° C and the sample was converted to oxychloride to check maximum upward displacement of the balance. The balance was designed so that a 200 µg change in weight, corresponding roughly to the change in weight of one milligram of oxychloride to the trichloride, would deflect the balance pointer two millimeters. This corresponded approximately to the field of the microscope at twentyfold magnification. After conversion of the oxide to either trichloride or oxychloride, a mixture of nitrogen, hydrogen chloride gas and water vapor of selected composition was passed through the reaction tube. The desired gas composition was obtained by bubbling nitrogen through the appropriate aqueous HCl solutions.

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, $K = (P_{HCl})^2/(P_{H_2O})$, for the reaction at a number of selected temperatures. Gas compositions in which the value of $(P_{HCl})^2/(P_{H_2O})$ exceeded K caused the reaction to proceed to the left, as was evidenced by an increase in weight of the sample. Conversely, when the value of $(P_{HCl})^2/(P_{H_2O})$ was less than K the sample lost weight. In practice the reactions were seldom carried to completion, but were continued for a length of time sufficient to ascertain whether trichloride or oxychloride was being formed, and to analyze the gas stream for H_2O and HCl under the conditions in which trichloride or oxychloride were formed.

In early experiments[15] it was established 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.

1. Accuracy of the measurements.—The experimental data should be divided into two groups. The measurements on lanthanum, samarium, gadolinium, terbium and americium were carried out under conditions involving probable errors in the equilibrium constant of the order of 5 to 10 percent. At the time this work was initiated it was felt that an accuracy of 2 to 5 percent in determining the composition of the gas stream was adequate in view of other probable errors of the experiments. As a consequence of this conclusion the apparatus was designed to meet these rather liberal requirements. In the course of the measurements it became apparent that the method was capable of considerably greater precision. The apparatus and technique were modified accordingly. The measurements involving the hydrolysis of praesodymium and neodymium trichlorides represent an effort to exact maximum precision in the measurements. For simplicity and clarity of discussion, the original method and the subsequent more precise one will be discussed separately.

2. The original apparatus.--a. Composition of the gas stream.--The partial pressures of $HCl_{(g)}$ and $H_2O_{(g)}$ were fixed at approximately the desired levels by bubbling tank nitrogen (Linde Air Products, 99.9 percent) through a series of gas bubblers (1,2,3 of Fig. 1B) filled with aqueous solutions of reagent grade hydrochloric acid or with this acid fortified by the addition of anhydrous hydrogen chloride obtained from a cylinder of the compressed gas. Aid in selecting a composition to produce a desired pressure of $HCl_{(g)}$ and $H_2O_{(g)}$ was obtained by reference to the data in the "International Critical Tables."[16] The

bubblers were immersed in a thermostat controlled by a mercury regulator. The temperature maintained by the regulator was consistent to ±0.1° C.

Early work[15] indicated that the vapor pressures obtained by bubbling nitrogen through the aqueous solutions were close to the saturation values given in the "International Critical Tables," but a more careful investigation revealed that they were significantly lower. Table 1 lists several experimental measurements together with values estimated from the data in the "International Critical Tables."

Table 1

Partial Pressures (in mm) of Aqueous Hydrochloric Acid Solutions

Thermostat Temp. (C)	P_{H_2O} Expt.	P_{HCl} Expt.	P_{H_2O} ICT	P_{HCl} ICT	% HCl
21.8	4.01 3.89	82.0 80.3	3.91	84.7	35.09
23.1	4.00 4.00	85.1 86.4	4.28	91.2	35.07
24.2	4.25	91.7	4.65	94.2	35.01

To determine whether or not the data in the Critical Tables are self-consistent, the Gibbs-Duhem equation was employed

$$\int_{1}^{11} d\log p_1 = -\int_{1}^{11} \frac{N_2}{N_1}\, d\log p_2.$$

Because the gas pressures were sufficiently low it was assumed that $HCl_{(g)}$ and $H_2O_{(g)}$ behaved as perfect gases and therefore that partial pressures could be substituted for fugacities.

Table 2 compares the vapor pressures of water listed in the Critical Tables with those calculated from the Gibbs-Duhem equation assuming the values for $HCl_{(g)}$ to be correct. These calculations indicate possible errors of the order of 10-20 percent in the data in the Critical Tables.

Table 2

Comparison of Critical Tables H_2O Partial Pressures with Those Calculated from the Gibbs-Duhem Equation, Assuming HCl Partial Pressures to be Correct

% HCl (wt.)	Temp. °C	N_2/N_1	HCl (ICT)	H_2O (ICT)	H_2O (Calc.)
30	5	0.2117	3.57	1.90	1.90
32		0.2325	8.3	1.57	1.53
34		0.2545	18.8	1.29	1.18
36		0.2779	41.0	1.03	0.89
38		0.3027	87.0	0.81	0.64
40		0.3293	176	0.63	0.45
42		0.3578	332	0.48	0.32
30	20	0.2117	10.6	5.41	5.41
32		0.2325	23.5	4.55	4.53
34		0.2545	50.5	3.81	3.76
36		0.2779	105.5	3.10	3.09
38		0.3027	210	2.51	2.53
40		0.3293	399	2.00	2.06
42		0.3578	709	1.56	1.69
30	35	0.2117	28.6	13.7	13.7
32		0.2325	60.0	11.7	12.0
34		0.2545	122	9.95	9.81
36		0.2779	246	8.33	8.16
38		0.3027	465	6.92	6.79
40		0.3293	830	5.68	5.67

Since the vapor pressures of $HCl_{(g)}$ and $H_2O_{(g)}$ in aqueous solutions listed in the Critical Tables are open to question, and also since there was no simple way to determine whether or not, with the bubbler system used, equilibrium conditions are obtained, 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 an empty bubbler in the line as shown in Fig. 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 experimental detail is not shown in 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 here, in which large thermal gradients exist.[17] The existence of an experimentally important thermal diffusion effect can be revealed empirically by altering the flow rate of the gas stream and noting the effect on the apparent value of K. This point was investigated at an early stage in the measurements. In addition, a series of experiments were carried out to determine whether appreciable amounts of spray were carried into the reaction chamber by the gas stream. Table 3 shows the observed change in the apparent value of the equilibrium constant for the lanthanum chloride hydrolysis reaction with change in flow rate when a spray trap was not used. The apparent value decreases roughly twofold when the flow rate is increased from 0.025 ml per second to 18 ml per second. Larger quantities of spray at a faster flow rate would produce the effect observed since this would introduce larger quantities of $H_2O_{(g)}$ than of $HCl_{(g)}$ into the gas stream in the furnace. It should also be pointed out that the use of vapor pressure values calculated from data in the "International Critical Tables" contributes to the lower values of K listed in Table 3 in comparison with subsequent data.

Table 3

Apparent Equilibrium Constants for the Lanthanum Trichloride Hydrolysis with no Attached Spray Trap

Equilibrium constants calculated from HCl concentrations and International Critical Tables data

Furnace Temp. °K	Flow Rate ml/sec	% HCl	K
843	0.025	34.00	1.21 1.20
843	0.4	34.02	1.25 1.20
843	1.5	34.07	1.14 1.11
843	7	33.59	0.80 0.77
843	12	33.51	0.70 0.67
846	18	33.38	0.66 0.62

Table 4 shows the values obtained when a spray trap is included in the line. No significant trend in the calculated values for K are detectable at flow rates from 0.28 to 7.7 ml/sec. The data in Table 4 were taken as representative of the experimental accuracy that could be realized with this apparatus. Subsequent flow rates for equilibrium constant measurements varying from 0.3 to 1.5 ml/sec were used.

Table 4

Effect of Flow Rate on the Equilibrium Constant for the Reaction
$LaCl_{3(s)} + H_2O_{(g)} = LaOCl_{(s)} + 2HCl_{(g)}$

Furnace Temp. °K	Flow Rate ml/sec	v.p. HCl[a] mm	v.p. H_2O[a] mm	K max. min.	K mean[b]
792	0.28	44.9 38.6	5.63 4.79	0.47 0.41	0.45
789	1	41.4 37.5	5.59 5.02	0.40 0.37	0.47
795	1.8	37.1 33.1	3.6 3.2	0.50 0.45	0.48
794.5	3.5	52.7 48.0	7.47 6.79	0.49 0.44	0.47
795	7.7	45.4 40.6	5.58 5.07	0.49 0.43	0.46

[a] The vapor pressures of $HCl_{(g)}$ and $H_2O_{(g)}$ were determined gravimetrically as discussed in a subsequent section.

[b] Corrected to 795° K from data obtained at a later date.

b. Temperature measurements.--The temperature of the sample was determined by means of an internal platinum; platinum-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 in place against a Bureau of Standards platinum; platinum-rhodium thermocouple. The correction to the working thermocouple varied nearly linearly over the temperature range from 450° to 675° C.

Typical data for the calibration of the reaction chamber thermocouple are listed in Table 5.

Table 5

Calibration of Reaction Chamber Thermocouple by Comparison to Bureau of Standards Calibrated Thermocouple

Bur. Stan. Thermocouple (microvolts)	Furnace Thermocouple (microvolts)	Difference between Thermocouples (microvolts)	T °C
6382 6382	6295 6295	87	711.5
5973 5972	5890 5888 5887	85	672.4
5609 5609	5528 5528	81	637.4
5310 5310	5232 5231	78	608.2
5043 5042	4966 4967	76	582.0
4783 4783	4711 4710	72	556.4
4475 4474	4407 4406	68	525.7
4099 4099	4029 4029	70	487.2
3776 3776	3709 3709	67	454.2

The leads from the thermocouple were soldered to No. 18 B and S gauge copper wire and connected to the binding posts of a Rubicon Precision Potentiometer. The soldered junctions were kept at 0° C 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. Changes in temperature of 0.3° were readily detected with this arrangement.

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

Because the thermocouple junction was exposed at all times to an atmosphere of $HCl_{(g)}$ and $H_2O_{(g)}$ it was recalibrated at the conclusion of the work on lanthanum, gadolinium and americium but not in the case of samarium and terbium. The maximum change found in the course of recalibration was 3°.

c. <u>Gas analyses</u>.--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, or by collecting a given quantity of water in a volumetric flask in the case of americium. The measured volume was converted to standard conditions by making appropriate corrections for temperature, barometric pressure, the hydrostatic pressure over the water in the Mariotte bottle, and the partial pressure of water in the Mariotte bottle. Traces of $HCl_{(g)}$ and $H_2O_{(g)}$ 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 for all measurements but those involving the americium hydrolysis. In the americium case the water was determined to within ±30 μg by weighing the absorption tube on an American Balance Company SM 1012-01 semimicro balance. It was shown in separate experiments that there was no appreciable absorption of HCl by either anhydrous or partially hydrated magnesium perchlorate. In earlier work it was shown that this is not the case when phosphorous pentoxide is used to absorb the water. No serious difficulty was encountered with respect to absorption of $HCl_{(g)}$ on anhydrous phosphorous pentoxide but the partially hydrated material absorbed appreciable quantities of $HCl_{(g)}$ which could be removed only by sweeping with nitrogen gas for relatively long periods of time. Due to the uncertainties associated with the use of phosphorous pentoxide, all gas analyses reported in this work were performed using magnesium perchlorate as the water absorbent.

Analyses for $HCl_{(g)}$ also were done gravimetrically by absorbing the $HCl_{(g)}$ in an absorption tube containing Ascarite. 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 carbon dioxide formed from carbonate previously present in the Ascarite, the tube was replaced when approximately one-half the Ascarite was used up.

d. Equilibrium measurements.--In a typical run the furnace was adjusted to the desired temperature and the bubblers were filled with a solution of hydrochloric acid sufficiently concentrated to convert the sample completely to the 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 five hours to go to completion at approximately 800° K.

The hydrochloric acid 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 $(P_{HCl})^2/(P_{H_2O})$ then caused that 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 reaction rate. By careful manipulation, maximum and minimum values of K, differing by only a few percent, could be obtained. The equilibrium 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 that the determination of the equilibrium constant by the balance method was impractical.

On several occasions it was noted that samples of the oxychloride which had been held at 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 change in heat content of the solid of the type suggested by Giauque,[18] but x-ray diffraction results on samples of lanthanum oxychloride taken from the equilibrium apparatus indicated a crystallite size of greater than 500 Å and hence a reasonable approach to the macrocrystalline state.

3. The refined apparatus.--a. Composition of the gas stream.--The partial pressures of $HCl_{(g)}$ and $H_2O_{(g)}$ were fixed as discussed previously under "The Original Apparatus." The changes involved in this phase of the refinement concern better temperature control of the thermostat, reduction of the pressure drop between the last two bubblers and the reaction chamber, and greater volume of the hydrochloric acid solution to diminish changes in the composition over the course of the 10-15 hours required to obtain both a maximum and minimum K value at a given temperature.

A toluene-mercury regulator having six fingers and an overall capacity of 500 ml proved adequate to maintain the thermostat to within ±0.005° C when used in conjunction with a stirrer having three 2-inch blades turning at 300 revolutions per minute in a bath 18 x 18 x 12 inches.

To saturate the gas stream with $HCl_{(g)}$ and $H_2O_{(g)}$ a total of six bubblers was used. The first three bubblers each had a capacity of one liter and contained fritted glass filters to disperse the gas into small bubbles. The fourth, fifth and sixth bubblers of 500 ml capacity did not contain fritted discs. In addition, a bottle containing glass wool was used to trap the spray. To be certain that the gas stream in the reaction chamber was at atmospheric pressure a small mercury manometer was placed in the line between the spray trap and the reaction tube. The gas flow was then adjusted at the start of a run so that atmospheric pressure was maintained throughout the course of the determination.

To check the reliability of analyses on composition, water analyses were carried out on nitrogen gas which had been bubbled through two solutions of sulfuric acid of different concentrations and on pure distilled water. The results of these measurements were compared with vapor pressure data listed in the "International Critical Tables." The uncertainty attached to the vapor pressures assigned to the two sulfuric acid solutions is probably quite large but the values reported for water should be reliable. A comparison of the vapor pressures obtained from the bubbling system used in making these measurements with the values obtained from the "International Critical Tables" shows a reasonable agreement as is seen in Table 6. In addition, several measurements were made on a solution of concentrated hydrochloric acid (approximately 37 percent) to determine the reproducibility that could be obtained from the analyses. This information is presented in Table 7.

Table 6

Determination of the Composition of Gas Stream Using the Refined Apparatus

Solution Conc.	Vol. N_2 Collected	Atmos. Pressure (mm)	Bath Temp. °C	v.p. H_2O found (mm)	v.p. H_2O reported[a] (mm)
H_2SO_4					
75.89%	6 liters	763	23.1	0.352	0.34-0.36
		765	23.1	0.364	
67.67%	4 liters	761	23.3	1.485	1.46-1.48
		760	23.3	1.483	
Distilled water					
	2 liters	756.4	22.4	20.26	20.34
		756.4	22.4	20.34	20.34
		756.1	23.3	20.93	21.47
		756.2	23.3	21.59	21.47
		765.9	22.7	20.91	20.97
		764.2	22.7	20.86	20.93

[a] International Critical Tables, McGraw-Hill Book Co., Inc., New York (1926).

Table 7

Partial Pressures of HCl Gas Over Concentrated Hydrochloric Acid

Thermostat Temp. °C	Barometric Pressure	Vol. N_2 Collected (ml)	v.p. HCl (mm)	v.p. H_2O (mm)
20.0	760.3	2000	188.3	2.764
	760.2	2000	184.1	2.740
	760.2	2000	187.6	2.751
	760.2	4000	187.3	2.759
	760.3	4000	187.7	2.766
Average			187.0	2.756
Mean Deviation			±1.2	±0.008

The data in Table 6 indicate that saturation conditions are closely approached with the new apparatus and that the reproducibility of the analyses warrants attempting greater precision in the equilibrium measurements. Table 7 also indicates great improvement in precision as compared with the initial apparatus as can be seen by comparison with Table 1.

b. <u>Temperature measurements</u>.--The only change in construction of the thermocouple in the refined apparatus was the enclosing of the thermocouple junction by a very thin quartz bubble so that the gas stream could not attack the platinum; platinum-rhodium wire. Greater accuracy in measuring the furnace temperature was achieved by using a more sensitive galvanometer. A Leeds and Northrup galvanometer having a deflection of three scale divisions per 0.1° change in temperature was used in place of the Rubicon. The greater sensitivity made the temperature fluctuations which occurred in the course of the run. It is not implied that absolute temperatures were known to tenths of degrees.

c. Gas analyses.--To obtain greater accuracy in the analyses 2-6 liters of gas were collected per determination, as compared with 300-500 ml measured with the initial apparatus. The same microabsorption tube was used to collect the water since only 10-50 mg were contained in the larger volume of gas. However, the increased amount of $HCl_{(g)}$ required a much larger HCl absorption tube than was used previously. To prevent swelling of the Ascarite to the point where gas flow was impaired, the tube packing consisted of a mixture of Ascarite and magnesium perchlorate followed by the conventional quantity of magnesium perchlorate to prevent water loss in the course of analysis. An absorption tube packed in this manner would usually permit the collection of 5-7 grams of $HCl_{(g)}$ before replacement of the packing was required.

To permit a more accurate estimate of the hydrostatic head over the Mariotte bottle, a simple mercury manometer was attached to the system so that the departure from atmospheric pressure could be measured precisely, rather than roughly estimated, as was the case in the initial apparatus.

d. Equilibrium measurements.--The procedure with the refined apparatus was identical with that used for the previous measurements, with one exception. With a manometer installed in the line, the pressure in the reaction chamber could now be adjusted to equal the external pressure during the course of the analysis on the gas stream. In the initial apparatus one could never be certain that this was the case.

III. EXPERIMENTAL RESULTS

A. Sources and Purity of Material

The sesquioxides used for the vapor phase hydrolysis of the trichlorides were analyzed spectrographically for traces of impurities. The analyses obtained for these samples are listed in Table 8 together with the source from which the rare earth oxide was obtained.

Table 8

Sources and Purity of the Sesquioxides Used for the Vapor Phase Hydrolysis of the Trichlorides

Rare Earth Oxide	Source	Impurities and Relative Amts.
La_2O_3	Iowa State College	No other constituent as great as 0.01 percent.
Pr_6O_{11}	Johnson, Matthey and Co., Ltd.	No other constituent as great as 0.01 percent.
Nd_2O_3		Fe 0.01-0.1%; Ca 0.01-0.1%; Ce 0.01-0.1%; Sm 0.01-0.1%.
Sm_2O_3	Iowa State College	Ca 0.01-0.1%; La 0.01-0.1%; Eu 0.01-0.1%.
Gd_2O_3	Adam Hilger and Sons, London	Fe 0.01-0.1%; Mg 0.01-0.1%; No other rare earths detected
Tb_4O_7	Johnson, Matthey and Co., Ltd.	No other constituent as great as 0.01%.
Am_2O_3		La 0.5%; Pu 0.2%; Al 0.15%; Ca 0.1%.

B. The Hydrolysis of Lanthanum Trichloride

The experimental observations and the necessary calculations for a typical determination of the equilibrium constant are given in the following section. Data obtained from a determination of the equilibrium constant for the vapor phase hydrolysis of lanthanum trichloride are used to illustrate the required calculations.

Before initiating the determination of an equilibrium constant at a given furnace temperature, the bubblers are filled with a hydrochloric acid solution having a concentration required to obtain a measurement in the desired temperature range. The bubblers are assembled as described previously in the section pertaining to the composition of the gas stream. The flow rate of nitrogen gas through the bubblers is adjusted to 20-50 ml per minute and the thermostat temperature is fixed at approximately 20° C. This temperature is selected only because it affords good control of the thermostat. If the temperature of the bath exceeds that of the room by more than ten degrees, greater precaution to avoid condensation of vapor is necessary and if the bath temperature is decreased below 10-15° C the water content of the gas stream becomes smaller than is easy to determine.

With the thermostat temperature fixed, the furnace temperature is slowly increased until the oxychloride starts to form which is shown by a loss of weight on the balance. The temperature of the furnace is then lowered 5-10° C. When the potentiometer readings indicate that the temperature in the reaction chamber is essentially constant, the direction of the reaction is determined and the thermostat temperature is altered until the direction is changed. A typical set of data is shown in Table 9.

Table 9

Data Illustrating the Formation of Lanthanum Oxychloride From Lanthanum Trichloride at 852° K

Time	Pointer Reading	Furnace Temp. °K	Thermostat Temp. °C
3:30	2.21	852	24.2
3:40	2.14	852	24.2
Changed thermostat temperature to:			20.6
4:00	2.00	852	20.6
4:40	1.89	852	20.6
Changed thermostat temperature to:			18.3
5:00	1.64	852	18.3
5:30	1.55	852	18.3
6:30	1.57	852	18.3
7:30	1.61	852	18.3
7:55	1.74	852	18.3
8:30	1.88	852	18.3
8:50	1.93	852	18.3
9:10	2.00	852	18.3
10:00	2.10	852	18.3

In the period of time that the formation of lanthanum oxychloride is followed, the water and hydrogen chloride absorption tubes are weighed, attached to the line at stopcock 14 of Fig. 1B and to the Mariotte bottle, 18, and the gas stream is diverted from passage through the HCl traps, 20 and 21, into the system containing the two absorption tubes. After approximately 500 ml of gas has been passed through the absorption tubes, traces of HCl and H_2O remaining in the line beyond the stopcock numbered 14 are flushed through the absorption tubes with dry, carbon dioxide-free nitrogen admitted through tube 16 which contains Ascarite and magnesium perchlorate. The absorption tubes are detached and weighed. The temperature of the thermostat and of the water displaced from the Mariotte bottle are noted together with the barometric pressure and average hydrostatic head. This completes the data required to determine the composition of the gas stream and is summarized below.

	Wt. H_2O absorption tube, mg		Wt. HCl absorption tube, g
Final	115.370		59.4787
Initial	113.706		59.4125
Wt. H_2O	1.664	Wt. HCl	0.0662

Wt. flask + H_2O	522.5 g	Bar. Pressure	754.3 mm
Wt. flask	6.8 g	Temp. Collected H_2O	26.0° C
Wt. H_2O	515.7 g	Temp. Thermostat	18.3° C
Buoy. Dens. Corr.	2.1 g	Hydrostatic Head, mm H_2O	213
Vol. H_2O Collected	517.8 ml	mm Hg	15.8
		Vapor pressure over H_2O at 26.0° C, mm Hg	25.2

The calculations to determine the partial pressures of $HCl_{(g)}$ and $H_2O_{(g)}$ in the gas stream in the temperature range of the thermostat assume that within the limits of accuracy nitrogen, water vapor and hydrogen chloride behave as perfect gases. The calculations follow.

$$\text{Vol. } N_2 \text{ gas} = \frac{(517.8)(754.3-25.2-15.8)(291.4)}{(754.3)(299.2)}$$

$$= 476.9 \text{ ml at } 18.3^\circ \text{ C and } 754.3 \text{ mm}$$

$$\text{Vol. } H_2O \text{ gas} = \frac{(1.664)(22.412)}{(18.02)}$$

$$= 2.07 \text{ ml at } 0^\circ \text{ C and } 760 \text{ mm}$$

$$= \frac{(2.07)(760)(291.4)}{(273.2)(754.3)}$$

$$= 2.22 \text{ ml at } 18.3^\circ \text{ C and } 754.3 \text{ mm}$$

$$\text{Vol. HCl gas} = \frac{(66.2)(22.412)}{(36.46)} = 40.7 \text{ ml at } 0^\circ \text{ C and } 760 \text{ mm}$$

$$= \frac{(40.7)(760)(291.4)}{(273.2)(754.3)}$$

$$= 43.7 \text{ ml at } 18.3^\circ \text{ C and } 754.3 \text{ mm}$$

$$\text{Total vol. gas} = 476.9 + 2.22 + 43.7$$

$$= 522.8 \text{ ml at } 18.3^\circ \text{ C and } 754.3 \text{ mm}$$

$$\text{Partial pressure } H_2O = \frac{(2.22)(754.3)}{(522.8)} = 3.20 \text{ mm}$$

$$\text{Partial pressure HCl} = \frac{(43.7)(754.3)}{(522.8)} = 63.1 \text{ mm}$$

$$\text{Minimum possible equilibrium constant} = \frac{(63.1)^2}{(3.20)(754.3)} = 1.65$$

The thermostat temperature is increased approximately 1° C to change the direction of the reaction. Table 10 illustrates the measurements made during the formation of lanthanum trichloride from lanthanum oxychloride to complete the determination initiated with data presented in Table 9.

Table 10

Data Illustrating the Formation of Lanthanum Trichloride From Lanthanum Oxychloride at 852° K

Time	Pointer Reading	Furnace Temp. °K	Thermostat Temp. °C
10:00	changed thermostat temp. to		19.5
11:15	1.90	852	19.5
11:45	1.60	852	19.5
12:25	1.47	852	19.5
1:15	1.14	852	19.5

The calculations to determine the partial pressures of $HCl_{(g)}$ and $H_2O_{(g)}$ are repeated in the same manner as described above.

The values obtained for the equilibrium constant for the vapor phase hydrolysis of lanthanum trichloride are summarized in Table 11. In this table, column 1 gives the number of the experiment in the order of decreasing temperature, column 2 lists the temperatures inside the reaction chamber. Column 3 lists the experimentally determined partial pressure of $HCl_{(g)}$; column 4 gives the experimentally determined

Table 11

Equilibrium Constants for the Reaction
$LaCl_3(s) + H_2O(g) = LaOCl(s) + 2HCl(g)$

Run. No.	T °K	v.p. HCl (mm)	v.p. H_2O (mm)	K_{max} K_{min}	ΔF_{expt} Kcal	ΔF_{calc} Kcal	Dev. Kcal
1	892	80.9 71.6	2.92 2.58	2.95 2.62	-1.82	-1.84	-0.02
2	880	72.6 66.8	2.94 2.72	2.36 2.16	-1.42	-1.46	-0.04
3	875	66.8 62.9	2.72 2.54	2.16 2.05	-1.30	-1.32	-0.02
4	859	66.2 63.0	3.47 3.21	1.66 1.63	-0.85	-0.81	+0.04
5	849	60.8 56.2	3.43 3.10	1.42 1.34	-0.54	-0.50	+0.04
6	843	61.0 55.2	3.89 3.37	1.26 1.19	-0.34	-0.32	+0.02
7	820	55.3 49.0	4.66 4.05	0.86 0.78	0.32	0.38	+0.06
8	804	48.35 44.6	4.75 4.21	0.65 0.62	0.73	0.89	+0.16
9	787	36.5 33.54	4.34 3.95	0.40 0.38	1.47	1.39	-0.08
10	770	33.4 31.3	5.20 4.98	0.28 0.26	2.00	1.94	-0.06
11	756	30.2 27.3	5.64 5.26	0.21 0.19	2.42	2.35	-0.07
12	733	23.7 21.8	5.70 5.42	0.13 0.12	3.07	3.07	0.00
					Average Deviation		±0.05

partial pressure of $H_2O_{(g)}$; column 5 lists maximum and minimum values for the equilibrium constants calculated as $P_{(HCl)}^2/P_{H_2O}$. Column 6 lists values of ΔF_T^o for the hydrolysis reaction calculated from the average K_{max} and K_{min}. Column 7 lists values of ΔF_T^o calculated from a free energy equation of the form

$$\Delta F_T^o = \Delta H_o - 2.30\ C_pT\log T + BT^2 - \frac{C}{T} + IT.$$

The ΔC_p equation used for these calculations will be discussed in a subsequent section. The measurements on the lanthanum trichloride hydrolysis were the first ones made with the original apparatus. Some of these results, particularly runs 4, 6 and 8, suggested the possibility of obtaining greater precision in the measurements than had originally been anticipated.

C. The Hydrolysis of Samarium Trichloride

The concentration of the hydrochloric acid used for these hydrolysis measurements had to be increased above that which is available commercially in order to obtain partial pressures of $HCl_{(g)}$ sufficient to permit formation of the trichloride. The precision of these measurements was perhaps somewhat less than those for the lanthanum trichloride because of difficulty in maintaining a constant concentration of HCl in the last bubbler, due to the large quantity of HCl removed by the gas stream. This resulted in a wider spread between maximum and minimum values of the equilibrium constant. The equilibrium constant values obtained are presented in Table 12. The headings in this table and all subsequent tables for the hydrolysis reactions of the trichlorides investigated have the same interpretation as those discussed under lanthanum in section A.

Table 12

Equilibrium Constants for the Reaction

$SmCl_{3(s)} + H_2O_{(g)} = SmOCl_{(s)} + 2HCl_{(g)}$

Run No.	T °K	v.p. HCl (mm)	v.p. H_2O (mm)	K_{max} K_{min}	ΔF_{expt} Kcal	ΔF_{calc} Kcal	Dev. Kcal
7	893	418.8 406.3	1.60 1.60	144 136	-8.77	-8.83	-0.06
8	885	423.7 390.8	1.77 1.74	133 116	-8.48	-8.55	-0.07
9	867	454.9 442.5	2.54 2.52	107 102	-8.01	-8.00	+0.01
10	848	441.9 407.8	2.99 2.89	85.9 75.7	-7.40	-7.40	0.00
11	830	363.7 347.3	2.70 2.59	64.4 61.3	-6.83	-6.84	-0.01
1	816	387.8 329.6	3.45 2.66	57.3 53.7	-6.51	-6.40	+0.09
12	811	326.1 309.8	2.65 2.53	52.8 49.9	-6.35	-6.24	+0.11
2	797	273.6 262.7	2.43 2.36	40.5 38.5	-5.82	-5.81	+0.01
13	774	298.2 272.1	4.14 3.64	28.3 26.8	-5.10	-5.08	+0.02
4	755	258.3 231.9	4.26 3.90	20.6 18.1	-4.44	-4.48	-0.04
5	727	205.3 193.6	4.37 4.22	12.7 11.7	-3.61	-3.70	-0.09
14	703	152.7 133.6	3.81 3.35	8.05 7.01	-2.82	-2.84	-0.02
				Average Deviation			±0.05

Table 13

Equilibrium Constants for the Reaction
$GdCl_{3(s)} + H_2O_{(g)} = GdOCl_{(s)} + 2HCl_{(g)}$

Run No.	T °K	v.p. HCl (mm)	v.p. H_2O (mm)	K_{max} K_{min}	ΔF_{expt} Kcal	ΔF_{calc} Kcal	Dev. Kcal
1	892	610	2.46	199	-9.32	-9.40	-0.08
		636	2.87	185			
8	877	472	1.80	163	-8.80	-8.95	-0.15
		397	1.40	148			
3	867	620	3.17	159	-8.69	-8.65	+0.04
		605	3.18	151			
9	855	453	1.97	137	-8.32	-8.29	+0.03
		415	1.72	132			
10	838	344	1.55	101	-7.67	-7.76	-0.09
		318	1.36	98			
11	819	346	1.84	86	-7.21	-7.19	+0.02
		300	1.42	83			
5	799	478	4.36	69	-6.63	-6.59	+0.04
		387	3.22	60			
12	754	322	4.16	32.8	-5.17	-5.20	-0.03
		303	4.01	30.1			
7	704	212	4.08	14.4	-3.69	-3.66	+0.03
		218	4.66	13.5			
				Average Deviation			±0.06

D. The Hydrolysis of Gadolinium Trichloride

The values obtained for the equilibrium constants for the vapor phase hydrolysis of gadolinium trichloride are summarized in Table 13. In the first determination of this series the temperature of the furnace exceeded the reported melting point of gadolinium trichloride by several degrees. The measurement proceeded satisfactorily and appeared to be readily reversible. Consequently, the results of this measurement are included with the other data obtained.

E. The Hydrolysis of Terbium Trichloride

The values obtained for the equilibrium constants for the vapor phase hydrolysis of terbium trichloride are summarized in Table 14. From the table it can be seen that these data contain greater variations than appeared in the previous measurements. There are several possible reasons why these measurements are less precise than the previous ones. First, terbium trichloride melts at 861° K and for that reason it was necessary to work in a lower temperature region where the reaction rate was very appreciably slower than was conducive to easy measurement. Secondly, the sample seemed much more inert than samples of the rare earths previously measured. Lastly, due to the slower reaction rate of the sample it was necessary to pass larger quantities of $HCl_{(g)}$ and $H_2O_{(g)}$ through the reaction chamber for a given determination than was the case with the previous rare earths. In the course of the verification of reaction direction and subsequent analytical work, this could result in a considerable change of concentration in the last bubbler. It is believed that a combination of these three factors is responsible for the greater deviations appearing in the terbium trichloride hydrolysis than in the other rare earth measurements.

Table 14

Equilibrium Constant for the Reaction
$TbCl_3(s) + H_2O(g) = TbOCl(s) + 2HCl(g)$

Run No.	T °K	v.p. HCl (mm)	v.p. H_2O (mm)	K_{max} K_{min}	ΔF_{expt} Kcal	ΔF_{calc} Kcal	Dev. Kcal
7	827	376.6 348.9	1.32 1.19	141.4 134.6	-8.10	-8.13	-0.03
1	808	428.0 439.7	2.62 3.19	92.0 79.7	-7.14	-7.54	-0.40
3	789	519.3 478.2	4.57 4.58	77.6 65.7	-6.74	-6.91	-0.17
8	786	360.0 333.8	2.16 1.95	78.9 75.2	-6.79	-6.82	-0.03
2	777	403.9 352.8	3.17 2.94	67.7 55.7	-6.41	-6.52	-0.11
10	770	400.9 373.8	3.20 3.07	66.1 59.9	-6.34	-6.29	+0.05
11	756	312.4 292.4	2.64 2.50	48.6 45.0	-5.78	-5.83	-0.05
9	742	281.9 262.2	2.59 2.30	40.4 39.4	-5.44	-5.36	+0.08
				Average Deviation			±0.11

F. The Hydrolysis of Americium Trichloride

Apparatus and experimental technique were essentially the same as described for previous work, 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. Also, one additional 500 ml bubbler containing a fritted glass filter was added to the three used in the previous experiments. If more bubblers were used the pressure developed in the first one in the series became great enough to force some of the gas mixture past the ground area of the ball joint which connected the first and second bubblers.

Approximately 0.8 mg of the 475 year alpha particle emitting nuclide $_{95}Am^{241}$ was used for the hydrolysis work. Equilibrium constants for the hydrolysis reaction were determined at eight different temperatures. The experimental results are summarized in Table 15.

Table 15

Equilibrium Constants for the Reaction
$AmCl_3(s) + H_2O(g) = AmOCl_{(s)} + 2HCl_{(g)}$

Run No.	T °K	v.p. HCl (mm)	v.p. H_2O (mm)	K_{max} K_{min}	ΔF_{expt} Kcal	ΔF_{calc} Kcal	Dev. Kcal
1	880	344	2.85	54.6	-6.93	-6.96	-0.03
		304	3.34	50.9			
3	841	323	4.12	33.3	-5.78	-5.77	+0.01
		306	4.07	30.3			
2	807	198	2.43	21.2	-4.76	-4.73	+0.03
		179	2.40	17.6			
5	789	225	4.91	13.6	-4.07	-4.18	-0.11
		212	4.46	13.3			
4	780	178	3.31	12.6	-3.89	-3.90	-0.01
		169	3.15	11.9			
6	739	153.6	4.89	6.27	-2.59	-2.66	-0.07
		139.8	4.76	5.40			
7	700	94.9	4.04	2.93	-1.46	-1.43	+0.03
		88.1	3.67	2.78			
8	682	73.3	3.43	2.07	-0.91	-0.87	+0.04
		67.4	3.24	1.85			
				Average Deviation			±0.04

G. The Hydrolysis of Praesodymium Trichloride

The measurements on the praesodymium trichloride hydrolysis were the first ones undertaken with a more elaborate apparatus. The same reaction chamber was used for the praesodymium trichloride measurements as for all the previous work. However, the other modifications discussed under "The Refined Apparatus" were incorporated for this set of measurements. The data are summarized in Table 16. It can be seen from the table that the difference between maximum and minimum values of the equilibrium constant has been very appreciably reduced and that at the same time the overall average deviation has also been diminished. The reliability of the measurements may exceed that estimated from the average deviation because of an incorrect choice for the ΔC_p function, as discussed later. The values listed for runs 1, 2 and 4 seem to be in accord with the general degree of precision anticipated in the measurements. The very small difference between maximum and minimum values in run 3 must be considered fortuitous.

It was originally intended that several more measurements be made on the praesodymium system. However, at the conclusion of the fourth determination the electric power was turned off for a period of 24 hours during which time the sample, the platinum pan and the platinum; platinum-rhodium thermocouple were exposed to the gas stream. At the end of this room temperature exposure to the gas stream the sample had become contaminated with platinum chloride and the thermocouple had been seriously attacked by the hydrogen chloride-water mixture. As a consequence of this attack on the platinum by the gas stream it was decided to modify the reaction chamber as discussed on page 18. Rather than repeat the work already completed on the praesodymium trichloride hydrolysis it was decided to use the new reaction chamber to measure the equilibrium constants for the neodymium trichloride hydrolysis.

Table 16

Equilibrium Constants for the Reaction
$PrCl_{3(s)} + H_2O_{(g)} = PrOCl_{(s)} + 2HCl_{(g)}$

Run No.	T °K	v.p. HCl (mm)	v.p. H_2O (mm)	K_{max} K_{min}	ΔF_{expt} Kcal	ΔF_{calc} Kcal	Dev. Kcal
1	864.7	169.5 167.1	2.830 2.790	13.36 13.17	-4.44	-4.48	-0.04
2	803.3	114.9 117.2	3.250 3.485	5.345 5.186	-2.65	-2.64	+0.01
3	760.0	75.67 75.41	3.092 3.078	2.437 2.431	-1.34	-1.33	+0.01
4	703.1	41.86 39.83	3.063 2.934	0.753 0.711	+0.44	+0.40	-0.04
				Average Deviation			±0.03

H. The Hydrolysis of Neodymium Trichloride

The values obtained for the equilibrium constants for the vapor phase hydrolysis of neodymium trichloride are summarized in Table 17. The data in the table confirm the conclusions drawn from the praesodymium measurements. The accuracy of the gas analyses serves to confine the uncertainty of the equilibrium constants to within 1-2 percent and no discrepancy from the calculated free energies greater than 0.05 kcal occurs. These measurements on the neodymium system indicate that an apparatus such as the one described here may be used to obtain thermodynamic data of good accuracy in those cases where a solid-gas interaction is involved and where the conditions are practicable for accurate gas analyses.

Table 17

Equilibrium Constants for the Reaction
$NdCl_3(s) + H_2O_{(g)} = NdOCl_{(s)} + 2HCl_{(g)}$

Run No.	T °K	v.p. HCl (mm)	v.p. H_2O (mm)	K_{max} K_{min}	ΔF_{expt} Kcal	ΔF_{calc} Kcal	Dev. Kcal
1	896.6	232.1	1.939	36.56	-6.41	-6.41	0.00
		230.4	1.919	36.40			
2	865.4	224.6	2.749	24.15	-5.47	-5.47	0.00
		219.4	2.655	23.86			
3	831.6	187.6	3.026	15.30	-4.50	-4.46	+0.04
		182.8	2.913	15.09			
4	802.1	170.2	4.072	9.360	-3.53	-3.55	-0.02
		166.4	4.080	8.930			
5	767.5	108.1	2.969	5.179	-2.50	-2.50	0.00
		105.1	2.836	5.125			
6	730.0	82.55	3.502	2.560	-1.35	-1.35	0.00
		80.72	3.422	2.505			
				Average Deviation			±0.01

IV. DISCUSSION AND CONCLUSIONS

A. The Heats and Entropies of the Hydrolysis Reactions

The experimental data themselves yield only the values of ΔF^o at various temperatures in the range from about 700° to 900° K. For thermodynamic purposes it is desirable to derive from these data the thermodynamic properties of the reaction at the standard temperature of 298.16° K. In such cases it is customary to express the experimental data by an empirical equation, usually of the type

$$\Delta F_T^o = \Delta H_o - RT \cdot \Delta C_p \ln T + IT \qquad (1)$$

(although additional temperature dependent terms may be added) in which the values of the constants ΔH_o, ΔC_p and I are chosen to give the minimum deviation from the observed ΔF values.

As an alternative, ΔC_p may be computed independently of the experimental data, from the known heat capacity functions of the substances involved in the reaction, or from estimated heat capacity values, such as those based on the additivity principle.[19] The two constants, ΔH_o and I are then evaluated from the data.

A third possibility is to choose the temperature coefficient of the entropy of the reaction, $\delta \Delta S/\delta T = \Delta C_p/T$, to give agreement of the extrapolated ΔS^o_{298} value with empirical entropy rules, such as those of Latimer,[20] for the entropies of the solids at room temperature.

The first alternative has been applied to all of the data reported in this thesis. Calculated free energy values listed in Tables 11 through 17 are based on the function

$$\Delta F_T^o \text{ (kcal)} = \Delta H_o + \frac{6.4 \text{ T} \log T}{1000} + 0.18 \cdot 10^{-6} \text{ T}^2 - \frac{22}{T} + IT \qquad (2)$$

which implies a

$$\Delta C_p = -2.8 - 0.36 \cdot 10^{-3} T + 0.44 \cdot 10^5 T^{-2}. \qquad (3)$$

The value of ΔC_p for the reactions was estimated by combining heat capacities of the solids computed from the additivity principle discussed by Lewis and Randall with the heat capacity equations given by Kelley[21] for $HCl_{(g)}$ and $H_2O_{(g)}$.

The thermodynamic constants for the vapor phase hydrolysis of the solid trichlorides of lanthanum, praesodymium, neodymium samarium, gadolinium, terbium and americium are summarized in Table 18.

Table 18

Summary of Thermodynamic Constants for the Trichloride Hydrolysis Reactions

Metal	ΔF^{o}_{785}	ΔH^{o}_{785}	ΔS^{o}_{785}	ΔF^{o}_{298}	ΔH^{o}_{298}	ΔS^{o}_{298}	ΔH_{o}	I
La	+1.4	25.6	30.8	17.0	27.0	33.5	27.9	-52.4
Pr	-2.1	21.6	30.2	13.2	23.0	32.8	24.0	-51.8
Nd	-3.0	20.8	30.4	12.4	22.2	33.0	23.2	-52.0
Sm	-5.4	19.2	31.4	10.4	20.6	34.0	21.6	-53.0
Gd	-6.2	17.8	30.6	9.3	19.2	33.2	20.2	-52.2
Tb	-6.7	18.8	32.6	9.7	20.2	35.3	21.2	-54.4
Am	-4.1	20.0	30.6	11.5	21.4	33.3	22.4	-52.3

No allowance has been made for differences in the ΔC_p functions for the hydrolysis reactions of the different rare earths and actinides. The lattice heat capacities of the isostructural rare earth trichlorides would be expected to differ but little since the lattice parameters and masses of the ions are nearly the same (see Table 22 and 23). The heat capacities of the oxychlorides would be expected to show similar behavior. Trends in heat capacity values as a function of atomic number probably would run nearly parallel in the two salts--trichlorides and oxychlorides. For this reason $C_{pMOCl}-C_{pMCl_3}$ may be taken as constant for all members of the series so far as the lattice heat capacities are concerned.

Small differences might be expected because of differences in the Stark splitting of the ground states and (probably higher levels for neodymium, plutonium and americium since the first excited state lies within a few hundred cm^{-1} of the ground state) for the trichlorides on one hand, and the oxychlorides on the other. Since these effects probably are of small magnitude in comparison with the uncertainty in the estimation of the lattice heat capacities of the solid, they are not considered further.

Terbium forms an exception to the arguments presented above, since its trichloride has a unique, unknown structure. For the other elements, however, no substantial differences in the ΔC_p function are to be expected.

It is of interest to compare estimates of the ΔC_p function made in various ways. The function

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

estimated from the additivity principle has already been discussed.

A one-term ΔC_p function may also be estimated from groups of three experimental free energy values by substitution into the free energy equation

$$\Delta F_T = \Delta H_o - RT\Delta C_p \ln T + IT$$

and solution of the three simultaneous equations for ΔH_o, ΔC_p and I. Since the temperature range covered is limited, the values of ΔC_p, ΔH_o and I determined in this way are quite sensitive to small errors in the measured free energies. Nevertheless, random choice of several groups of three free energy values from the data on neodymium give an average ΔC_p of -3.3 for the first term of the ΔC_p function, in fair agreement with the value of -2.8 estimated as described previously. The preliminary treatment of the data suggests that the mean value of ΔC_p from all possible combinations probably would be approximately -2.0 rather than -3.3, as the small number of groups chosen included the free energy value for 831.6° K, which yields a large value of approximately -8 for the ΔC_p term.

Extensive calculations, using all of the data for all of the rare earths investigated probably would yield a better value of ΔC_p than that estimated independently of the data. A revision of this kind could not materially improve the calculated free energy values in the experimental temperature range but could effect significantly the values at 298° K. Errors in the ΔC_p function affect all of the values at 298° K to the same extent.

The third method of estimating ΔC_p is based on the relation

$$\frac{\delta \Delta S}{\delta T_p} = \frac{\Delta C_p}{T}$$

Approximately: $\Delta S_{T_2} - \Delta S_1 = \Delta C_p \ln \frac{T_2}{T_1}$.

ΔS_{298} is chosen to agree with Latimer's rules,[20] whence

S^o_{298} for $LaCl_3 = 13.8 + 6.9 \times 3 = 34.5$ e.u.
S^o_{298} for $LaOCl = 13.8 + 6.9 + 0.5 = 21.2$ e.u.
S^o_{298} for $H_2O = 45.1$ e.u.
S^o_{298} for $2HCl = 89.2$ e.u.
$\Delta S^o_{298} = 30.8$ e.u.

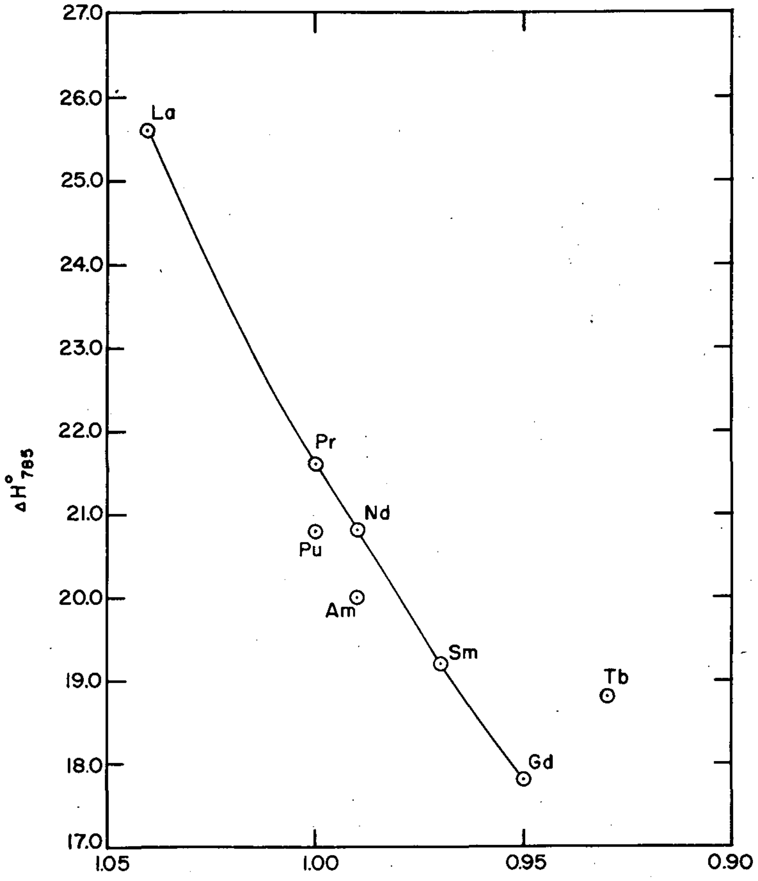
Substituting into the above equation the ΔS^{o}_{298} obtained from Latimer's rules and the experimentally determined ΔS^{o}_{881} from the neodymium data one calculates for ΔC_p a value of -0.6 calories/degree mole. This value for the first term of the ΔC_p function is materially lower than the estimated value of -2.8 or the values obtained by calculation from the experimental data, but the disagreement is not highly significant since the empirical rules probably are not reliable to better than one entropy unit.

To study the reaction over a wider temperature range using the method described herein to obtain a better experimental ΔC_p value is limited on the one extreme by the melting points of the trichlorides and the temperature at which the balance is no longer stable and on the other by the rapidly decreasing rate of reaction below 700° K.

In Fig. 3, ΔH^{o}_{785} for the various hydrolysis reactions has been plotted as a function of the ionic radii of the metal cation. The points for lanthanum, praesodymium, neodymium, samarium and gadolinium fall along a smooth curve, while terbium does not lie along this curve. The anamolous behavior of terbium is undoubtedly to be correlated with the novel crystal structure of terbium trichloride.

The data illustrate in quantitative fashion the changes in thermodynamic properties of the reaction brought about by slight changes in crystal parameters of the solids, and by a change in nuclear charge on the cation. The experimentally determined free energies do not fit a smooth curve (Fig. 4) as well as the calculated ΔH^{o}_{785} values. ΔF^{o}_{785} for the hydrolysis of samarium trichloride appears to be the furthest out of line. There is no obvious reason why this should be the case and until the work is confirmed by using the more refined apparatus one is forced to say that the deviation is within the experimental error.

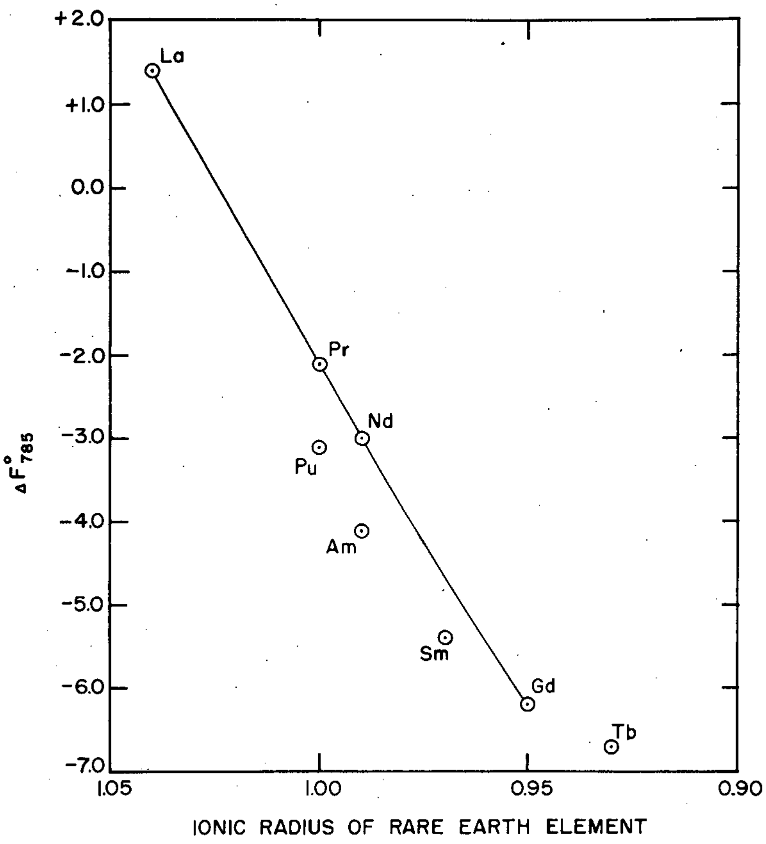
For the purpose of comparison, an average value of ΔS^{o}_{785} equal to 30.5 ± 0.3 and of I, the integration constant, equal to 52.1 ± 0.3 were assumed for the hydrolysis of all the lanthanide trichlorides through gadolinium and of the trichlorides of neptunium, plutonium, americium and curium. The ΔF^{o}_{785} values were assigned for the hydrolysis of each of the seven lanthanide trichlorides from a smooth line drawn through the points for lanthanum, praesodymium, neodymium and gadolinium, as shown in Fig. 4. In addition to the data on americium, in the actinide series, Sheft and Davidson[22] have reported for plutonium, $\Delta H^{o}_{298} = 22.2$ kcal and $\Delta S^{o}_{298} = 33.5$ entropy units. These data when substituted into the free energy equation gives a ΔF^{o}_{785} value which lies one kilocalorie below the lanthanide values for comparable radii. The experimentally determined ΔF^{o}_{785} value found in Table 18 for the hydrolysis of americium trichloride also lies one kilocalorie below the lanthanide curve for an atom of comparable radius. On this basis values along a line parallel to the lanthanide curve and one kilocalorie below the lanthanide data have been assigned for neptunium and curium. The ionic radius used for neptunium was assigned by Zachariasen[23] and that of curium was estimated as 0.98 Å. The compilation of this information is found in Table 19. All values which have been assigned rather than experimentally determined are enclosed in parentheses.



PLOT OF THE CHANGE OF ΔH°_{785} WITH IONIC RADIUS OF THE METAL ION

FIG. 3

MU-6062



PLOT OF THE CHANGE OF ΔF°_{785} WITH IONIC RADIUS OF THE METAL ION

FIG. 4

MU-6063

Table 19

Compilation of the Estimated Thermodynamic Data for the Hydrolysis of some Lanthanide and Actinide Trichlorides

Metal	ΔF^{o}_{785}	ΔH^{o}_{785}	ΔS^{o}_{785}	ΔF^{o}_{298}	ΔH^{o}_{298}	ΔS^{o}_{298}	ΔH_{o}	I
La	+1.4	25.3	30.5	16.9	26.8	33.3	27.8	-52.1
Ce	(-0.6)	(23.3)	"	(14.9)	(24.7)	"	(25.8)	"
Pr	-2.1	21.8	"	13.4	23.2	"	24.3	"
Nd	-3.0	20.9	"	12.5	22.3	"	23.4	"
Pm	(-3.9)	(20.0)	"	(11.6)	(21.4)	"	(22.5)	"
Sm	-4.8	19.1	"	10.7	20.5	"	21.6	"
Eu	(-5.6)	(18.3)	"	(9.9)	(19.7)	"	(20.8)	"
Gd	-6.2	17.7	"	9.3	19.1	"	20.2	"
Np	(-2.2)	(21.7)	"	(13.3)	(23.2)	"	(24.2)	"
Pu	-3.1	20.9	"	12.3	22.2	"	23.2	"
Am	-4.1	19.8	"	11.4	21.2	"	22.3	"
Cm	(-4.9)	(19.0)	"	(10.6)	(20.4)	"	(21.4)	"

B. The Heats of Reactions Involving Lanthanide and Actinide Oxychlorides

With the aid of the values obtained for the hydrolysis of the various lanthanide and actinide trichlorides, it is possible to calculate heats of several reactions of interest. Additional information needed for these calculations include values for the heats of the trichlorides and oxides and of the various gases involved in the reactions considered. Values for $HCl_{(g)}$, $H_2O_{(g)}$, $Cl_{2(g)}$, $O_{2(g)}$ and $H_{2(g)}$

are found in the National Bureau of Standards Tables, which also include values for the heats of formation of the oxides of lanthanum, praesodymium and neodymium. The heats of formation of the trichlorides were obtained as follows. The heat of formation of lanthanum and gadolinium trichlorides listed in Table 20 are the values reported by F. Spedding, et al.[24] The values listed for cerium and neodymium trichlorides are those reported by Spedding and Miller.[25] The values listed for the other trichlorides are extrapolated ones obtained by drawing a smooth curve through the points listed by Spedding for lanthanum, cerium, neodymium and gadolinium trichlorides.

Of interest in the reactions listed in Table 20 are reaction (3) which gives the heat of formation of the respective oxychlorides. Reaction (4) illustrates the stability of the oxychlorides against disproportionation to the trichlorides and oxides. Reaction (5) shows the further hydrolysis of the oxychloride to the oxide and reactions (6), (7) and (8) list several methods of forming the oxychloride. Parentheses have been used to enclose values which have been assigned rather than experimentally determined.

For the data listed in Table 21, the heats of formation for the actinide trichlorides were taken from Latimer.[20]

Table 20

ΔH^{o}_{298} for Reactions Involving Lanthanide Oxychlorides

No.	Reaction	La (Kcal)	Ce (Kcal)	Pr (Kcal)	Nd (Kcal)	Pm (Kcal)	Sm (Kcal)	Eu (Kcal)	Gd (Kcal)
1.	$MCl_3(s) + H_2O_{(g)} = MOCl(s) + 2HCl_{(g)}$	27.0	(24.9)	23.0	22.2	(21.4)	20.6	(19.7)	19.2
2.	$M(s) + 3/2Cl_2(g) = MCl_3(g)$	-250.8	-250.6	(-247.6)	-244.1	(-240.2)	(-236.5)	(-232.8)	(-234.7)
3.	$M(s) + 1/2O_2(g) + 1/2Cl_2(g) = MOCl_{(s)}$	-237.5	(-239.4)	(-237.9)	-235.2	(-232.1)	(-229.2)	(-226.4)	(-223.4)
4.	$MOCl_{(s)} = 1/3M_2O_3\ (s) + 1/3MCl_3(s)$	+0.9	--	(+7.2)	+6.5	--	--	--	--
5.	$MOCl_{(s)} + 1/2H_2O_{(g)} = 1/2M_2O_3(s) + HCl_{(g)}$	15.3	--	(22.5)	20.8	--	--	--	--
6.	$MCl_3(s) + 1/2O_2(g) = MOCl(s) + Cl_2(g)$	13.3	(11.2)	(9.7)	8.9	(8.1)	(7.3)	(6.4)	5.9
7.	$1/2M_2O_3(s) + 1/2Cl_2(g) = MOCl_{(s)} + 1/4O_2(g)$	-8.5	--	(-15.6)	-14.2	--	--	--	--
8.	$M_{(s)} + HCl_{(g)} + H_2O_{(g)} = MOCl_{(s)} + 3/2H_2(g)$	-157.6	(-159.5)	(-158.0)	-155.3	(-152.2)	(-149.3)	(-146.5)	(-143.5)

Table 21

ΔH^{o}_{298} for Reactions Involving Actinide Oxychlorides

No.	Reaction	Np (Kcal)	Pu (Kcal)	Am (Kcal)
1.	$MCl_3(s) + H_2O_{(g)} = MOCl_{(s)} + 2HCl_{(g)}$	(23.2)	22.2	21.2
2.	$M_{(s)} + 1/2Cl_{2(g)} + 1/2O_2(g) = MOCl_{(s)}$	(-206.5)	-221.5	-243.8
3.	$MCl_3(s) + 1/2O_2(g) = MOCl_{(s)} + Cl_2(g)$	(9.5)	8.5	7.5
4.	$M_{(s)} + HCl_{(g)} + H_2O_{(g)} = MOCl_{(s)} + 3/2H_{2(g)}$	(-126.6)	-141.6	-171.4

Table 22

Reactions Involving Lanthanum Oxychloride

No.		ΔS^{o}_{298} e.u.	ΔF^{o}_{298} Kcal
1.	$LaCl_3(s) + H_2O_{(g)} = LaOCl_{(s)} + 2HCl_{(g)}$	33.3	17.0
2.	$La_{(s)} + 1/2O_{2(g)} + 1/2Cl_{2(g)} = LaOCl_{(s)}$	-41.1	-225.3
3.	$LaOCl_{(s)} = 1/3La_2O_{3(s)} + 1/3LaCl_{3(s)}$	-2.5	1.6
4.	$LaOCl_{(s)} + 1/2H_2O_{(g)} = 1/2La_2O_3(s) + HCl_{(g)}$	12.9	11.5
5.	$LaCl_3(s) + 1/2O_{2(g)} = LaOCl_{(s)} + Cl_{2(g)}$	18.0	7.9
6.	$1/2La_2O_3(s) + 1/2Cl_{2(s)} = LaOCl_{(s)} + 1/4O_{2(g)}$	-5.2	7.0
7.	$La_{(s)} + HCl_{(g)} + H_2O_{(g)} = LaOCl_{(s)} + 3/2H_{2(g)}$	-32.9	-147.8

The ΔS^o_{298} and ΔF^o_{298} values for the reactions listed in Table 20 are compiled for lanthanum oxychloride in Table 22. The entropies of lanthanum trichloride and lanthanum oxychloride at 298° K were calculated using Latimer's rules. The calculated entropy at 298° K for lanthanum oxychloride was obtained from equation 1 of Table 22 using the previously estimated value for lanthanum trichloride. The entropy values for $H_2O_{(g)}$, $HCl_{(g)}$, $O_{2(g)}$, $Cl_{2(g)}$ and $H_{2(g)}$ were taken from the National Bureau of Standards Tables.

In the course of the preparation of lanthanum oxychloride for crystallographic investigation it was observed that disproportionation of the sample to the oxide and trichloride occurred relatively rapidly in vacuum above 1000° C. It is of interest to compare qualitatively the observed pressure for the disproportionation with a pressure one would calculate for the effusion of the lanthanum trichloride from the Knudsen equation:

$$q = \frac{5.83 \times 10^{-2}}{(MT)^{1/2}} \times pa$$

where q represents the number of moles effusing per second, M the molecular weight of the gas, T the absolute temperature of the source, p the pressure in the source expressed in millimeters of mercury, and a the cross sectional area of the slit. Although the equation holds only for small slit widths and long mean free paths, the conditions of the experiment should permit a rough comparison of the observations and the theory.

At a temperature of approximately 1300° K and a pressure of 10^{-3} mm, it was found that 10 minutes were required to quantitatively convert 5 mg of lanthanum oxychloride to lanthanum oxide and lanthanum trichloride in a 2 mm inner diameter quartz tube. From these data one estimates an effusion rate of 1×10^{-8} moles per second. Substitution into the Knudsen equation yields the following result:

$$p = \frac{(1 \times 10^{-8})(245 \times 1300)^{1/2}}{(5.83 \times 10^{-2})(0.12)}$$

$$p = 0.8 \times 10^{-3} \text{ mm.}$$

This value is in good agreement with the experimentally observed pressure of 10^{-3} mm at 1300° K.

C. Crystal Energy Calculations

The data presented in the preceding sections afford an opportunity to test theoretical equations which have been used to calculate from crystallographic data a quantity--variously called the "crystal energy," the "cohesive energy" or the "binding energy" of ionic crystals--which may be taken here as equal to the heat of formation per mole of the solid crystal from its component ions in the gaseous state, at the standard temperature of 298° K, although literature references to this quantity sometimes refer to the hypothetical heat for the process at 0° K. When the required thermodynamic data--standard heats of formation of ions and crystal--are available direct comparison between calculation and experiment is possible. However, even in the most favorable cases the thermodynamic data are uncertain by several kilocalories, since accurate measurements of electron affinities have not been made. In such calculations uncertainties of this kind may be eliminated by adopting a scheme of comparison between calculated and observed thermodynamic properties which will be discussed in a subsequent section of this thesis.

1. Derivation of General Equation.--The simple models that have been used for crystal energy calculations permit one to perform the required arithmetic without clearly understanding the procedure necessary for such a calculation. Consequently, at the risk of excessive elaboration, the procedure used for the various calculations is discussed in detail.

The expressions given by Kittel[23] for the calculation of interionic forces and crystal energy are adopted herein with minor alterations. If ϕ_{ij} is the interaction energy between ions i and j, the total energy of any one ion is

$$\phi = \sum_{j}{}' \phi_{ij}$$

where the prime indicates that the summation is to include all ions except $j = i$. The ϕ_{ij} is written as the sum of a central field repulsive potential varying as r_{ij}^{-n} and a Coulomb potential:

$$\phi_{ij} = \frac{\lambda}{r_{ij}^{n}} \pm \frac{e^2}{r_{ij}}$$

The repulsive term describes the fact that at small distances the ions repel each other with a force which varies much more rapidly with interionic distance than does the point charge coulombic interaction. It is a convenient approximation to regard the ions as spheres of slight compressibility. The constants λ and n are determined generally from lattice parameters and compressibility data. In principle the interaction energies of ions in a crystal may be calculated precisely from quantum mechanical considerations, but the computational labor involved is very great, and has been carried out only for sodium chloride and lithium hydride. The results differ but slightly from values obtained by the classical approach.

The total potential energy of an ionic crystal is obtained by summing the terms ϕ_{ij} over all the pairs of ions in the crystal. In a crystal all of the interionic distances are related rather simply to a crystallographic parameter. The calculations for the trichlorides and oxychlorides have been based on the length of the a axis, because this distance is known with reasonable precision while the nearest neighbor distance is defined less precisely. It is convenient to introduce quantities p_{ij} such that

$$r_{ij} = p_{ij} \cdot R_a$$

where R_a is the length of the a axis. Then

$$\phi_{ij} = \frac{1}{p_{ij}^{n}} \cdot \frac{\lambda}{R_a^{n}} \pm \frac{1}{p_{ij}} \cdot \frac{e^2}{R_a}$$

$$\phi = \sum_{j}^{\prime} \frac{1}{p_{ij}^{n}} \circ \frac{\lambda}{R_a^{n}} + \sum_{j}^{\prime} \frac{1}{p_{ij}} \circ \frac{e^2}{R_a}$$

or

$$\phi = \frac{\lambda A_n}{R_a^{n}} - \frac{\alpha e^2}{R_a} \quad ,$$

where $A_n = 0.5 \sum_{j}^{\prime} \left(\frac{z' z''}{p_{ij}} \right)^{n}$ $\qquad \alpha = 0.5 \sum_{j}^{\prime} \frac{z' z''}{p_{ij}}$

The symbols z' and z" denote the charges on the two ions of the pair which is summed. The term 0.5 appears because in the course of the summation procedure every interaction has been counted twice.

The constants A_n and α (α is commonly called the Madelung constant) represent the sums of a series of terms obtained by writing each ion pair interaction as the product of charges on the ions (in units of e^2) divided by the interionic distance in terms of R_a, each term being raised to a power appropriate to the dependence on R_a of the energy. Since the repulsive potential due to ion "contact" has a large exponential dependence on R_{ij} the terms of the

$$0.5 \sum_{j}^{\prime} \left(\frac{z' z''}{p_{ij}} \right)^{n}$$

series converge very rapidly and the value of A_n is obtained with sufficient precision by considering "nearest neighbor" interactions. The constant A_n has no real significance, however, since the interactions do not in general show any regular z'z" dependence.

A_n and α both have the same values for all crystals having the same structure and ion charges but different values of R_a. The α summation converges rather slowly, and necessitates the consideration of interactions at relatively large distances for its accurate evaluation.

The product λA_n will not be calculated directly but will be eliminated from the equation by allowing $d\phi/dR$ to equal zero at the equilibrium distance in the crystal so that

$$-\frac{n\lambda A_n}{R_a^{n+1}} + \frac{\alpha e^2}{R_a^2} = 0$$

Eliminating λA_n the following expression is obtained

$$\phi = \frac{\alpha e^2}{R_a}\left(\frac{1}{n} - 1\right)$$

The total cohesive energy of a mole of the crystal is then

$$U_o = N\phi = -\frac{N\alpha e^2}{R_a}\left(1 - \frac{1}{n}\right)$$

2. Evaluation of the Madelung Constant.--The definition of the Madelung constant, α, from the previous derivation is:

$$\alpha = 0.5 \sum_{j}{}' \frac{z'z''}{\rho_{ij}}$$

where as previously stated the prime indicates that the summation is to include all ions except $j = i$. The sign for a particular term in the summation will then depend on the respective charges on the ion pair being considered--positive-negative (attractive) terms being counted as negative, and positive-positive and negative-negative as positive (repulsive) terms. For a stable arrangement of ions, the crystal energy will be negative and consequently α must always be negative in such cases. Sodium chloride is used as an example to illustrate the several points discussed.

Reference atom is sodium

$\sum_{Na}{}' \frac{1}{\rho_{Na-Na}}$	When all sodium sites have been considered every Na-Na interaction will have appeared twice.
$-\sum_{Na}{}' \frac{1}{\rho_{Na-Cl}}$	When all sodium sites have been considered every Na-Cl interaction will have appeared once.

Reference atom is chlorine

$$\sum_{Cl}{}' \frac{1}{\rho_{Cl-Cl}}$$

When all chlorine sites have been considered every Cl-Cl interaction will have appeared twice.

$$-\sum_{Cl}{}' \frac{1}{\rho_{Cl-Na}}$$

When all chlorine sites have been considered every Na-Cl interaction will have appeared once.

For the sodium chloride structure

$$-\sum_{Na}{}' \frac{1}{\rho_{Na-Cl}} = -\sum_{Cl}{}' \frac{1}{\rho_{Cl-Na}}$$

Therefore, in the total summation every interaction has appeared twice. Then to obtain the Madelung constant each summation much be divided by two.

$$\alpha = 0.5 \sum_{Na}{}' \frac{1}{\rho_{Na-Na}} + 0.5 \sum_{Cl}{}' \frac{1}{\rho_{Cl-Cl}} - 2(0.5) \sum_{Na}{}' \frac{1}{\rho_{Na-Cl}}$$

In this example, the problem is further simplified because

$$\sum_{Na}{}' \frac{1}{\rho_{Na-Na}} = \sum_{Cl}{}' \frac{1}{\rho_{Cl-Cl}}$$

and so the Madelung constant can be calculated from the summation using one of the ions only as a reference ion. Hence, for sodium chloride

$$\alpha = \sum_{Na}' \frac{1}{\rho_{Na-Na}} - \sum_{Na}' \frac{1}{\rho_{Na-Cl}}$$

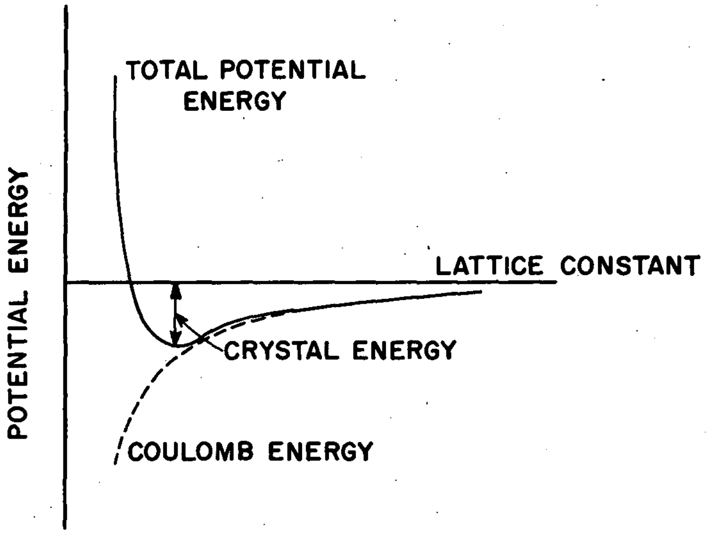
For the rare earth and actinide trichlorides:

$$\alpha = 4.5 + \sum \frac{1}{\rho_{La-La}} + 1.5 \sum \frac{1}{\rho_{Cl-Cl}} - 6.0 \sum \frac{1}{\rho_{La-Cl}}$$

For the oxychlorides the expression is as follows:

$$\alpha = 4.5 \sum \frac{1}{\rho_{La-La}} + 2 \sum \frac{1}{\rho_{O-O}} + 0.5 \sum \frac{1}{\rho_{Cl-Cl}} + 2 \sum \frac{1}{\rho_{O-Cl}} - 6 \sum \frac{1}{\rho_{La-O}} - 3 \sum \frac{1}{\rho_{La-Cl}}$$

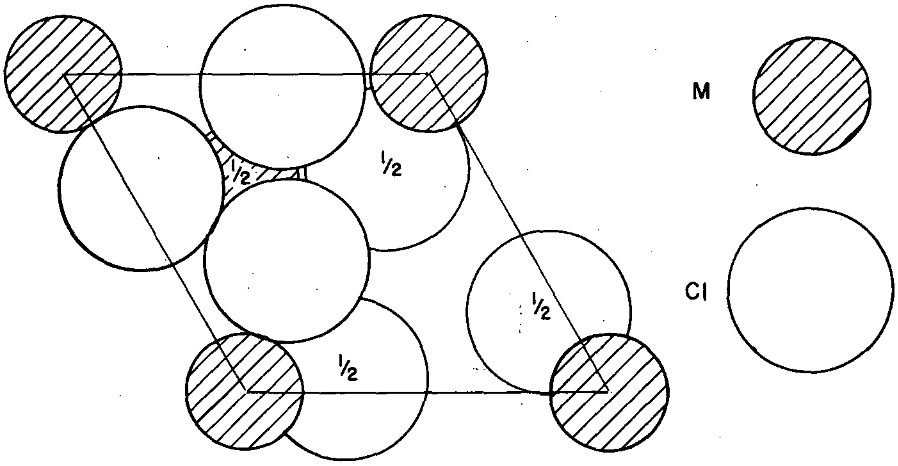
The crystallographic data used for the Madelung constant calculations were believed to be the best available at the time the calculations were undertaken. The two sources for the values listed are W. H. Zachariasen[26] and D. H. Templeton and C. Dauben.[27] Several of the values listed for the trichlorides were obtained from D. H. Templeton and C. Dauben and are not as yet in the literature. Pictures of the hexagonal trichlorides and tetragonal oxychlorides are shown in Figs. 6 and 7. Table 23 contains the crystallographic data of some of the rare earth and actinide trichlorides used for the Madelung constant calculations.



DEPENDENCE OF POTENTIAL ENERGY OF AN IONIC CRYSTAL
ON THE LATTICE CONSTANT

FIG. 5

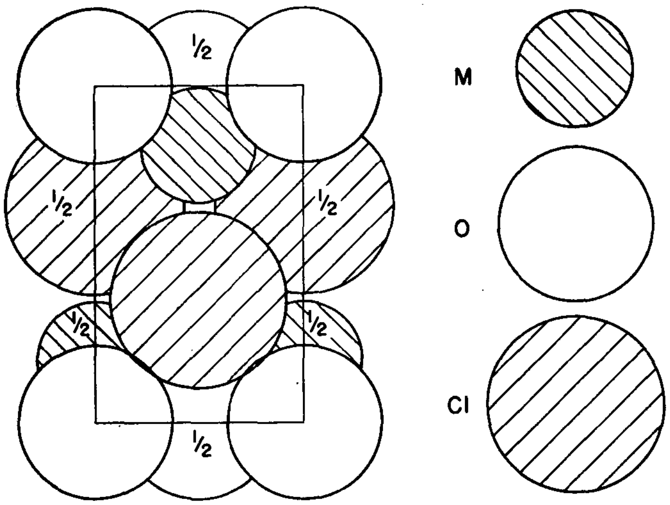
MU-6064



CRYSTAL STRUCTURE OF THE HEXAGONAL LANTHANIDE
AND ACTINIDE TRICHLORIDES

FIG. 6

MU-6145



CRYSTAL STRUCTURE OF THE TETRAGONAL LANTHANIDE AND ACTINIDE OXYCHLORIDES

FIG. 7

MU-6146

Table 23

Crystallographic Data for Some Lanthanide and Actinide Trichlorides

Metal Trichloride	a Å	c Å	x in terms of a	y in terms of a
La	7.468	4.366	0.292 ± 0.014	0.375 ± 0.014
Ce	7.436	4.304	"	"
Pr	7.407	4.267	"	"
Nd	7.381	4.231	"	"
Sm	7.362	4.151	"	"
Eu	7.34	4.13	"	"
Gd	7.321	4.100	"	"
Np	7.405	4.273	"	"
Pu	7.380	4.238	"	"
Am	7.37	4.23	"	"

From Fig. 6 it is seen that the structure of the trichlorides is unusual in that the metal atoms are in positions 0,0,0 and 1/3,2/3,1/2 but that one does not appear at the position 2/3,1/3,1/2. As a consequence of this "vacancy" in the structure the summations converge very slowly. For this reason, the complete summation was carried out for only lanthanum trichloride. Two procedures were employed to estimate the Madelung constants listed in Table 24 for the other lanthanide and actinide trichlorides. The first method involved selecting a minimum number of unit cells which would provide a value for the individual summations in agreement with the result found for the more complete summation for lanthanum trichloride. The same number of unit cells were not used for each summation. Most of the cells chosen had one boundary in which values for c were equal to zero and so it is probable that the change in Madelung constant from member to member in the series is not sufficiently rapid. Since time did not permit the use of the more lengthy calculation to prove or disprove the shorter summations and since it was believed that the rate of change using the shorter summations was not sufficiently great, a second set of Madelung constants were calculated assuming that the change from member to member would be proportional to the rate of change of the c axis as compared to the a axis.

From the two procedures used, the Madelung constants change by approximately four percent from lanthanum to gadolinium trichloride using the abbreviated summation method and by comparison of the rate of change of c/a the constant changes by slightly less than seven percent over the same lanthanide trichlorides.

In subsequent comparisons between the crystal energies of the oxychlorides and trichlorides, both sets of values for the trichlorides listed in Table 24 will be used to illustrate the possible discrepancies present in the calculations due to the uncertainty associated with the Madelung constants that have been calculated for the respective trichlorides.

Table 24

Madelung Constants for Some Lanthanide and Actinide Trichlorides

Metal Trichloride	Abbreviated summation		Change of α proportional to change of c/a		
	$-\alpha$	$-\alpha/R_a$	c/a	$-\alpha$	$-\alpha/R_a$
La	23.4295	3.1373	0.58460	23.4295	3.1373
Ce	23.5222	3.1633	0.57880	23.6638	3.1823
Pr	23.5656	3.1815	0.57608	23.7763	3.2100
Nd	23.6092	3.1986	0.57323	23.8934	3.2371
Sm	23.7556	3.2268	0.56384	24.2917	3.2996
Eu	23.7752	3.2391	0.56267	24.3433	3.3165
Gd	23.8168	3.2532	0.56003	24.4581	3.3408
Np	23.5486	3.1801	0.57704	23.7364	3.2055
Pu	23.5922	3.1968	0.57425	23.8512	3.2319
Am	23.5977	3.2019	0.57395	23.8653	3.2382

The crystallographic data and Madelung constants for some lanthanide and actinide oxychlorides are listed in Table 25. For each value listed for the oxychlorides, the extensive summation procedure has been used.

Table 25

Crystallographic Data and Madelung Constants
for Some Lanthanide and Actinide Oxychlorides

Metal Oxychloride	a Å	c Å	u in terms of c	v in terms of c	$-\alpha$	$-\alpha/R_a$
La	4.119	6.883	0.179	0.639	20.7693	5.0423
Ce	4.080	6.831	0.178	0.638	20.9609	5.1375
Pr	4.051	6.810	0.1766	0.6366	20.9387	5.1688
Sm(1)	3.982	6.721	0.172	0.632	21.0320	5.2818
Sm(2)	"	"	0.175	0.635	20.9294	5.2560
Gd(1)	3.950	6.672	0.170	0.630	21.3273	5.3993
Gd(2)	"	"	0.179	0.639	20.9259	5.2977
Pu	4.004	6.779	0.180	0.640	20.8561	5.2088
Am	3.99	6.77	0.179	0.639	21.0228	5.2689

The change in Madelung constant from member to member in the series of oxychlorides is due primarily to a greater rate of change of the a axis as compared to the c axis. This change is roughly comparable to that of the two axes is the trichlorides. Slight changes also may occur due to the relative changes of position of the parameters u and v. The values listed in Table 25 for u and v were assigned on the basis that intensity measurements on the lines obtained from x-ray powder patterns for the oxychlorides indicate that the parameters for lanthanum oxychloride should be $u = 0.18 \pm 0.01$ c and $v = 0.64 \pm 0.01$ c in accord with values listed in the literature.[28]

Samarium and holmium oxychloride powder patterns suggest that the parameters for these two salts should be $u = 0.17 \pm 0.01$ c and $v = 0.63 \pm 0.01$ c. The second samarium oxychloride summation serves to illustrate the effect of halving the rate of change of the two parameters. The second gadolinium oxychloride summation illustrates the change of the Madelung constants from lanthanum to gadolinium if the parameters are constant. In a subsequent section concerning crystal energies, the second summations of samarium and gadolinium oxychlorides will be discussed further.

3. Evaluation of the Repulsive Term.--The repulsive force between ions becomes appreciable only when their centers are not more than a few Angstroms apart. It increases more rapidly than the interionic distance of two ions is illustrated in Fig. 5.

Two forms of the repulsive interaction term have been considered in the course of the development of the theory of interionic forces and crystal energy. The first has no independent foundation. It was assumed by Born[2] that the repulsive forces between ions gave rise to an interaction energy of the type

$$\phi_r = \frac{b}{r^n} .$$

The second form of the repulsive term was introduced by Born and Mayer as a result of quantum theoretical treatments of ionic interactions. They replaced the above term by an exponential expression of the type

$$\phi_r = ae^{-r/\rho}$$

The symbols a and ρ are constants.

For the first calculations included in this thesis it was felt that the earlier Born expression might be satisfactory. The values of n used for the repulsive term are those determined by use of Pauling's rules. These values are listed in Table 26. For a crystal of mixed ion type an average of values of this table should be used.

Table 26

Values of the Born Exponent, n

Ion Type	n
He	5
Ne	7
A, Cu^+	9
Kr, Ag^+	10
Xe, Au^+	12
Rn	13

An examination of the literature indicates that the only repulsive interactions ordinarily considered are those between neighboring ions of opposite charge. For example, in the reported crystal energy calculations on the alkali halides, the average n values for anion-cation interactions are used throughout. This probably is a satisfactory estimate for the halides of sodium, potassium and rubidium since the positive ions are sufficiently large that the cations do not touch. However, for LiCl, LiBr and LiI, one should not be concerned with anion-cation repulsions but rather with overlapping of the respective halides, since the anion-cation distance is greater than the combined equilibrium radii assigned to the lithium and corresponding halide ions. If the anion-anion repulsions are considered only in these three cases rather than the anion-cation repulsion, better agreement is obtained with the experimental data obtained from the thermodynamic cycle,

$$U_{0298} = \Delta H_{f298} \text{ of } RX - \Delta H_{f298} \text{ of } R^{+}_{(g)} - \Delta H_{f298} \text{ of } X^{-}_{(g)} ,$$

if the crystal energies are corrected to 298° K. Table 27 lists calculated energies considering anion-cation repulsion as reported in the literature, the calculated crystal energies considering only anion-anion repulsions and the experimentally determined energies obtained from the thermodynamic cycle for LiCl, LiBr and LiI.
A consideration of both repulsions to obtain some intermediate value should represent more nearly the average repulsion of ions in the crystal.

Table 27

Crystal Energies of Lithium Chloride, Lithium Bromide and Lithium Iodide

Salt	n from cation-anion interaction	U_{calc} Kcal/mole	n from anion-anion interaction	U_{calc} Kcal/mole	U_{expt} Kcal/mole
LiCl	7.0	193.3	9.0	201.1	200.3
LiBr	7.5	183.1	10.0	190.2	189.3
LiI	8.5	170.7	12.0	177.3	175.5

In the cases of the lanthanide and actinide trichlorides and oxychlorides there is an overlapping of the negative ions as well as anion-cation contact. In the trichlorides, the metal ions are surrounded by nine approximately equidistant chloride ions but in addition half of the chloride ions overlap other chlorides while the other half do not touch. The oxychlorides are even more complex in that the metal ion is surrounded by four equally spaced oxygen atoms on one side and by five equally spaced chlorine atoms on the other side. In addition, the oxygen-oxygen distances approximate the conventionally assigned oxygen diameter, the chlorine-chlorine and chlorine-oxygen distances are less than the usually assigned combined equilibrium radii. Therefore, the various repulsive terms have been considered separately.

The procedure used in calculating the energy due to repulsions of the b/r^n type was the following:

Univalent radii* computed by Pauling for lanthanum, oxygen and chlorine are 1.39, 1.76 and 1.81 Å, respectively. These values were used as guides to modify the radii so that agreement was obtained with the thermodynamic cycle for lanthum oxychloride. It was found that an additional correction of 0.11 Å was required for each ion-pair

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*These radii are computed to give the correct interionic distances for hypothetical crystals, having the sodium chloride arrangement, composed of univalent ions of the elements but with exponential repulsive forces corresponding to the actual ionic structures of the multivalent ions.

interaction to obtain a crystal energy in accord with the thermodynamic cycle.

The point charge coulombic energy of a hypothetical $La^{+}\ O^{-}$ crystal having the sodium chloride arrangment, therefore, is equal to

$$\frac{1.7476e^{2} \times 6.023 \times 10^{23} \times 10^{-3}}{(3.15 + 0.11)10^{-8} \times 4.185 \times 10^{7}} = 177.97 \text{ kcal.}$$

At equilibrium the "contact" repulsion energy is equal to

$$\frac{1}{\frac{n_{La^{+3}} + n_{O^{-2}}}{2}} \times 177.97 = \frac{1}{\frac{12 + 7}{2}} \times 177.97 = 18.73 \text{ kcal.}$$

Since this energy varies as $b/r^{9.5}$, the repulsive energy at any value of r will be equal to

$$18.73 \times \frac{\frac{b}{r^{9.5}}}{\frac{b}{(3.15 + 0.11)^{9.5}}}$$

for a crystal with the sodium chloride arrangment. For other crystals, if only nearest neighbor interactions are considered, the energy will be proportional to the number of the nearest neighbor La-O contacts, divided by the number of such contacts (6) in the hypothetical sodium chloride type LaO crystal. Thus in lanthanum oxychloride the La-O repulsion energy is

$$18.73 \times \frac{3.26 \times 10^{-8}}{2.40 \times 10^{-8}} \; r^{9.5} \times \frac{4}{6} = 229.2 \text{ kcal.}$$

The other repulsions were computed in a similar manner.

The same radii for lanthanum and chlorine and the correction term were used to calculate the repulsive terms for the trichlorides. The radius assigned to the metal ion was altered in accord with the change of radius usually assigned to the ions from lanthanum through gadolinium. Plutonium and americium were assigned univalent radii equal to those of praesodymium and neodymium, respectively.

The results of the calculations for the repulsive energies of individual ion pairs are summarized in Tables 28 and 29 for the oxychlorides and trichlorides respectively of some lanthanides and actinides.

Table 28

Repulsive Energy Terms for Individual Ion Pairs for some Lanthanide and Actinide Oxychlorides

Metal Oxy-Chloride	Individual Repulsive Energies M-O Kcal	M-Cl Kcal	M-M Kcal	O-O Kcal	O-Cl Kcal	Cl-Cl Kcal	Total Repulsive Energy Kcal
La	229.2	21.9	0.4	71.0	37.5	21.2	334.9
Ce	244.2	22.0	0.4	76.0	39.1	23.9	353.9
Pr	245.9	21.9	0.4	79.8	40.3	25.4	360.9
Sm(1)	273.1	22.2	0.4	86.0	42.8	32.2	397.4
Sm(2)	262.9	23.2	0.4	86.0	44.3	30.5	388.8
Gd(1)	297.7	22.0	0.4	95.4	44.2	35.9	429.8
Gd(2)	261.8	25.3	0.3	95.4	49.8	30.1	399.8
Pu	247.4	25.1	0.3	86.8	44.9	25.9	373.9
Am	254.2	24.6	0.3	88.9	45.0	27.2	382.0

4. Crystal Energies.--The results of the calculations of the Coulombic and repulsive interaction energies are summarized for the lanthanide and actinide trichlorides and oxychlorides in Tables 30 and 31.

Table 29

Repulsive Energy Terms for Individual Ion Pairs for some Lanthanide and Actinide Trichlorides

Metal Tri-chloride	Individual Repulsive Energies M-Cl Kcal	M-M Kcal	Cl-Cl Kcal	Cl-M Kcal	Total Repulsive Energy Kcal
La	72.6	0.0	41.6	24.2	135.0
Ce	75.9	"	44.6	25.3	142.9
Pr	76.3	"	46.7	25.4	146.4
Sm	83.8	"	52.2	27.9	159.1
Gd	87.1	"	55.9	29.0	171.0
Pu	82.5	"	49.7	27.5	155.6
Am	81.4	"	50.4	27.1	155.5

Table 30

Crystal Energies for Some Lanthanide and Actinide Oxychlorides

Metal Oxy-chloride	Coulombic Energy Kcal	Total Repulsive Energy Kcal	U_o Kcal
La	1674.0	334.9	1339
Ce	1705.6	353.9	1352
Pr	1716.0	360.9	1355
Sm(1)	1753.5	397.4	1356
Sm(2)	1745.0	388.8	1356
Gd(1)	1792.5	429.8	1363
Gd(2)	1758.8	399.8	1359
Pu	1729.3	373.9	1355
Am	1749.2	382.0	1367

Table 31

Crystal Energies for Some
Lanthanide and Actinide Trichlorides

	Abreviated Summation			Change of α proportional to c/a		
Metal Tri-chloride	Coulombic Energy Kcal	Total Repulsive Energy Kcal	U_o Kcal	Coulombic Energy Kcal	Total Repulsive Energy Kcal	U_o Kcal
La	1041.6	135.0	907	1041.6	135.0	907
Ce	1050.2	142.9	907	1056.5	142.9	914
Pr	1056.2	146.4	910	1065.7	146.4	919
Sm	1071.3	159.1	912	1095.4	159.1	936
Gd	1080.0	171.0	909	1109.1	171.0	938
Pu	1061.3	155.6	906	1073.0	155.6	917
Am	1063.0	155.5	908	1075.1	155.5	920

It can be seen from Table 30 that the two series of values listed for the Coulombic and repulsive energies of samarium oxychloride afford the same number for the resulting crystal energy. Reference to Table 25 shows that the rate of change of the assigned parameters, u and v, from one lanthanide to the next was halved as compared with that suggested by the crystallographic data. Since the crystal energy is the same for the two sets of parameters they represent a close approximation to the minimum of the potential energy curve shown in Fig. 5. It is interesting to compare the results of these calculations with the two of gadolinium oxychloride in which the second calculation used the same us and v parameters that have been assigned to lanthanum oxychloride. Here, it is seen that what has been lost from the total Coulombic energy exceeds the decrease in repulsive energy. The overall decrease of the repulsive energy is due primarily to the decrease in repulsion of the metal-oxygen pair. The fact that the first set of values leads to a greater crystal energy is in accord with the observation from the crystallographic data which indicate that a gradual change of the parameters should occur in the oxychloride series from lanthanum to gadolinium. A comparable adjustment of the parameters to obtain a maximum value for the crystal energy of the trichlorides was not undertaken due to the very lengthy calculations required to obtain the values. Likewise, it would be desirable to re-examine the crystallographic data of the oxychlorides and trichlorides to obtain the maximum possible experimental accuracy for the parameters before undertaking further calculations.

5. <u>Comparison of Crystal Energy Calculations and Experimental Results</u>.--The results of the crystal energy calculations can be compared to the experimental values determined for the hydrolysis of the individual trichlorides to their respective oxychlorides. In these calculations, uncertainties of such terms as electron affinities, heats of dissociation, heats of vaporization and ionization potentials may be eliminated, by adopting the following scheme of comparison between calculated and observed thermodynamic properties:

$$\Delta H^{\circ}_{f_{298}} MX(s) - \Delta H^{\circ}_{f_{298}} MY(s) - \left[\Delta H^{\circ}_{f_{298}} NX(s) - \Delta H^{\circ}_{f_{298}} NY(s)\right] \qquad (1)$$

to be compared with

$$U_{o_{298}}^{MX} + U_{o_{298}}^{NY} - \left[U_{o_{298}}^{MY} + U_{o_{298}}^{NX}\right] \qquad (2)$$

where Uo_{298}^{MX} is the calculated crystal energy of the salt MX at 298° K, and the terms following have corresponding meanings. The expression (2) results merely from the definitions:

$$\Delta H^{o}_{f_{298}} MX = Uo_{298}^{MX} - \Delta H^{o}_{f_{298}} M^{+}(g) - \Delta H^{o}_{f_{298}} X^{-}(g)$$

etc., and its value must equal the value given by (1) if the calculated crystal energies are correct.

The rare earth salts would appear to form an exceptionally suitable group of compounds for comparisons of this kind, for the chloride salts on the one hand form a group of close crystallographic similarity, as do the oxychlorides on the other.

The thermodynamic data required by schematic expression (1) have been obtained in the research described in this thesis.

Specifically for the reactions

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

$$GdCl_{3(s)} + H_2O_{(g)} = GdOCl_{(s)} + 2HCl_{(g)} \qquad (4)$$

ΔH^{o}_{298} for reaction (3) - ΔH^{o}_{298} for reaction (4) is equal to

$$\Delta H^{o}_{f_{298}} LaOCl - \Delta H^{o}_{f_{298}} GdOCl - \left[\Delta H^{o}_{f_{298}} LaCl_3 - \Delta H^{o}_{f_{298}} GdCl_3\right]$$

$$= \Delta H^{o}_{f_{298}} LaOCl - \Delta H^{o}_{f_{298}} LaCl_3 - \left[\Delta H^{o}_{f_{298}} GdOCl - \Delta H^{o}_{f_{298}} GdCl_3\right]$$

corresponding to expression (1).

This quantity observed experimentally should be equal to the sum of the calculated crystal energies of lanthanum oxychloride and gadolinium trichloride, less the sum of the crystal energies of lanthanum trichloride and gadolinium oxychloride.

Some of the data appearing in the literature may be compared in this way. Thus

ΔH_f^o of KCl = -104.17 kcal.

ΔH_f^o of KBr = -93.73 kcal.

ΔH_f^o of NaCl = -98.23 kcal.

ΔH_f^o of NaBr = -86.03 kcal.

$-104.17 + 93.73 - [-98.23 + 86.03] = -0.24$ kcal.

$U_{o_{KCl}} + U_{o_{NaBr}} - [U_{o_{KBr}} + U_{o_{NaCl}}]$

$- 164.4 - 171.7 - [-157.8 - 180.4] = +2.1$ kcal.

The crystal energies are those computed by Sherman, for room temperature. The disagreement between the crystal energy relationships and the thermodynamic data amounts to about 2.3 kcals., and can therefore be considered as reasonably good, since the various ions involved are quite dissimilar.

A still more severe test is the following comparison:

ΔH_f^o of KF = -134.46 kcal.

ΔH_f^o of KI = -78.31 kcal.

ΔH_f^o of NaF = -136.0 kcal.

ΔH_f^o of NaI = -68.84 kcal.

$-134.46 + 78.31 - [-67.16 + 68.84] = 11.01$ kcal.

$U_{o_{KF}} + U_{o_{NaI}} - [U_{o_{KI}} + U_{o_{NaF}}] - 190.4 - 160.8 - [-149.0 - 215.0]$

= 12.8 kcal.

Here the disagreement amounts to only 1.7 kcals.

Table 32 compares the differences between ΔH_{hydr} for lanthanum trichloride and one of the other lanthanide or actinide trichlorides with the differences between $U_{o_{LaOCl}} - U_{o_{LaCl_3}}$ and the crystal energies for another lanthanide or actinide oxychloride and trichloride. The Madelung constants for the trichlorides were calculated by the abbreviated summation procedure. Table 33 compares the same differences if the change in Madelung constants from member to member is for the trichlorides considered to be proportional to the axial ratio, c/a.

Table 32

Comparison of Experimentally Determined Heats of Hydrolysis with Results of Crystal Energy Calculations

		Abreviated Trichloride Summation			
Metal	$\Delta H^{o}_{hLaCl_3} - \Delta H^{o}_{hMCl_3}$ Kcal	$U_{oLaOCl} - U_{oLaCl_3}$ Kcal	$U_{oMOCl} - U_{oMCl_3}$ Kcal	Δ Kcal	Diff Kcal
Ce	2.1	432	445	+13	+11
Pr	4.0	"	445	+13	+9
Sm(1 and 2)	6.4	"	444	+12	+6
Gd(1)	7.8	"	454	+22	+14
Gd(2)	7.8	"	450	+18	+10
Pu	4.8	"	449	+17	+12
Am	5.6	"	459	+27	+21
		Average Difference			+12
		Maximum Deviation			9

Table 33

Comparison of Experimentally Determined Heats of Hydrolysis with Results of Crystal Energy Calculations

		α proportional to c/a for the trichlorides			
Metal	$\Delta H^{o}_{hLaCl_3}-\Delta H^{o}_{hMCl_3}$ Kcal	$U_{oLaOCl}-U_{oLaCl_3}$ Kcal	$U_{oMOCl}-U_{oMCl_3}$ Kcal	Δ Kcal	Δ Kcal
Ce	2.1	432	438	+6	+4
Pr	4.0	"	436	+4	0
Sm(1 and 2)	6.4	"	420	-12	-18
Gd (1)	7.8	"	425	-7	-15
Gd (2)	7.8	"	421	-11	-19
Pu	4.8	"	438	+6	+1
Am	5.6	"	447	+15	+9
		Average Difference			-6
		Maximum Deviation			15

From Table 32, it is seen that the discrepancies between the experimentally determined heats and the calculated values for the crystal energies range from 6 to 21 kcals, resulting in a net positive difference of 12 kcals. The largest discrepancy in the crystal energies appears in the difference of the two lanthanum salts. If the difference in crystal energies of the cerium salts was selected as the reference energy, the average difference would correspond to -1 kcal with a maximum deviation of 11 kcal. The values listed in Table 33 show an increasing discrepancy between the reference lanthanum trichloride and lanthanum oxychloride crystal energies and those of a second salt pair in the series between lanthanum and gadolinium. Comparison of Tables 32 and 33 indicate that the actual Madelung constants for the trichlorides may lie between the two sets of values calculated by these simplified procedures.

While the crystal energy differences exceed the experimentally observed changes in the vapor phase hydrolysis of the trichlorides, the differences do not seem unreasonable when one considers that there are uncertainties in the crystallographic data of the order of 0.01 Å for the a and c axes and of nearly 0.1 Å in the u and v parameters of the oxychlorides and in the x and y parameters of the trichlorides. In addition, the choice of equilibrium radii for the metal, oxygen and chloride ions to calculate the repulsive energies for the two structural types has very little foundation and could easily result in considerable error in the individual crystal energies, shown in Tables 30 and 31. However, the crystal energy differences would indicate that error due to these assumed radii used in both systems is not large.

6. <u>Estimation of the Sum of the First Three Ionization Potentials of the Metal Ions</u>.--Since ionization potentials are reported in the literature only for lanthanum and cerium, it is of interest to compute them for some of the lanthanides and actinides from the crystal energy calculations of the oxychlorides and trichlorides. The thermodynamic data required for the calculations were obtained from the National Bureau of Standards Tables. To obtain the experimentally

determined value for the ionization potential of lanthanum trichloride by means of the thermodynamic cycle, it was necessary to add 97 kcals to the crystal energy value listed in Table 31. Therefore, 97 kcals were added to each of the crystal energies calculated for the trichlorides. Using Sherman's value of 168 kcals for the electron affinity of oxygen it was necessary to subtract 5 kcals in order to make the thermodynamic cycle coincide with the U_0 value calculated for lanthanum oxychloride. Consequently 5 kcals were subtracted from each crystal energy of the oxychlorides listed in Table 30. The ionization potentials calculated using these corrections are listed in Table 34. Values from the trichloride crystal energy calculations are listed only from those values assuming that the change in Madelung constant was proportional to the axial ratio, c/a. The ionization potential listed for cerium from these calculations deviates from the value listed in the National Bureau of Standards Tables (909 kcal) by 52 kcals.

Table 34

Calculated Ionization Potentials for Some Lanthanides and Actinides

Metal	From Crystal Energies of Trichlorides Kcal	From Crystal Energies of Oxychlorides Kcal	Ave. Value Kcal
La	840	840	840
Ce	850	864	857
Pr	856	866	861
Sm	886	876	881
Gd	896	887	892
Pu*	959	970	965
Am*	941	959	950

*Heats of vaporization for plutonium and americium are not listed. The values given above represent the heats of formation of the gaseous ions.

The nitrides of lanthanum, cerium, praesodymium, zirconium, chromium and vanadium all have the sodium chloride structure. Using the known ionization potentials of zirconium, chromium and vanadium in addition to the estimated values for lanthanum, cerium and praesodymium, an electron affinity can be estimated for nitride ion. Conventional anion-cation interactions were considered to calculate the repulsive energies for lanthanum, cerium, praesodymium, and zirconium. For chromium and vanadium, anion-anion interactions were the only ones considered. The thermodynamic data were obtained from the National Bureau of Standards Tables and the crystallographic data from Volume I of Wyckoff's "Crystal Structure." The results of the calculations are listed in Table 35.

Table 35

An Estimation of the Electron Affinity of Nitride Ion

Metal Nitride	a_o Å	Repulsive Term	U_o Kcal	$\Delta H_{f_{MN}}$ Kcal	$\Delta H_{f_{M^{+3}}}$ Kcal	$\Delta H_{f_{N^{-3}}}$ Kcal
La	5.275	9.5	1767	-72	928	767
Ce	5.211	9.5	1793	-78	942	773
Pr	5.155	9.5	1813	-84	948	781
Zr	4.61	8.5	1999	-82	1180	737
Cr	4.14	7	2162	-30	1330	802
V	4.129	7	2168	-41	1289	838
			Average value		783 kcal	
			Average deviation		$\pm$24 kcal	

Subtracting the heat of dissociation of nitrogen gas from the average value for the heat of formation of nitride ion, one obtains a value of 697 kcal for the electron affinity of nitride ion.

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