would seem that such a technique would reduce the accuracy of the heat leak corrections; furthermore, potassium dissolved or occluded by the rare earth metals would lead to high results. The presence of varying amounts of oxides in the metals used by the other authors would explain the differences in their results; the lanthanum metal used by Sieverts and Gotta[8] was only 84% pure. The metals used in the present work were prepared by reducing the anhydrous fluorides with calcium; the reductions were made in tantalum containers in an inert atmosphere. Unfortunately, a reliable method for the determination of oxygen in rare earth metals is not presently available. Since precautions were taken to keep oxygen out of the reactant materials and away from the reduction reaction, it is believed the metals contained a minimum of this element. Oxide impurities would produce lower results in the data reported here.

In general, the heats of formation of the rare earth chlorides and ions studied in this work decrease with increasing atomic number of the rare earth. The heat formation of the aqueous praseodymium ion is nearly equal to that of lanthanum, making a sharp break in the plot in Fig. 1. This break is not as sharply manifested when the heats of formation of the chlorides (Fig.1) are considered; the reason for this is that the heat of solution of the anhydrous chloride, which enters into the calculations, is greater for praseodymium chloride than it is for lanthanum chloride. The heats of formation presented here do not agree with those given in the tabulations of the National Bureau of Standards[2] since the values reported there are based upon the heat of solution data of Bommer and Hohmann.[3]

The free energies of formation of the compounds given in Tables III and V are based upon estimates of the entropies of the compounds. These values are subject to revision as more accurate entropy values for the compounds become available.

The plot in Fig. 2 of the heats of solution of the hydrates shows some interesting features of these compounds. Praseodymium chloride forms the most stable seven-hydrate and gadolinium chloride the most stable six-hydrate under ordinary laboratory conditions. There is a regular decrease in ΔH with atomic number in the case of $PrCl_3 \cdot 6H_2O$, $SmCl_3 \cdot 6H_2O$ and $GdCl_3 \cdot 6H_2O$. That $ErCl_3 \cdot 6H_2O$ and $YbCl_3 \cdot 6H_2O$ were observed to have higher heats of solution than expected indicates a possible structural change. Such a change could probably be brought about by changes in packing due to the smaller erbium ion. An X-ray study of the structures of the hydrated chlorides of the rare earths is presently under way at this Laboratory; when completed, the anomalous behavior in the thermal data reported here may be resolved.

Acknowledgments.—The authors wish to thank Mr. A. W. Naumann for his capable assistance in making the measurements and Dr. A. H. Daane, Mr. D. Dennison and Mr. K. Gschneidner for preparing the metals.

AMES, IOWA

[CONTRIBUTION NO. 289 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

Integral Heats of Solution of Some Rare Earth Trichlorides

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

RECEIVED AUGUST 6, 1953

The integral heats of solution of the trichlorides of lanthanum, praseodymium, samarium, gadolinium, erbium, ytterbium and yttrium have been measured in water at 25°. Using the limiting slope given by the Debye–Hückel theory, the data have been extrapolated to infinite dilution.

Introduction

Recent work[2] on the heats of solution of the anhydrous chlorides of cerium and neodymium gave results one to two kcal. per mole higher than those reported elsewhere.[3,4] It therefore seemed advisable to extend the work on the heats of solution of the rare earth trichlorides. The present paper presents the results obtained for the trichlorides of lanthanum, praseodymium, samarium, gadolinium, erbium, ytterbium and yttrium.

Experimental

The source materials were in the form of spectrographically pure oxides. The preparation of the anhydrous chlorides has been described.[5] The apparatus and general experimental procedure were discussed in the paper[2] on cerium and neodymium. However, several changes in the isothermal solution calorimeter were made. The single large tube leading from the calorimeter in the bath to the outside was replaced by a number of small tubes to house the stirrer shaft, electrical leads and breaker assembly. As a result, each element had better thermal contact with the constant temperature bath, and much of the dead air space was eliminated. The calibrating heater was made separately rather than winding it on the same tube as the thermometer coils. A new thermometer was constructed of nickel and manganin rather than the copper manganin used previously. Nickel wire was chosen in place of copper because of its larger temperature coefficient of resistance and its larger specific resistance. The thermometer had a sensitivity of 2×10^{-4} degree per microvolt and was calibrated *versus* a platinum resistance thermometer in the region of 25°. An electronic timer built at this Laboratory was used to measure the total time of electrical energy inputs during calibrations. The frequency of the oscillator used in the timer was calibrated against the Bureau of Standards

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

[2] F. H. Spedding and Carl F. Miller, THIS JOURNAL, **74**, 3158 (1952).

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

[4] C. A. Matignon, *Compt. rend.*, **141**, 53 (1905).

[5] F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2055 (1952).

Station WWV. The performance of the timer was further checked for intervals of time up to 25 minutes by comparing the same intervals given by a calibrated pendulum clock. The timer was found to be reproducible to about 0.005 second in a 25-minute interval. This is somewhat misleading, however, since the uncertainty of the relay system in the clock circuit was estimated to be 0.008 second.

Results

Since there were several changes in the calorimeter, the performance of the apparatus was tested by measuring the heat of solution of potassium nitrate in water, extrapolating the data to infinite dilution, and comparing the results with those of other investigators.[6-11] The unweighted arithmetic average of the L_2's reported by these investigators was found to be 8397 ± 63 cal. per mole. Table I lists the data obtained in this work. A set of three samples was run and each measured value converted to L_2 by adding the corresponding ϕ_L value for the final concentration of the experiment. The results agree within experimental errors with the adiabatic work of Lange and Monheim.[6]

TABLE I

HEATS OF SOLUTION OF POTASSIUM NITRATE AT 25°

m	$m^{1/2}$	ΔH, heat absorbed	ϕ_L	$-L_2$
0.04239	0.2059	8394	10	8384
0.09904	0.3147	8329	−37	8366
0.1588	0.3985	8320	−83	8403
			Av.	8384 ± 12

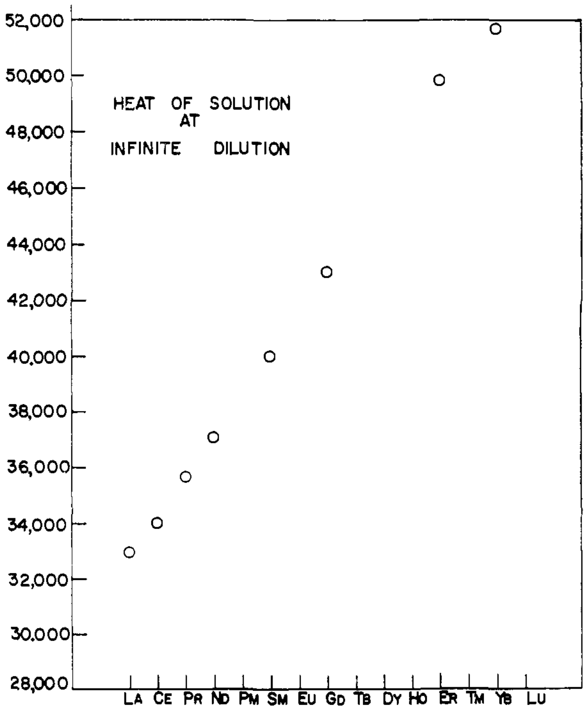

Fig. 1.—Heats of solution at infinite dilution of the rare earth trichlorides in cal./mole.

The data of other investigators on the heats of solution of anhydrous rare earth trichlorides in water are given in Table II.

TABLE II

HEATS OF SOLUTION OF RARE EARTH TRICHLORIDES BY OTHER INVESTIGATORS

Cpd.	Investigators	t, °C.	$-\Delta H$, cal./mole
$LaCl_3$	Bommer and Hohmann[3]	20	31.6 ± 0.05
	Matignon[12a]	17	31.4
$PrCl_3$	Bommer and Hohmann	20	33.9 ± 0.05
	Matignon[12a]	17	33.5
$SmCl_3$	Bommer and Hohmann	20	39.0 ± 0.05
	Matignon[12b]	17	37.4
$GdCl_3$	Bommer and Hohmann	20	42.4 ± 0.05
$ErCl_3$	Bommer and Hohmann	20	49.55 ± 0.05
$YbCl_3$	Bommer and Hohmann	20	50.95 ± 0.05
YCl_3	Bommer and Hohmann	20	52.3 ± 0.05
	Matignon[12a]	17	45.4

The results obtained in the present work are given in Table III. For the heat of solution data, an equation of the general form

$$\Delta H = a + bm^{1/2} + cm \qquad (1)$$

was formulated, by an approximate least squares method, to represent the heat of solution as a function of the molality. The constant, b, was taken as the theoretical limiting slope given by the Debye–Hückel theory for a 3–1 electrolyte. It was believed that the extrapolation to infinite dilution would be more accurate if the limiting slope were used. The procedure is justified to some extent on the basis of work on activity coefficients of rare earth halides at high dilutions.[13,14] This work indicates approach to the limiting laws of the Debye–Hückel theory for these salts. The extrapolated constant, a, is the value of the heat of solution at infinite dilution. Table IV lists the values of the constants in equation 1 for the trichlorides studied in this work.

A few remarks on oxychlorides are in order, since their presence in the original materials or their formation by hydrolysis would lead to low results. Final solutions obtained from rare earth chloride experiments showed no obvious evidences of insolubility and Tyndall light tests indicated the absence of colloidal oxychloride particles. This was not true in the case of yttrium chloride; final solutions showed strong Tyndall effects probably due to the scattering of light by insoluble oxychloride particles. The anhydrous salt was prepared three times and each time the final solutions gave Tyndall cones. To eliminate the Tyndall effect it was found necessary to run the yttrium experiments in solutions made to a pH of about three with hydrochloric acid. Since analyses showed the ratio of yttrium ion to chloride ion to correspond to YCl_3, and since the presence of oxychloride was observable only in the Tyndall effect, it was believed that the oxychloride content was very small and no corrections were attempted. The increase in ionic strength due

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(9) A. Colson, *Compt. rend.*, **161**, 458 (1915).

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(12) (a) C. A. Matignon, *Ann. chim. phys.*, **8**, 402 (1906); (b) *ibid.*, **8**, 426 (1906).

(13) F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2781 (1952).

(14) F. H. Spedding and I. S. Yaffe, *ibid.*, **74**, 4751 (1952).

TABLE III

INTEGRAL HEATS OF SOLUTION OF RARE EARTH TRICHLORIDES IN WATER AT 25°

$LaCl_3$	$m^{1/2}$	0.09287	0.1106	0.1343	0.1640	0.1745	0.2071
	$-\Delta H$	32306	32260	32134	31932	31969	31687
	$m^{1/2}$	0.2085	0.2320	0.2423	0.2596	0.2797	0.2854
	$-\Delta H$	31711	31581	31622	31485	31476	31425
$PrCl_3$	$m^{1/2}$	0.1020	0.1425	0.1544	0.1705	0.1904	0.1976
	$-\Delta H$	35045	34824	34750	34622	34559	34643
	$m^{1/2}$	0.2109	0.2247	0.2490	0.2804	0.3058	
	$-\Delta H$	34455	34433	34290	34166	34129	
$SmCl_3$	$m^{1/2}$	0.07119	0.1154	0.1258	0.1575	0.1775	0.2081
	$-\Delta H$	39490	39270	39204	39030	38981	38859
	$m^{1/2}$	0.2251	0.2518	0.3027			
	$-\Delta H$	38851	38774	38647			
$GdCl_3$	$m^{1/2}$	0.09126	0.1026	0.1041	0.1470	0.1556	0.1696
	$-\Delta H$	42392	42356	42277	42177	41879	41913
	$m^{1/2}$	0.1947	0.1991	0.2198	0.2235	0.2461	
	$-\Delta H$	41830	41780	41694	41623	41546	
$ErCl_3$	$m^{1/2}$	0.09904	0.09964	0.1486	0.1515	0.1895	0.1951
	$-\Delta H$	49138	49270	48960	48914	48794	48773
	$m^{1/2}$	0.2135	0.2384	0.2610			
	$-\Delta H$	48611	48558	48486			
YCl_3	$m^{1/2}$	0.08684	0.09528	0.1020	0.1167	0.1324	0.1459
	$-\Delta H$	48145	48052	48148	47945	47850	47701
	$m^{1/2}$	0.1598	0.1712	0.2114	0.2681	0.2907	
	$-\Delta H$	47678	47645	47502	47270	47073	
$YbCl_3$	$m^{1/2}$	0.1120	0.1191	0.1663	0.1733	0.2149	0.2178
	$-\Delta H$	50922	50880	50691	50537	50529	50427
	$m^{1/2}$	0.2458	0.2693	0.2969			
	$-\Delta H$	50230	50234	50014			

TABLE IV

VALUES OF THE CONSTANTS IN EQUATION 1

Cpd.	a	b	c	Δ^a	Highest molality studied
$LaCl_3$	−32,933	6925	−5640	35	0.08145
$PrCl_3$	−35,672	6925	−5774	21	.09351
$SmCl_3$	−39,932	6925	−8949	15	.09163
$GdCl_3$	−42,992	6925	−4027	39	.06350
$ErCl_3$	−49,792	6925	−7873	40	.06812
$YbCl_3$	−51,638	6925	−5433	40	.08815
YCl_3	−48,690	6925	−5223	40	.08451

[a] Δ is the average deviation in cal./mole of calculated from experimental values,

$$\Delta = \frac{\sum_{i=1}^{n} [\Delta H_i(\text{obsd.}) - \Delta H_i(\text{calcd.})]}{n}$$

to the presence of the hydrochloric acid had a negligibly small effect on the heat of solution values.

Discussion

In general, the data reported here agree reasonably well with those of Bommer and Hohmann[3] and Matignon.[12] The most serious discrepancy arises with yttrium chloride; the value reported here falls midway between the values found by the above authors. On the basis of ionic size, one would predict that yttrium chloride would fall between dysprosium and holmium in the rare earth group. The unusually high value of Bommer and Hohmann[3] cannot be explained. The plot in Fig. 1 of the heats of solution at infinite dilution indicates a linear relationship from lanthanum through gadolinium. The values for cerium and neodymium chlorides obtained by Spedding and Miller[2] were drawn in for comparison. The size of the circles represents average experimental errors.

Bommer and Hohmann[3] reported the trichlorides to exist in alpha, beta and gamma forms, but did not give further information concerning the structures. From their work, the chlorides of lanthanum through gadolinium have the alpha form, terbium chloride the beta form, and the remaining members of the series and yttrium chloride, the gamma form. Zachariasen[15] reported the chlorides of lanthanum, cerium, praseodymium and neodymium as iso-structural having hexagonal type lattices; the crystal system of cerium chloride was confirmed by Kojima, *et al.*[16] Recently, Carter[17] identified the gamma form as monoclinic by working out the crystal structure of yttrium chloride in detail using single crystals. By comparing X-ray powder diffraction patterns of the trichlorides of dysprosium through lutetium with a powder diagram of yttrium chloride, Carter showed these chlorides to be iso-structural. The lattice constants of dysprosium, holmium, erbium and thulium chlorides decrease almost linearly with increasing atomic number in accordance with the lanthanide contraction. Marked expansions of the *a*- and *c*-axes of ytterbium and lutetium chlorides were observed while the *b*-axis continued to shrink as expected. Although powder diagrams of the chlorides used in the present work are not yet available, it is believed that their structures should be identical with those studied by the aforementioned au-

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(15) W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).

(16) T. Kojima, T. Inoue and T. Ishiyama, *J. Electrochem. Soc., Japan*, **19**, 383 (1951).

(17) G. F. Carter, United States Atomic Energy Commission, UCRL-1908 (1952).

thors. The crystallographic observations are in qualitative agreement with the heat of solution data presented here. Thus, one would predict a regular relationship from lanthanum through gadolinium since these chlorides are iso-structural. Erbium and ytterbium chlorides would not be expected to fall on a line with the lighter rare earths because of the change from hexagonal to monoclinic structures. That ytterbium chloride breaks back sharply toward the straight line through the light rare earths is in qualitative agreement with the sudden change in volume of the unit cell observed by Carter.[17]

The total hydration energy of the chloride ion at infinite dilution is the same for the series of compounds studied in this work. For this reason, the differences in the heats of solution of the anhydrous chlorides at infinite dilution are a measure of the differences in lattice energies of the crystals and total hydration energies of the cations. On the basis of the lanthanide contraction, one would predict that the lattice energy would increase positively for the seven hexagonal rare earth chlorides. Since the heats of solution increase negatively for the same group, it is seen that the differences in total hydration energies are greater than the differences in lattice energies. The same observation is true in the case of erbium and ytterbium. A quantitative measure of these differences will be possible once the lattice energies have been calculated.

Acknowledgments.—The authors wish to thank Mr. A. W. Naumann for his capable assistance in making the calorimetric measurements and preparing the anhydrous chlorides, and Dr. J. Powell and J. L. Evans for furnishing the pure rare earth oxides.

AMES, IOWA

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High Temperature Heat Contents of Calcium and Magnesium Ferrites

BY K. R. BONNICKSON

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High temperature heat content measurements of two calcium ferrites ($CaFe_2O_4$ and $Ca_2Fe_2O_5$) and magnesium ferrite ($MgFe_2O_4$) were conducted throughout the temperature range 298–1850°K. The heat of fusion of $CaFe_2O_4$ was determined as 25,870 cal./mole at 1510°K., and that of $Ca_2Fe_2O_5$ as 36,110 cal./mole at 1750°K. The compound $MgFe_2O_4$ has two transformations in the crystalline state—a heat capacity peak at 665°K. and an isothermal transformation at 1230°K. involving a heat absorption of 350 cal./mole.

Interoxidic compounds of the commoner metals have not been studied extensively by thermodynamic means, and in many instances thermodynamic data are entirely lacking. This paper presents the results of high temperature heat content measurements in the range 298–1850°K. for two calcium–iron–oxygen compounds ($CaFe_2O_4$ and $Ca_2Fe_2O_5$) and one magnesium–iron–oxygen compound ($MgFe_2O_4$). No previous, similar data exist for any of these substances.

Materials

The compound $CaFe_2O_4$[1] was prepared from reagent grade ferric oxide and calcium carbonate. A stoichiometric mixture was repeatedly heated, for several hours each time, at temperatures between 1000 and 1210°. The material was ground, mixed and analyzed, and the composition adjusted as necessary between heats. The final product contained 74.05% ferric oxide and 26.05% calcium oxide, as compared with the theoretical 74.01 and 25.99%. The X-Ray diffraction pattern agreed with that in the A.S.T.M. catalog.

The compound $Ca_2Fe_2O_5$[2] also was prepared from reagent grade ferric oxide and calcium carbonate. A stoichiometric mixture was formed into pellets and heated repeatedly, for several hours each time, at temperatures between 850 and 1230°. Between heats, the substance was ground, mixed, analyzed, composition adjusted, and repelletized. The final product contained 58.71% ferric oxide and 41.27% calcium oxide, as compared with the theoretical 58.74 and 41.26%. The X-ray diffraction pattern agreed with the A.S.T.M. catalog.

The compound $MgFe_2O_4$[1] was prepared from reagent grade ferric oxide and magnesia. A stoichiometric mixture, in pellet form, was heated repeatedly for periods of several hours in the temperature range 900 to 1,300°, the treatment between heats being the same as for the calcium compounds. The final product contained 79.74% ferric oxide, 20.22% magnesia and 0.14% silica. (Theoretical contents of ferric oxide and magnesia are 79.84 and 20.16%.) The X-ray diffraction pattern agreed with the A.S.T.M. catalog.

Measurements and Results

Previously described apparatus and methods[3] were used in the high temperature heat content measurements. The samples were enclosed in platinum–rhodium capsules during the measurements, the heat contents of the capsules having been determined by separate experiments. The furnace thermocouple was calibrated frequently against the melting point of pure gold. The results are expressed in defined calories (1 cal. = 4.1840 abs. joules) per mole. Molecular weights accord with the 1951 International Atomic Weights,[4] and all weighings were reduced to vacuum. The experimental heat content results are listed in Table I and plotted in Fig. 1.

According to the existing phase diagram for the $CaO–Fe_2O_3$ system,[5] the compound $CaFe_2O_4$ melts incongruently over a range of temperature. There is some evidence in the present results of beginning

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(1) This substance was prepared and analyzed by R. E. Lorenson, Minerals Thermodynamics Branch, Bureau of Mines.

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(3) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

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