The calculated thermodynamic constants of the reaction are

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

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

Discussion

Within the experimental temperature range, agreement between observed and calculated free energy values is quite good. Close agreement would not be expected to be maintained at temperatures much outside this range, if the assumed ΔC_p relation is substantially in error.

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

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

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

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

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

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

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

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

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

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

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

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

RECEIVED NOVEMBER 21, 1953

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

$PrCl_3$(s): $\Delta F^0_{785} = -2.07$ kcal.; $\Delta H^0_{785} = 21.53$ kcal.; $\Delta S^0_{785} = 30.07$ e.u.
$\Delta F^0_{298} = 13.22$ kcal.; $\Delta H^0_{298} = 22.98$ kcal.; $\Delta S^0_{298} = 32.75$ e.u.
$NdCl_3$(s): $\Delta F^0_{785} = -2.88$ kcal.; $\Delta H^0_{785} = 20.91$ kcal.; $\Delta S^0_{785} = 30.31$ e.u.
$\Delta F^0_{298} = 12.41$ kcal.; $\Delta H^0_{298} = 22.24$ kcal.; $\Delta S^0_{298} = 32.99$ e.u.

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

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

Experimental

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

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

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

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

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

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

(2) The number of units in the nitrogen bubbler train was increased from three to six, of which the first three were of the fritted disk type of one-liter capacity and the last three of the open-tube type of 500-ml. capacity. A seventh 500-ml. bottle, lightly packed with glass wool, served as a spray trap. All of these units, except the first, were contained in the thermostat.

(3) A small mercury manometer was connected to the gas line between the spray trap and reaction chamber to measure the pressure in the chamber relative to atmospheric pressure.

(4) The platinum, platinum–rhodium thermocouple, which previously had been exposed to the gas stream, was enclosed in a thin protective bubble of fused silica, blown at the end of the thermocouple insert tube.

(5) The platinum pan used previously to contain the sample was replaced by a hemispherical pan of fused silica. The silica pan was made from a thin-walled bubble blown from 2-mm. quartz tubing. Changes 4 and 5 were prompted by the observation that corrosion of the platinum pan and thermocouple by condensed hydrochloric acid solution occurred during a period of temporary shutdown, although no corrosion had occurred during weeks of exposure to hot gaseous HCl–H_2O mixtures.

(6) A mercury manometer was attached to the Marriotte bottle so that the gas pressure could be measured directly, relative to atmospheric pressure, rather than calculated from the roughly estimated hydrostatic head.

(7) A Leeds and Northrup galvanometer (Type E, sensitivity 0.0034 μÅ./mm., CDRX 470 Ω) was substituted for the Rubicon instrument used previously. The more sensitive galvanometer permitted fluctuations in reaction chamber temperature of ±0.03° to be detected, and this in turn facilitated the maintenance of a constant temperature during the course of a measurement. It is not implied, of course, that absolute temperatures in the neighborhood of 800°K. were known to ±0.03°.

Gas Analyses.—In previous work the accuracy realized in the analysis of the gas mixture for HCl(g) and H_2O(g) was not regarded as entirely satisfactory, particularly in the case of water, which was present in little more than trace amounts. The increased capacity of the hydrochloric acid reservoir system made it feasible to take much larger samples of gas for analysis, without danger of a significant change in composition during sampling. The volume of gas taken for analysis was therefore increased from about 500 ml. to 2–6 liters. The increased amount of hydrochloric acid required a much larger absorption tube than was used previously. To prevent swelling of the ascarite to the point where gas flow was impaired, the tube packing was made from a mixture of approximately two parts of ascarite to one part of magnesium perchlorate, followed by the conventional quantity of magnesium perchlorate to prevent loss of water from the tube.

TABLE I

ANALYSES FOR WATER VAPOR IN N_2(g) BUBBLED THROUGH VARIOUS AQUEOUS SOLUTIONS

Solution, %	Vol. N_2 collected, l.	Total pressure, mm.	Bath temp., °C.	Partial pressure H_2O, mm. Found	Reported[a]
75.89 H_2SO_4	6	763	23.1	0.352	0.34–0.36
75.89 H_2SO_4	6	765	23.1	0.364	
67.67 H_2SO_4	4	761	23.3	1.485	1.46–1.48
67.67 H_2SO_4	4	760	23.3	1.483	
Water	2	756.4	22.4	20.26	20.34
Water	2	756.4	22.4	20.34	
Water	2	756.1	23.3	20.93	21.47
Water	2	756.2	23.3	21.59	
Water	2	765.9	22.7	20.91	20.97
Water	2	764.2	22.7	20.86	20.93

[a] "International Critical Tables," McGraw–Hill Book Co., Inc., New York, N. Y., 1926.

TABLE II

ANALYSES FOR H_2O(g) AND HCl(g) IN N_2(g) BUBBLED THROUGH 37–38% HYDROCHLORIC ACID SOLUTION

Temp., °C.	Total pressure, mm.	Vol. N_2 collected, l.	Partial pressure, mm. HCl	H_2O
20	760.3	2	188.3	2.764
20	760.2	2	184.1	2.740
20	760.2	2	187.6	2.751
20	760.2	4	187.3	2.759
20	760.3	4	187.7	2.766
		Av.	187.0	2.756
		Mean dev.	±1.2	±0.008

The accuracy of analysis for water vapor was checked on samples of nitrogen which had been bubbled through aqueous solutions of known vapor pressure. These solutions were: distilled water, 75.89% sulfuric acid and 67.67% sulfuric acid. In addition, analyses were made on nitrogen passed through 37–38% hydrochloric acid in order to check the reproducibility of analyses for HCl(g) and H_2O(g) mixed with nitrogen.

The analytical data are summarized in Tables I and II.

The results presented in Tables I and II indicated that errors of analysis on two- to six-liter samples would not exceed one per cent. except for water at a partial pressure below one millimeter.

Materials.—Praseodymium was purchased as "Pr_6O_{11}" from Johnson, Matthey and Co., Ltd., of London, England. This oxide was found to contain about 4% of sodium and potassium and 0.5% of other rare earths, principally neodymium. The oxide was dissolved in hydrochloric acid and further purified by D. C. Stewart and R. C. Lilly of the Radiation Laboratory by elution from a cation-exchange column, using Dowex-50. The separated praseodymium fraction was found to be free of any impurity in excess of 0.01%, according to spectrographic analysis.

The neodymium used was a sample of the oxalate from an unidentified source. Spectrographic analysis detected the following impurities: Fe, 0.01–0.1%, Ca, 0.01–0.1%, Ce, 0.01–0.1% and Sm, 0.01–0.1%.

Results and Discussion

The results of the measurements on $PrCl_3$(s) and $NdCl_3$(s) are summarized in Tables III and IV, respectively.

TABLE III

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}	$\Delta F^0_{expt.}$, kcal.	$\Delta F^0_{calcd.}$, kcal.	Dev., kcal.
1	864.7	169.5	2.830	13.36	−4.44	−4.48	−0.04
		167.1	2.790	13.17			
2	803.3	114.9	3.250	5.345	−2.65	−2.64	+ .01
		117.2	3.485	5.186			
3	760.0	75.67	3.092	2.437	−1.34	−1.33	+ .01
		75.41	3.078	2.431			
4	703.1	41.86	3.063	0.753	+0.44	+0.40	− .04
		39.83	2.934	0.711			
						Av. dev.	± .03

TABLE IV

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}	$\Delta F^0_{expt.}$, kcal.	$\Delta F^0_{calcd.}$, 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	.00
		219.4	2.655	23.86			
3	831.6	187.6	3.026	15.30	−4.50	−4.46	+ .04
		182.8	2.913	15.09			
4	802.1	170.2	4.072	9.360	−3.53	−3.55	− .02
		166.4	4.080	8.930			
5	767.5	108.1	2.969	5.179	−2.50	−2.50	.00
		105.1	2.836	5.125			
6	730.0	82.55	3.502	2.560	−1.35	−1.35	.00
		80.72	3.422	2.505		av. dev.	± .01

Calculated free energy values (in kcal. mole^{-1}) based on the function

$$\Delta F^\circ_T = \Delta H_0 + \frac{6.4T \log T}{1000} + 1.8 \times 10^{-7}T^2 - \frac{22}{T} + \frac{IT}{1000} \quad (1)^5$$

are given for comparison.

Calculated thermodynamic properties of the reactions are summarized in Table V.

TABLE V

THERMODYNAMIC CONSTANTS[a] FOR THE HYDROLYSIS OF $PrCl_3(s)$ AND $NdCl_3(s)$

	Pr	Nd
ΔH°_0, kcal./mole	24.01	23.20
I, cal./mole/deg.	−51.86	−52.10
ΔH°_{298}, kcal./mole	22.98	22.24
ΔH°_{785}, kcal./mole	21.53	20.91
ΔF°_{298}, kcal./mole	13.22	12.41
ΔF°_{785}, kcal./mole	−2.07	−2.88
ΔS°_{298}, kcal./mole/deg.	32.75	32.99
ΔS°_{785}, kcal./mole/deg.	30.07	30.31

[a] The probable errors in the constants at 785°K. are about ±0.3 e.u. for ΔS^0 and ±0.2 kcal. in ΔF^0 and ΔH^0. The low temperature values are less certain, as explained in the text.

The ΔC_p function implicit in equation 1 is the same as that estimated previously[3] for the hydrolysis of $LaCl_3(s)$. In estimating this function we have retained second order terms derived from the accurately known heat capacity functions of $H_2O(g)$ and $HCl(g)$, even though the high temperature heat capacities of the rare earth trichlorides and oxychlorides can be estimated only very roughly.

For each hydrolysis reaction the constants ΔH^0_0 and I were evaluated by the method described in an earlier paper.[4]

As shown by the figures appearing in the last column of Tables III and IV, the derived free energy functions are in very good agreement with the experimental data, the mean deviation amounting to only ±30 cal. for the praseodymium reaction, and ±10 cal. for the neodymium reaction. This improvement in the internal consistency of the data, in comparison with earlier work, is attributed to the refinements of apparatus and technique discussed in the Experimental section of this paper.

As we have emphasized before,[3,4] the agreement between free energies calculated from the derived free energy functions and "observed" values calculated from the experimentally determined equilibrium constants is relatively insensitive to the choice of constants in the assumed ΔC_p relation. For example, free energy equations based on any value between −1 and −3 for the first term of the ΔC_p relation reproduce the experimental data on samarium within about the same mean deviation of ±70 cal.

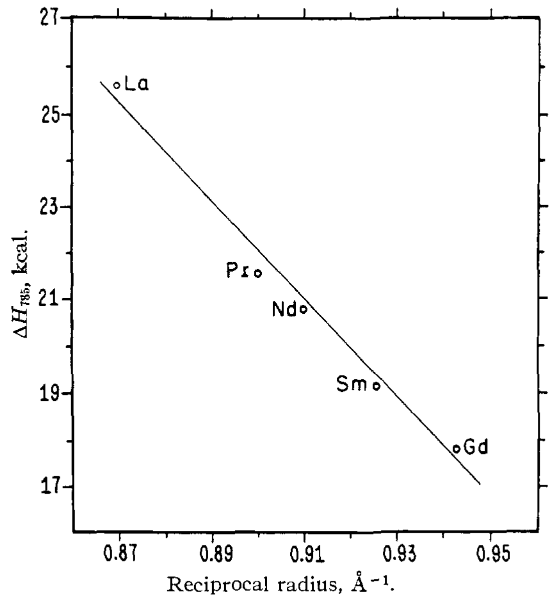

Fig. 1.—Heat of hydrolysis at 785°K. *vs.* reciprocal of cation radius for some rare earth trichlorides.

These various equations give significantly different free energy values at 298°K., however. Thus, for samarium, the calculated free energy at 298°K. is about 600 cal. more positive for a free energy equation based on a ΔC_p of −3 than for one based on a ΔC_p of −1.

However, the more accurate experimental data on neodymium are better represented by assuming $\Delta C_p = -3$ rather than by $\Delta C_p = -1$. For this reason we believe that the uncertainties in our previously calculated free energies at 298°K. are less than the 600 cal. referred to above.

Multiplication of equation 1 by 1000 and differentiation with respect to temperature gives the entropy relation

$$-\Delta S^\circ_T \text{ (cal. mole}^{-1}\text{ deg.}^{-1}) = 2.8\,[1 + \ln T] + 3.6 \times 10^{-4}\,T + \frac{2.2 \times 10^4}{T^2} + I \quad (2)$$

Using the values of I given in Table V and equation 2: $\Delta S^0_{785} = +30.31$ e.u., $\Delta S^0_{298} = +32.99$ e.u for the hydrolysis of neodymium trichloride and $\Delta S^0_{785} = +30.07$ e.u., $\Delta S^0_{298} = 32.75$ e.u. for the praseodymium hydrolysis. The uncertainties in the ΔS^0_{785} are estimated to be about ±0.3 e.u., while the room temperature values may be in error by as much as 2 e.u., if the ΔC_p relation which we have used is grossly in error.

The ΔS^0_{298} values given above, in combination with the known entropies of $H_2O(g)$ and $HCl(g)$ give $S^0NdOCl(s) - S^0NdCl_3(s) = -11.1$ e.u. and $S^0PrOCl(s) - S^0PrCl_3(s) = -11.3$ e.u., in fair agreement with Latimer's[6] rules, which predict an entropy difference of −13.3 e.u. at room temperature. Close agreement with Latimer's rules would have been obtained by using a free energy equation based on a ΔC_p of −0.6, but in view of the approximate nature of the rules this does not seem to be a sufficient reason for altering our heat capacity function.

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(5) The free energy equation published in a previous paper[4] contains two errors. The coefficient of the T^2 term was given incorrectly as 1.8×10^{-6}, and division of the last term by 1000, to make the equation appropriate for ΔF°_T values in kcal. was omitted. The published thermodynamic properties of the lanthanum, samarium and gadolinium hydrolysis reactions were calculated from the correct equation, however, and no error appears in these values.

(6) W. M. Latimer, "Oxidation Potentials," Second Edition, Appendix III, Prentice-Hall, Inc., New York, N. Y., 1952.

The entropies at 785°K. for the two hydrolysis reactions are found to be identical within ±0.12 e.u., as seems reasonable for reactions as closely similar as these, in which the corresponding solids have the same crystal structures, and nearly the same lattice parameters and atomic weights.

Since neither the trichlorides nor the oxychlorides are "magnetically dilute" compounds the magnetic entropy of a trichloride may be somewhat different from the magnetic entropy of the oxychloride of the same rare earth, but these effects probably would not be evident above our experimental errors.

The data presented here are in agreement with the observation reported previously[4] that the heats and free energies of reaction exhibit a steady trend toward more negative values with increasing atomic number of the metal cation.

The assumption that the rare earth trichlorides and oxychlorides are predominantly ionic compounds appears reasonable in view of their known physical and crystallographic properties. It seems plausible therefore to seek for a quantitative explanation of the variation in the heat of reaction in terms of the relative variation in coulombic interaction energy in the two solids as the metal cation undergoes contraction. The examination of our data from this point of view is in progress, and will be presented when the Madelung constant calculations for the solids have been completed.

An interesting empirical correlation, which is not obvious from detailed crystal energy considerations, is presented in Fig. 1, in which the heats of reaction are plotted as a function of the reciprocal of the cation radius. The radii are from Zachariasen[7] and are corrected to coördination number 9. The correlation is seen to be approximated rather closely by a straight line having a slope of ~ -100 kcal. per reciprocal ångström. It is clear, however, that the heats of reaction deviate significantly from the straight line curve. In view of the fact that it is meaningless to assign exact values to the radii of ions no special interpretation of these deviations seems warranted.

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

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[CONTRIBUTION NO. 288 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE][1]

Thermochemistry of the Rare Earths. II. Lanthanum, Praseodymium, Samarium, Gadolinium, Erbium, Ytterbium and Yttrium

BY F. H. SPEDDING AND J. P. FLYNN

RECEIVED AUGUST 3, 1953

The integral heats of solution of the metals and anhydrous chlorides, in hydrochloric acid solutions, and the hydrated chlorides in water, have been measured at 25°. From these data the standard heats of formation of the anhydrous and hydrated chlorides have been calculated. In addition, estimates have been made of the free energies of formation of the same compounds.

Introduction

The values tabulated by the Bureau of Standards[2] for the heats of formation of rare earth compounds are based upon the heat of solution data of Bommer and Hohmann.[3] A recent paper[4] from this Laboratory indicated that the accepted values in the case of cerium and neodymium may be too high by 8 to 10 kcal. Lohr and Cunningham[5] reported values for lanthanum and praseodymium which are also lower than those of Bommer and Hohmann.[3] In each case the heats of formation were calculated from heats of solution. The major contribution to the heat of formation came from the heat of solution of the metal in hydrochloric acid. It is in the latter value that the largest discrepancy occurs. The present paper extends the thermochemical work to include several other members of the rare earth group. Care was taken to use the best materials available for all measurements.

Experimental

The calorimeter and the preparation of the anhydrous chlorides have been described.[6] The hydrated chloride samples were prepared by the method described earlier.[4] The hydrate, $PrCl_3 \cdot 6H_2O$, was prepared by desiccation of powdered $PrCl_3 \cdot 7H_2O$ over calcium chloride. The metals were prepared in tantalum containers by the method described by Spedding and Daane.[7] They were found, by spectrographic analysis, to be free of other rare earths and all common elements. Metal samples were prepared as fine lathe turnings in a dry helium atmosphere. In the case of metal experiments, only one sample was mounted in the calorimeter.

Results

The heats of solution of rare earth metals obtained by other authors are given in Table I and the results of the present investigation in Table II. From these data and the heats of formation in solution of hydrogen chloride given by the National Bureau of Standards,[1] the heats of formation at 25° were calculated by the method set forth in the earlier paper.[4] The heats of reaction of the following reactions were used to calculate the heats of formation of the rare earth chlorides.

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, 1952.

[3] H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **248**, 357 (1941).

[4] F. H. Spedding and Carl F. Miller, THIS JOURNAL, **74**, 4195 (1952).

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

[6] F. H. Spedding and Carl F. Miller, *ibid.*, **74**, 3158 (1952).

[7] F. H. Spedding and A. H. Daane, *ibid.*, **74**, 2783 (1952).