0.5% above 3 mol kg^{-1}. If more reliable standard data become available for H_2SO_4 at high concentrations, a corresponding improvement will occur in the $CaCl_2$ osmotic coefficients. It should be noted that the data reported here exhibit less scatter than Stokes' results, especially below 7.0 mol kg^{-1}. This presumably occurs because of the longer equilibration times used by us. The osmotic coefficients from this research also agree reasonably well with those from other sources below 3 mol kg^{-1}.

Acknowledgment

The authors thank Herman O. Weber for preparing and analyzing the $CaCl_2$ stock solution and Tony Habenschuss for preparing the conductivity water.

Literature Cited

(1) Rard, J. A., Habenschuss, A., Spedding, F. H., *J. Chem. Eng. Data,* **21,** 374 (1976).
(2) Rard, J. A., Habenschuss, A., Spedding, F. H., *J. Chem. Eng. Data,* submitted.
(3) Spedding, F. H., Weber, H. O., Saeger, V. W., Petheram, H. H., Rard, J. A., Habenschuss, A., *J. Chem. Eng. Data,* **21,** 341 (1976).
(4) Stokes, R. H., *Trans. Faraday Soc.,* **41,** 637 (1945).

Received for review April 30, 1976. Accepted August 13, 1976. This work was performed for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

Heats of Dilution of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 3. Rare Earth Chlorides

Frank H. Spedding,* Carroll W. DeKock, George W. Pepple, and Anton Habenschuss
Ames Laboratory-ERDA and Department of Chemistry, Iowa State University, Ames, Iowa 50011

The heats of dilution of aqueous $LaCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $EuCl_3$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$, $YbCl_3$, and $LuCl_3$ solutions have been measured up to saturation at 25 °C. The integral heats of solution of $LaCl_3 \cdot 7H_2O$, $PrCl_3 \cdot 7H_2O$, $NdCl_3 \cdot 6H_2O$, $SmCl_3 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$, $GdCl_3 \cdot 6H_2O$, $TbCl_3 \cdot 6H_2O$, $DyCl_3 \cdot 6H_2O$, $HoCl_3 \cdot 6H_2O$, $ErCl_3 \cdot 6H_2O$, $TmCl_3 \cdot 6H_2O$, $YbCl_3 \cdot 6H_2O$, and $LuCl_3 \cdot 6H_2O$ in water at 25 °C have also been measured. The heat of dilution data are represented by empirical equations, and relative partial molal heat contents are calculated. The heat content trends across the rare earth chloride series are similar to the trends found for the rare earth perchlorate heat data, and can be correlated with a change in the inner sphere cation water coordination across the rare earth cation series.

The heats of dilution of aqueous rare earth chloride solutions up to 0.2 m have been reported (*28, 32*). These dilute data for the chlorides were shown to conform to the Debye-Hückel limiting law, and the heat content trends across the rare earth chloride series showed the two series effect attributed to a change in the inner sphere water coordination of the rare earth cations between Nd and Tb (*28*).

Recently, we have extended many of the dilute thermodynamic and transport measurements to higher concentrations (*13, 23, 27, 36, 37*) where short range ion-ion interactions become important. The heats of dilution reported for the rare earth perchlorates (*31*) up to saturation show that the two-series effect across the rare earth perchlorate series persists to high concentrations virtually unchanged. In contrast, although the two-series effect is observable in very dilute nitrate solutions, the heats of dilution for the rare earth nitrates outside this region were found to be correlated with the available stability constants of the rare earth nitrate complexes (*30*). In this report we present the heats of dilution measurements for the rare earth chlorides up to saturation, and compare these to the results of the perchlorate and nitrate studies.

Experimental Section

The apparatus, an adiabatically jacketed differential calorimeter similar to that of Gucker, Pickard, and Planck (*12*), was the same one used for the rare earth perchlorate (*31*) and nitrate (*30*) experiments and has been previously described (*28, 32*). The calorimeter was operated at a sensitivity of about 4×10^{-4} cal/mm chart displacement. The accuracy of the calorimeter has been established and was monitored throughout the present experiments by measuring the heat of neutralization of HCl by NaOH. From a total of ten measurements at 25.00 ± 0.02° we obtained $\Delta H^{\circ} = -13.334 \pm 0.018$ kcal mol^{-1} for the heat of neutralization corrected to infinite dilution. This is in good agreement with -13.34 kcal mol^{-1} recommended by Hepler and Woolley (*14*).

The stock solutions were prepared from the rare earth oxides and C.P. grade HCl. The oxides were purified by ion exchange methods by the Rare Earth Separation Group of the Ames Laboratory. The pH of the stock solutions was adjusted to guarantee a 1:3 ratio of rare earth to chloride ions. All secondary solutions were prepared by weight from the stock solutions and conductivity water with a specific conductance of less than 1×10^{-6} mho cm^{-1}, all weights being converted to mass. The stock, saturated, and some of the secondary solutions were analyzed by gravimetric oxide (*33*), sulfate (*33*), and/or EDTA (*29*) for the rare earth content and by a potentiometric $AgNO_3$ (*33*) method for the chloride content. The agreement between the anion and cation analyses was within 0.1%, showing that the stoichiometry was 1:3 for the rare earth to chloride ratio. The analyses indicated that the concentrations were known to better than ±0.1% in terms of the molality.

Hydrated crystals of the rare earth chlorides were grown from saturated solutions at 25.00 °C and were dried over $BaCl_2$ or $CaCl_2$. The ratio of rare earth chloride to number of water molecules was determined by EDTA titrations. $LaCl_3$ and $PrCl_3$ crystallized as the heptahydrate, while the rest crystallized as the hexahydrates, all within ±0.1% of the theoretical water content.

The experimental procedure for the heats of dilution and heats of solution measurements was similar to that employed for the rare earth perchlorate (*31*) and rare earth nitrate (*30*) experiments and is fully described elsewhere (*28, 32*). One or two samples of rare earth chloride solution were diluted into about 900 g of water. Diluting the first sample of initial molality m_1, containing n' moles of rare earth chloride, into the water giving a final concentration of m_2, evolves a quantity of heat q'. Diluting a second sample of the same initial concentration m_1, containing n'' moles of rare earth chloride, into the solution of molality m_2, resulting from the first dilution, to give a final concentration of m_3, evolves a quantity of heat q''. The integral heats of dilution, $\Delta H_{i,f}$, and the relative apparent molal heat content, ϕ_L, are related to the heats evolved, q' and q'', by

$$\Delta H_{1,2} = \phi_L(m_2) - \phi_L(m_1) = q'/n' \quad (1)$$

$$\Delta H_{1,3} = \phi_L(m_3) - \phi_L(m_1) = (q' + q'')/(n' + n'') \quad (2)$$

For samples with dilute initial concentrations, only the first dilution was made, eq 1, since the size of the sample bulb precluded a second dilution.

Similarly, dissolving two samples of the rare earth hydrate successively we obtain for the integral heats of solution, $\Delta H_{x,f}$,

$$\Delta H_{x,2} = \phi_L(m_2) - \bar{L}^{\cdot} = q'/n' \quad (3)$$

$$\Delta H_{x,3} = \phi_L(m_3) - \bar{L}^{\cdot} = (q' + q'')/(n' + n'') \quad (4)$$

where $\bar{L}^{\cdot}$ is the molal enthalpy of the hydrate relative to infinite dilution, and the $\phi_L(m_f)$ in eq 3 and 4 are obtained from the heat of dilution experiments. The heats evolved, q' and q'', were corrected for the change in vapor pressure over the solutions in the sample bulbs, the heat of breaking the glass sample bulbs, and for variation of the ratio of the heat capacities of the two calorimeter containers and their contents. The defined thermochemical calorie, 4.1840 absolute J, was used throughout this work. All measurements refer to 25.00 ± 0.02 °C.

Calculations and Results

The experimental heats of dilution and solution are given in Tables I and II, respectively. For those groups of dilutions having the same initial concentration, m_i, the initial concentration is listed only once. The first set of entries for each salt refers to the saturated solution. The samples with an asterisk in Tables I and II, referring to eq 2 and 4, were diluted into the solution resulting from the dilution of the immediately preceding sample, which refers to eq 1 and 3.

The heats of dilution $\Delta H_{1,2}$ and $\Delta H_{1,3}$, the "long chords", were used to obtain the "short chords", $\Delta H_{3,2}$,

$$\Delta H_{3,2} = \Delta H_{1,2} - \Delta H_{1,3} = \phi_L(m_2) - \phi_L(m_3) \quad (5)$$

For these short chords, m_2 is considered the final, and m_3 the initial concentration of the dilution. The $\Delta H_{3,2}$ values are listed in Table I immediately following the $\Delta H_{1,2}$ and $\Delta H_{1,3}$ data. For $LaCl_3$ the initial concentrations of the two-break runs were not the same and no $\Delta H_{3,2}$ values could be calculated. For $HoCl_3$ only one two-break run was made. However, except for $EuCl_3$ and $LuCl_3$, heat of dilution data up to 0.2 m are available from previous work in this laboratory (*28, 32*). These previous data were added to the presently reported ΔH values for fitting purposes. For the combined data sets the lowest final concentrations ranged from 0.0001 to 0.001 m. Some of the dilutions for $LaCl_3$ were made with very dilute HCl (pH 4.4) to check if appreciable hydrolysis occurs in rare earth chloride solutions. The results for $LaCl_3$ in Table I indicate that the heats of dilution are insensitive to slight variation in pH due to the addition of very small amounts of HCl, showing that the heat contribuion from hydrolysis under these conditions is negligible.

As was the case for the rare earth perchlorates (*31*) and the rare earth nitrates (*30*) the heats of dilution for the rare earth chlorides were successfully fitted directly to a power series in multiples of $m^{1/4}$ over the whole concentration range,

$$\Delta H_{i,f} = \sum_{j=1}^{6} A_j(m_f^{p_j} - m_i^{p_j}) \quad (6)$$

which can be used to calculate ϕ_L by setting $m_i = 0$ and letting m_f be any concentration desired (since $\Delta\phi_L = -\Delta H$)

$$\phi_L = \sum_{j=1}^{6} A_j m^{p_j} \quad (7)$$

As before, the first term is $A_1 = 6990$ (7) with $p_1 = 1/2$, the Debye–Hückel limiting law constraint. In contrast to the perchlorates and nitrates, only five empirical terms were necessary to fit the chlorides adequately. The coefficients A_j and powers p_j to be used with eq 6 and 7 are given in Table III. The differences between the calculated and experimental ΔH values are listed in the fourth column in Table I, and are plotted for $TbCl_3$ in Figure 1, which is typical of the other salts. The dilute range for $TbCl_3$ is illustrated in Figure 2 on a $\bar{P}_l$ plot. The criteria for the choice of powers in the least-squares fits were the same as given in the perchlorate work (*31*).

The relative partial molal heat contents of the solute, $\bar{L}_2$, and the solvent, $\bar{L}_1$, were calculated from

$$\bar{L}_2 = \phi_L + m\left(\frac{\partial \phi_L}{\partial m}\right)_{T,P,n_1} \quad (8)$$

$$\bar{L}_1 = -\frac{M_1 m^2}{1000}\left(\frac{\partial \phi_L}{\partial m}\right)_{T,P,n_1} \quad (9)$$

where M_1 is the molecular weight of water, 18.0154 g mol^{-1}. The results for ϕ_L, $\bar{L}_2$, and $\bar{L}_1$ calculated from eq 7, 8, and 9 are illustrated in Figures 3–7, and are given in Table IV. The ϕ_L, $\bar{L}_2$, and $\bar{L}_1$ for the rare earth nitrates and perchlorates at even concentrations are given in Tables V and VI. Tables IV, V, and VI are available from the ACS Microfilm Depository Service; see paragraph at end of paper regarding supplementary material.

The heats of solution to infinite dilution for the rare earth chloride hydrates, $-\bar{L}^{\cdot}$, were calculated from eq 3 and 4 with $\Delta H_{x,f}$ and $\phi_L(m_f)$ taken from Table II. $\phi_L(m_f)$ was calculated from eq 7. The $\bar{L}^{\cdot}$ are listed in Table II. The standard heats of solution for $EuCl_3 \cdot 6H_2O$ and $LuCl_3 \cdot 6H_2O$, reported by Hinchey and Cobble (*15*) are −8770 ± 30 and −11 910 ± 20 cal mol^{-1}, respectively. These are in reasonable agreement with −8714 and −11 860 cal mol^{-1} reported in Table II for these two hydrates.

The standard deviations, σ, expected for the ΔH values are listed in column five in Table I and are discussed in the perchlorate paper (*31*). The weighting factors in the least-squares fits were taken as $1/\sigma^2$. The standard deviations in the fits ranged from 4.5 to 10 cal. The main cause of the slightly larger deviations in the chloride fits as compared to the perchlorate and nitrate fits is due to small mismatches between the data reported here and the previous dilute measurements that were included in the fits. The random and systematic errors in ϕ_L, $\bar{L}_2$, and $\bar{L}_1$ are similar to those reported and discussed in the perchlorate measurements (*31*).

Discussion

The heats of dilution for 11 rare earth chloride solutions in the dilute concentration range have been discussed by Spedding, Csejka, and DeKock (*28*). The present measurements extend these data to saturation and also give the results for $EuCl_3$ and $LuCl_3$. Analysis of the combined data shows that all of the rare earth chlorides conform to the Debye–Hückel limiting law in dilute solutions, within experimental error, as judged by $\bar{P}_l$ plots.

The ϕ_L curves for $LaCl_3$, $SmCl_3$, and $LuCl_3$ are compared to the ϕ_L curves of the respective nitrates (*30*) and perchlorates (*31*) in Figures 3–5. The chloride curves remain above the perchlorates and nitrates throughout the concentration range. The pronounced inflection points in the perchlorates are much smaller in the chlorides. These relative shapes of the chloride and perchlorate ϕ_L curves also appear in the divalent alkaline earth chlorides and perchlorates, particularly with respect to the severity of the inflection points (*43*).

Table I. Heats of Dilution of Some Aqueous Rare Earth Chloride Solutions at 25 °C

m_i	$10^4 m_f$	$-\Delta H_{i,f}$, cal mol^{-1}	Exptl − calcd (cal mol^{-1})	σ, cal mol^{-1}
Lanthanum Chloride				
3.896[a]	18.490	—	—	—
3.600[a]	9.897	6768.8	−0.4	4.6
3.290[a]	10.491	6135.6	−5.1	4.5
3.600[a]	25.040*[b]	6671.0	7.1	8.0
3.290	12.773	6117.9	−3.2	4.5
3.896	22.212*	7278.0	0.9	5.9
2.565	19.963	4694.8	9.9	5.4
2.832	37.418*	5098.0	7.5	7.5
2.565[a]	18.387	4700.1	5.1	5.4
2.832[a]	36.301*	5103.0	7.8	8.1
1.975	19.874	3686.6	1.1	4.4
2.252	38.477*	4038.0	−7.4	6.2
1.975[a]	19.874	3685.8	0.2	4.2
2.252[a]	38.477*	4038.0	−7.4	6.0
1.411	22.515	2839.2	1.7	4.1
1.693	48.832*	3111.0	−11.8	6.6
1.209	30.492	2529.7	7.4	4.8
1.693	59.352*	3086.0	−2.2	7.1
1.411	27.900	2804.2	−4.2	5.4
1.209	27.689	2531.1	−5.0	4.8
1.008	32.844	2244.5	−3.0	5.1
0.8102	34.199	1984.4	−0.7	4.7
0.6469	38.713	1759.7	8.0	4.7
0.4038	47.748	1392.1	13.3	4.6
Praseodymium Chloride				
3.891	11.256	7271.9	−5.2	5.2
	24.900*	7187.3	−0.0	8.0
	9.505	—	—	—
	21.188*	7207.9	0.0	6.9
3.475	9.872	6360.3	4.4	4.0
	21.734*	6279.1	7.8	6.1
3.095	14.145	5524.1	−1.4	4.7
	29.236*	5432.3	−4.8	6.8
2.871	14.822	5080.6	−0.4	4.5
	30.625*	4986.8	−4.3	6.5
2.479	17.389	—	—	—
	35.892*	4259.0	4.7	6.5
	18.801	4329.6	−10.9	4.9
	39.213*	4240.6	−0.2	7.1
2.232	19.492	3931.1	7.4	4.6
	39.740*	3829.8	3.7	6.4
1.931	20.259	3452.7	−1.4	4.2
	41.371*	3356.8	1.9	5.9
1.718	27.019	3113.9	2.0	4.9
	54.435*	3002.5	−1.8	6.8
1.433	25.543	2733.4	−4.4	4.1
	51.395*	2627.9	−4.6	5.6
1.198	31.326	2416.5	2.9	4.4
	63.696*	2299.5	0.7	6.1
0.9880	34.445	2146.7	2.4	4.4
	72.029*	2021.5	1.1	6.1
	32.673	2149.5	−2.5	4.8
0.8110	43.020	1898.5	1.9	5.6
0.6240	46.335	1656.9	2.4	5.3
0.5182	49.886	1514.1	8.0	5.2
0.3671	40.297	1335.3	5.1	3.8
0.002 490[c]	11.256	84.6	−5.2	9.5
0.002 173	9.872	81.2	−3.4	7.3
0.002 924	14.145	91.8	3.3	8.3
0.003 063	14.822	93.8	3.9	7.9
0.003 589	17.389	61.4	−34.0	8.0
0.003 921	18.801	89.0	−10.8	8.7
0.003 974	19.492	101.3	3.7	7.9
0.004 137	20.259	95.9	−3.3	7.2
0.005 443	27.019	111.4	3.8	8.4
0.005 139	25.543	105.5	0.2	6.9
0.006 370	31.326	117.0	2.2	7.5
0.007 203	34.445	125.1	1.3	7.5
Neodymium Chloride				
3.929	10.916	7272.2	9.2	4.9
	23.542*	7179.1	−0.3	7.4
	10.949	—	—	—
	22.677*	7181.7	−2.4	7.0
3.590	10.323	6488.2	−4.0	4.1
	21.437*	6415.3	0.2	5.9
	10.049	6480.7	−14.0	4.2
	22.562*	6400.0	−8.8	6.6
	9.722	6505.7	8.1	3.8
	19.563*	6429.1	3.1	5.3
3.250	12.852	5744.6	−5.3	4.4
	26.255*	5661.8	−6.2	6.3
	13.162	5754.2	6.6	4.5
	26.307*	5669.8	2.0	6.2
2.897	14.266	5055.2	5.6	4.4
	29.648*	4966.0	3.9	6.3
	14.018	5056.0	4.5	4.3
	29.171*	4962.1	−2.2	6.2
2.552	15.461	4414.3	−9.6	4.1
	31.438*	4326.2	−10.5	5.8
	15.761	4417.8	−4.1	4.1
	31.764*	4332.1	−3.2	5.8
	13.891	4440.7	5.6	3.7
	27.984*	4353.5	0.9	5.1
2.257	15.856	3940.3	4.1	3.8
	32.524*	3845.8	−1.2	5.3
	16.540	3929.2	−2.5	4.5
1.948	15.587	3478.8	8.8	3.3
	32.104*	3383.2	2.4	4.6
	16.492	3468.6	4.7	3.4
	33.178*	3375.4	−0.8	4.7
1.702	17.606	3108.4	−2.5	3.3
	36.168*	3011.2	−6.6	4.6
	17.556	3110.6	−0.6	3.8
1.455	20.766	2768.6	2.8	3.4
	41.551*	2670.3	−0.8	4.6
	20.052	2771.5	1.6	3.3
	40.322*	2672.5	−3.1	4.5
1.221	22.582	2465.5	2.4	3.3
	45.522*	2362.4	−1.9	4.5
	22.572	2460.1	−3.1	3.3
	45.118*	2358.9	−6.9	4.4
1.006	28.676	2171.9	−1.7	3.6
	57.578*	2061.9	−5.0	4.9
	29.095	2167.5	−4.2	3.7
	58.415*	2057.5	−6.8	5.0
0.8008	33.155	1914.3	3.7	4.4
0.6407	33.686	1720.7	4.5	3.4
	71.200*	1592.6	−1.5	4.8
	40.666	1694.1	5.8	3.8
	79.139*	1571.7	−2.6	5.0
0.4927	52.172	1463.6	1.3	5.3
	47.142	1480.8	1.9	4.8
0.3597	50.410	1283.3	−0.8	4.5
	53.714	1275.1	1.5	4.7
0.2532	43.139	1137.5	0.1	3.4
0.1726	27.605	1038.4	−2.2	2.1
	32.948	1014.8	−1.5	2.4
0.09959	19.501	878.1	−4.6	1.3
0.05293	12.131	732.2	1.7	2.8
0.002 354[c]	10.916	93.0	9.4	8.9
0.002 144	10.323	73.0	−4.2	7.2
0.002 256	10.049	80.7	−5.2	7.8
0.001 956	9.722	76.6	5.0	6.5
0.002 626	12.852	82.8	0.9	7.7
0.002 631	13.162	84.3	4.6	7.7
0.002 965	14.266	89.3	1.7	7.7
0.002 917	14.018	93.9	6.7	7.5
0.003 144	15.461	88.1	0.9	7.1

Table I. Continued

m_i	$10^4 m_f$	$-\Delta H_{i,f}$, cal mol^{-1}	Exptl − calcd (cal mol^{-1})	σ, cal mol^{-1}
0.003 176	15.761	85.7	−0.9	7.1
0.002 798	13.891	87.2	4.7	6.3
0.003 252	15.856	94.5	5.2	6.5
0.003 210	15.587	95.6	6.4	5.7
0.003 318	16.492	93.2	5.4	5.8
0.003 617	17.606	97.1	4.1	5.7
0.004 155	20.766	98.3	3.6	5.7
0.004 032	20.052	99.0	4.7	5.6
0.004 552	22.582	103.1	4.3	5.6
0.004 512	22.572	101.3	3.8	5.5
0.005 758	28.676	110.0	3.2	6.1
0.005 842	29.095	109.9	2.7	6.2
0.007 120	33.686	128.1	6.0	5.9
0.007 914	40.666	122.4	8.4	6.3
Samarium Chloride				
3.641	9.672	6922.1	2.1	4.1
	19.963*	6844.6	0.3	5.9
	8.317	—	—	—
	18.284*	6855.8	1.1	5.6
3.507	9.505	—	—	—
	19.519*	6568.0	6.3	5.5
	9.096	6637.4	−2.8	4.2
	9.660	—	—	—
	19.430*	6568.5	6.2	5.4
3.179	10.131	5943.3	−5.3	4.2
	10.452	5941.7	−4.1	3.7
	21.354*	5859.7	−9.3	5.3
2.865	11.162	5319.6	3.4	3.6
	22.868*	5238.3	1.3	5.1
2.523	12.781	4662.5	−2.8	3.6
	25.959*	4580.7	−2.3	5.0
2.116	15.618	—	—	—
	32.070*	3858.6	−0.7	5.3
	15.595	3955.5	5.5	3.7
	31.528*	3864.6	2.9	5.1
1.945	16.492	3682.0	8.2	3.6
	33.628*	3587.3	4.9	5.1
1.666	19.536	3240.6	0.4	3.8
	40.373*	3133.5	−7.5	5.4
	19.395	—	—	—
	39.038*	3144.1	−2.0	5.1
1.437	21.548	2911.7	1.0	4.3
	21.492	—	—	—
	43.626*	2808.4	−2.7	5.1
1.137	25.685	2494.4	−0.5	3.8
	51.797*	2382.9	−6.6	5.2
	25.543	2495.3	−0.3	3.7
	51.552*	2384.6	−5.7	5.1
1.063	26.812	2389.2	−5.4	3.7
	53.802*	2279.8	−8.8	5.1
	26.214	2397.0	−0.6	3.7
	52.621*	2288.1	−4.2	5.0
0.8527	30.947	2109.4	2.4	3.8
	61.701*	1998.1	1.4	5.1
	31.573	2112.6	8.4	3.9
	65.109*	1996.3	9.3	5.4
0.6702	38.094	1834.6	−4.1	4.0
	77.036*	1709.4	−8.4	5.4
	40.170	1826.7	−3.9	4.2
	80.856*	1705.0	−3.4	5.6
0.5158	33.536	1647.2	2.7	3.2
	69.572*	1522.6	−1.2	4.4
	33.028	1650.8	4.2	3.1
	66.048*	1533.5	0.1	4.2
0.3604	51.768	1339.9	1.9	4.8
0.2687	44.890	1204.6	5.0	3.8
	46.036	1203.0	7.5	3.9
0.1596	32.661	1019.9	9.5	2.4
	28.260	1038.6	7.9	2.2
0.09711	27.269	858.6	11.4	1.7
0.001 996^c	9.672	77.5	1.8	7.2
0.002 135	10.452	82.0	5.2	6.5
0.002 287	11.162	81.3	2.1	6.3
0.002 596	12.781	81.9	−0.5	6.2
0.003 153	15.595	90.8	2.6	6.3
0.003 363	16.492	94.6	3.3	6.3
0.004 037	19.536	107.2	7.9	6.6
0.005 180	25.685	111.4	6.1	6.4
0.005 155	25.543	110.7	5.4	6.3
0.005 380	26.812	109.4	3.4	6.3
0.005 262	26.214	108.9	3.6	6.2
0.006 170	30.947	111.3	1.0	6.3
0.006 511	31.573	116.3	−0.8	6.7
0.007 704	38.094	125.1	4.2	6.7
0.008 086	40.170	121.6	−0.5	7.0
0.006 957	33.536	124.5	3.9	5.5
0.006 605	33.028	117.3	4.1	5.2
Europium Chloride				
3.587	10.266	7083.1	−4.4	4.4
	20.757*	7004.4	−7.1	6.2
	10.963	7084.4	3.2	4.6
	22.241*	7000.0	−2.7	6.6
3.066	9.102	6016.1	8.2	3.4
	18.922*	5943.4	11.3	4.9
	9.163	6013.4	6.1	3.8
2.889	12.348	5615.5	−10.2	4.0
	23.922*	5538.6	−10.9	5.5
2.573	14.033	5004.3	−3.4	4.2
	28.069*	4916.4	−6.8	5.8
2.147	13.344	4258.7	3.6	3.4
	27.280*	4161.7	−7.5	4.8
	13.432	4253.2	−1.3	3.5
	27.931*	4161.5	−4.5	5.0
1.980	16.532	3953.8	0.5	3.9
	33.201*	3858.9	−3.7	5.4
	16.273	3960.6	5.5	3.9
	33.270*	3863.0	0.6	5.4
1.694	17.531	3495.9	3.0	4.3
	18.749	3491.4	6.4	3.7
	36.445*	3390.5	−4.4	5.2
1.526	19.246	3227.6	−0.4	3.7
	38.552*	3128.6	−3.8	5.1
	19.722	3217.6	−7.5	3.7
	39.489*	3121.6	−7.0	5.1
1.182	22.944	2727.8	18.2	3.8
	49.801*	2600.1	6.0	5.6
1.042	25.674	2495.9	−3.0	3.8
	52.809*	2382.9	−5.1	5.3
0.8286	31.573	2172.0	−0.6	4.0
	64.609*	2052.0	−2.4	5.5
	30.316	2179.6	1.1	3.8
	61.246*	2061.9	−2.3	5.2
0.6733	29.160	1964.6	0.7	3.5
	62.790*	1836.4	−3.1	5.0
	28.794	1962.5	−3.2	3.4
	62.157*	1836.3	−5.1	4.9
0.5187	29.279	1737.5	2.8	3.1
	63.091*	1610.6	0.6	4.4
0.3866	39.892	1477.5	0.2	4.1
	47.211	1447.2	−2.7	4.7
0.2819	41.448	1282.7	−0.6	3.7
	39.829	1292.4	2.8	3.6
0.1662	25.786	1098.9	0.9	2.0
	26.595	1094.1	0.4	2.1
0.09530	15.817	937.3	−0.4	1.6
	16.305	932.0	−2.3	1.5
0.02154	3.375	614.3	11.8	4.2
	3.877	602.2	8.0	4.2
0.002 076^c	10.266	78.7	2.7	7.5
0.002 224	10.963	84.4	5.9	8.1

Table I. Continued

m_i	$10^4 m_f$	$-\Delta H_{i,f}$, cal mol^{-1}	Exptl − calcd (cal mol^{-1})	σ, cal mol^{-1}
0.001 892	9.102	72.7	−3.1	5.9
0.002 392	12.348	77.0	0.8	6.8
0.002 807	14.033	87.9	3.3	7.1
0.002 728	13.344	97.0	11.1	5.9
0.002 793	13.432	91.7	3.2	6.1
0.003 320	16.532	94.9	4.2	6.6
0.003 327	16.273	97.6	4.8	6.7
0.003 645	18.749	100.9	10.8	6.4
0.003 855	19.246	99.0	3.4	6.2
0.003 949	19.722	96.0	−0.4	6.4
0.004 980	22.944	127.8	12.2	6.8
0.005 281	25.674	112.9	2.0	6.5
0.006 461	31.573	120.0	1.7	6.8
0.006 125	30.316	117.7	3.4	6.5
0.006 279	29.160	128.1	3.8	6.0
0.006 216	28.794	126.2	1.9	6.0
0.006 309	29.279	126.9	2.2	5.3
Gadolinium Chloride				
3.590	10.713	7358.0	−7.2	4.7
	21.632*	7274.1	−13.5	6.6
3.436	9.272	7055.4	14.5	3.9
	18.602*	6977.2	8.7	5.5
3.201	8.468	6548.9	4.5	3.4
	17.422*	6467.7	−4.2	4.8
	9.941	6521.9	−8.2	3.9
	20.061*	6446.5	−8.5	5.5
2.868	10.910	5828.9	−3.9	3.9
	22.506*	5750.6	−1.5	5.6
2.551	12.546	5199.6	3.4	4.0
	26.615*	5109.5	2.5	5.9
2.148	14.379	4446.1	6.0	3.9
	29.943*	4347.5	−1.1	5.6
1.858	15.832	3933.3	2.7	3.7
	31.945*	3840.5	0.2	5.2
1.524	19.018	3372.3	4.1	3.8
	38.701*	3258.3	−11.8	5.3
	17.497	3385.1	7.1	4.1
1.438	20.467	3209.2	−15.7	3.9
	40.883*	3109.2	−17.8	5.3
1.209	21.977	2871.0	4.7	3.7
	44.622*	2762.9	−0.2	5.2
0.9756	24.562	2507.5	4.4	3.6
	49.196*	2398.0	0.1	4.9
0.8087	29.031	2230.5	−0.7	3.7
	58.003*	2119.1	−0.9	5.1
0.6390	33.954	1955.7	5.3	3.8
	67.585*	1833.5	−0.1	5.1
0.4448	30.914	1657.5	5.9	3.0
	63.250*	1537.3	3.7	4.0
0.3590	29.301	1519.4	10.4	2.6
	61.732*	1394.1	6.4	3.7
0.2484	54.509	1196.5	3.1	4.5
	59.290	1181.3	3.0	4.8
0.1593	36.289	1053.2	6.5	2.7
	37.847	1047.4	7.2	2.8
0.09913	21.123	933.1	3.8	1.5
0.002 163^c	10.713	83.8	6.4	8.1
0.001 860	9.272	78.1	5.9	6.7
0.001 742	8.468	81.2	8.7	5.9
0.002 006	9.941	75.4	0.3	6.7
0.002 251	10.910	78.3	−2.5	6.8
0.002 662	12.546	90.1	0.9	7.2
0.002 994	14.379	98.6	7.1	6.8
0.003 195	15.832	92.8	2.6	6.4
0.003 870	19.018	114.0	15.9	6.5
0.004 088	20.467	99.9	2.1	6.5
0.004 462	21.977	108.1	4.9	6.4
0.004 920	24.562	109.5	4.3	6.1
0.005 800	29.031	111.4	0.2	6.3
0.006 758	33.954	122.2	5.5	6.3
0.006 325	30.914	120.2	2.1	5.0
0.006 173	29.301	125.2	4.0	4.5
Terbium Chloride				
3.571	10.259	7664.6	3.8	4.7
	20.448*	7575.9	−9.8	6.5
3.380	13.513	7175.9	−12.7	5.9
	28.324*	7105.1	7.5	8.7
	12.652	7204.3	8.9	5.5
	25.959*	7112.1	2.4	7.8
2.932	17.389	6164.1	−3.2	6.5
	36.457*	6068.6	1.7	9.5
2.509	16.687	5305.2	5.5	5.4
	35.557*	5202.1	3.8	8.0
2.049	21.818	4382.7	−6.1	5.7
	45.105*	4275.0	−6.7	8.2
1.694	49.688	3629.2	−4.4	10.2
	97.911*	3491.5	−10.0	13.8
	17.868	3780.0	−1.7	4.7
1.588	35.165	3517.2	8.8	7.3
	35.248*	3510.7	2.6	10.3
1.139	21.772	2829.6	−4.5	3.5
	42.068*	2737.5	−0.8	4.7
0.9855	42.523	2507.2	16.8	6.1
	84.327*	2375.5	11.9	8.1
0.7544	32.821	2165.8	3.7	4.1
	65.270*	2050.5	4.9	5.5
0.4492	24.661	1697.9	−2.4	2.4
	49.028*	1595.4	0.3	3.3
	24.671	1696.1	−4.2	2.4
	49.112*	1592.5	−2.4	3.3
0.002 045^c	10.259	88.7	13.5	8.0
0.002 832	13.513	70.7	−20.3	10.5
0.002 596	12.652	92.2	6.5	9.6
0.003 646	17.389	95.4	−5.0	11.5
0.003 556	16.687	103.1	1.7	9.7
0.045 510	21.818	107.6	0.6	10.0
0.009 791	49.688	137.6	5.5	17.2
0.003 525	35.165	6.5	6.2	12.7
0.004 207	21.772	92.1	−3.6	5.9
0.008 433	42.523	131.7	4.9	10.1
0.006 527	32.821	115.4	−1.2	6.8
0.004 903	24.661	102.5	−2.6	4.1
0.004 911	24.671	103.6	−1.8	4.1
Dysprosium Chloride				
3.631	8.404	7762.7	−10.4	4.0
	17.733*	7691.2	−5.0	6.0
	7.612	7785.7	4.2	3.6
	15.484*	7718.2	6.3	5.1
3.098	8.521	6622.4	11.2	3.5
	18.353*	6532.9	1.6	5.3
2.783	11.216	5917.7	1.3	4.6
	6.828	5957.8	−2.9	2.7
	15.500*	5884.5	2.4	4.3
2.494	10.621	5315.1	−14.3	3.4
	21.289*	5239.2	−12.2	4.9
2.172	10.713	4699.2	−0.4	3.0
	21.595*	4622.6	2.0	4.3
	9.126	4720.1	5.4	3.0
1.910	16.614	—	—	—
	33.109*	4072.1	−3.5	5.6
	10.798	4221.1	7.1	2.7
	21.604*	4142.2	6.4	3.8
	9.986	4219.5	−2.0	2.6
	20.133*	4147.6	2.8	3.6
1.669	20.612	—	—	—
	42.211*	3607.0	−5.6	6.4
	13.727	3767.4	2.4	3.1
	27.931*	3673.5	−2.9	4.4
	11.972	3781.8	2.4	2.7
	24.236*	3696.4	0.3	3.8

Table I. Continued

m_i	$10^4 m_f$	$-\Delta H_{i,f}$, cal mol^{-1}	Exptl − calcd (cal mol^{-1})	σ, cal mol^{-1}
1.443	14.258	3374.4	−6.0	2.9
	28.740*	3289.8	−1.9	4.0
1.163	18.593	2893.2	−3.8	3.2
	37.295*	2795.4	−4.3	4.4
0.974 1	21.206	2581.1	−1.6	3.2
	41.861*	2483.3	0.3	4.3
0.564 7	18.473	1952.9	5.0	2.2
	36.954*	1857.8	6.7	2.9
0.364 9	14.153	1627.3	−3.7	1.4
	27.521*	1550.9	3.0	1.8
0.236 9	39.138	1247.1	10.0	3.4
	42.393	1237.0	13.0	3.7
0.166 8	31.584	1108.7	7.8	2.5
	35.581	1093.6	10.9	2.7
0.091 26	21.289	913.4	1.2	1.4
	19.202	929.0	3.9	1.3
0.042 34	9.973	742.5	6.5	3.1
	11.236	724.5	0.1	3.0
	10.765	738.3	9.7	3.0
0.001 773^c	8.404	71.5	−5.4	7.2
0.001 548	7.612	67.5	−2.1	6.2
0.001 835	8.521	89.4	9.6	6.4
0.001 550	6.828	73.3	−5.4	5.0
0.002 129	10.621	75.9	−2.1	6.0
0.002 159	10.713	76.6	−2.4	5.2
0.002 160	10.798	79.0	0.6	4.7
0.002 013	9.986	72.0	−4.9	4.4
0.002 793	13.727	93.9	5.3	5.4
0.002 424	11.972	85.4	2.1	4.7
0.002 874	14.258	84.5	−4.1	5.0
0.003 730	18.593	97.9	0.4	5.4
0.004 186	21.206	97.8	−2.0	5.4
0.003 695	18.473	95.1	−1.7	3.6
0.002 752	14.153	76.5	−6.8	2.3
Holmium Chloride				
3.694	52.215	7644.8	3.4	10.0
	45.455	7648.5	−16.9	10.0
	45.468	7677.1	11.8	10.0
3.323	42.850	6839.2	−8.1	10.0
	40.348	6870.6	13.4	10.0
2.913	44.302	5949.2	2.7	10.0
	45.051	5940.1	−3.6	10.0
2.669	42.380	5430.3	−10.4	10.0
	43.481	5440.4	4.0	10.0
2.365	46.922	4817.4	5.7	10.0
	46.458	4806.3	−7.1	10.0
2.007	42.497	4150.0	−2.6	10.0
	42.811	4165.6	14.2	10.0
1.685	36.566	3622.5	10.9	9.0
	36.506	3591.0	−20.9	8.9
1.349	44.529	3020.1	−8.2	9.2
	44.556	3043.3	15.1	9.2
1.013	33.432	2547.5	−1.5	5.9
	33.270	2553.4	3.7	5.8
0.819 5	34.857	2243.3	−0.1	4.6
	73.102*	2114.0	0.3	6.5
0.518 3	47.156	1704.1	−7.5	5.5
0.007 310^c	34.857	129.4	−0.4	8.0
Erbium Chloride				
3.782	11.096	—	—	—
	22.496*	7824.1	−14.5	7.4
	11.391	7917.9	3.2	5.4
	23.040*	7839.1	3.5	7.6
3.535	8.474	7390.3	−4.1	3.7
	16.950*	7330.0	4.5	5.3
	7.497	7401.3	−3.4	3.4
	15.531*	7341.2	5.9	4.9
3.222	8.934	6709.7	0.9	3.7
	18.576*	6637.2	3.4	5.3
	8.833	6718.7	8.9	3.6
	17.817*	6646.7	8.0	5.0
2.904	11.662	5998.7	−14.8	4.2
	23.668*	5920.0	−13.1	6.0
	11.418	6013.3	−2.3	4.1
	23.232*	5933.2	−2.3	5.9
2.695	10.890	5596.1	1.9	3.8
	23.223*	5513.3	3.6	5.6
2.343	10.936	4909.2	1.7	3.7
	12.145	4896.0	−1.3	3.6
	24.562*	4811.2	−4.9	5.0
2.067	12.996	4386.4	4.7	3.4
	26.194*	4296.8	−2.0	4.8
	12.781	4378.6	−4.8	3.4
	25.888*	4293.8	−6.6	4.7
1.805	12.967	3927.0	3.7	3.1
	26.235*	3844.0	4.0	4.3
	12.390	3935.9	7.9	2.9
	25.210*	3854.7	9.4	4.2
1.453	14.884	3327.6	0.3	3.0
	30.371*	3234.4	−3.7	4.2
	15.351	3323.4	−0.5	3.1
	31.136*	3231.6	−2.9	4.3
1.218	15.587	2951.3	−0.8	2.7
	31.192*	2859.7	−4.4	3.8
	15.445	2950.4	−2.7	2.7
	31.326*	2859.5	−4.0	3.8
1.030	21.800	2622.4	−0.6	3.4
	44.183*	2515.8	−5.3	4.7
	22.184	2617.7	−3.1	3.4
	44.556*	2513.3	−6.5	4.7
0.872 3	18.888	2400.4	1.1	2.7
	38.007*	2301.5	−2.3	3.7
	18.836	2398.8	−0.9	2.7
	38.131*	2301.4	−1.9	3.7
0.631 1	36.675	1937.1	2.8	4.1
	74.494*	1808.8	−2.8	5.5
	34.328	1945.6	1.3	3.8
	68.873*	1823.8	−2.8	5.1
0.476 4	34.893	1696.8	8.4	3.5
	74.270*	1563.0	4.3	4.9
	38.032	1682.1	6.8	3.7
	76.527*	1556.0	3.1	4.9
0.387 4	29.041	1569.5	10.0	2.6
	58.706*	1453.5	6.5	3.5
	30.239	1563.2	9.5	2.8
	62.600*	1440.8	5.4	3.8
0.266 6	65.206	1201.1	7.0	5.4
	65.400	1201.4	7.8	5.4
0.167 4	29.084	1106.0	13.2	2.3
	27.752	1112.4	13.0	2.2
0.086 89	16.281	913.2	10.7	1.6
	19.018	892.1	7.6	1.3
0.045 84	10.439	753.1	19.7	3.0
	9.499	756.0	13.9	3.2
0.002 304^c	11.391	78.9	−0.3	9.3
0.001 695	8.474	60.3	−8.7	6.5
0.001 553	7.497	60.1	−9.3	6.0
0.001 858	8.934	72.5	−2.5	6.5
0.001 782	8.833	72.0	0.9	6.2
0.002 367	11.662	78.7	−1.6	7.3
0.002 323	11.418	80.1	0.1	7.2
0.002 322	10.890	82.8	−1.7	6.8
0.002 456	12.145	84.9	3.7	6.1
0.002 619	12.996	89.6	6.7	5.9
0.002 589	12.781	84.9	1.8	5.8
0.002 623	12.967	83.1	−0.3	5.3

Table I. Continued

m_i	$10^4 m_f$	$-\Delta H_{i,f}$, cal mol^{-1}	Exptl − calcd (cal mol^{-1})	σ, cal mol^{-1}
0.002 521	12.390	81.1	−1.5	5.1
0.003 037	14.884	93.3	4.1	5.2
0.003 114	15.351	91.8	2.4	5.2
0.003 119	15.587	91.6	3.7	4.7
0.003 133	15.445	90.9	1.3	4.7
0.004 418	21.800	106.6	4.7	5.8
0.004 456	22.184	104.4	3.4	5.8
0.003 801	18.888	98.9	3.4	4.6
0.003 813	18.836	97.4	1.1	4.6
0.007 449	36.675	128.3	5.6	6.9
0.006 887	34.328	121.8	4.1	6.4
0.007 427	34.893	133.8	4.1	6.0
0.007 653	38.032	126.1	3.7	6.1
0.005 871	29.041	115.9	3.5	4.4
0.006 260	30.239	122.5	4.1	4.7
Thulium Chloride				
3.881	8.486	8048.1	17.1	4.7
	4.347	8041.6	−39.4	4.2
	17.978*	7967.1	12.0	6.4
3.700	8.845	7674.4	46.2	4.1
	17.749*	7591.4	34.0	5.7
	8.277	7670.0	36.1	3.9
	17.115*	7598.8	37.2	5.6
3.620	6.802	7454.3	−20.3	3.1
	14.033*	7382.9	−25.3	4.5
	7.690	7435.3	−29.4	3.5
	15.539*	7373.7	−23.5	4.9
3.328	7.333	6842.1	4.9	3.1
	14.884*	6774.2	3.7	4.3
	8.300	6826.3	−0.6	3.5
	17.231*	6750.2	−3.8	5.0
2.916	9.885	—	—	—
	19.572*	5853.8	−25.3	4.8
	9.967	5955.6	4.8	3.6
	20.259*	5880.3	5.3	5.1
2.599	10.550	5313.4	−2.4	3.4
	21.142*	5242.3	2.4	4.7
	9.716	5320.7	−2.7	3.6
	20.702	—	—	—
2.225	14.040	4584.4	−1.3	4.5
	13.668	—	—	—
	28.005*	4502.1	0.7	5.4
1.953	15.602	4096.7	2.7	3.9
	32.285*	4005.4	4.5	5.5
	16.281	4101.0	11.7	4.0
	33.247*	4006.1	9.6	5.6
1.712	17.506	3692.5	16.3	3.9
	36.277*	3591.0	12.4	5.6
	18.029	—	—	—
	36.470*	3574.9	−2.9	5.5
1.458	18.114	3258.9	−5.8	3.5
	36.772*	3166.5	−2.6	4.9
	18.533	3262.5	0.5	3.6
	37.528*	3165.7	−0.3	5.0
1.037	19.501	2611.9	−1.4	3.0
	39.539*	2510.6	−4.5	4.2
	19.687	2605.8	−6.3	3.1
	40.526*	2506.3	−5.0	4.3
0.823 2	19.325	2282.2	−12.3	2.6
	39.125*	2186.0	−11.0	3.6
	19.785	2287.9	−3.8	2.7
	39.829*	2187.1	−7.1	3.7
0.640 5	21.050	2009.4	3.1	2.5
	43.086*	1904.3	0.6	3.5
	21.391	2009.5	5.2	2.5
	43.099*	1905.1	1.4	3.4
0.515 6	21.492	1806.9	0.6	2.7
	23.184	1799.1	2.5	2.4
	46.145*	1699.9	4.9	3.3
0.370 0	16.008	1598.0	3.6	1.6
	32.160*	1509.7	5.0	2.1
	14.432	—	—	—
	30.714*	1519.0	7.7	2.1
0.280 1	10.420	1469.7	1.2	1.3
	21.344*	1396.4	6.0	2.0
	9.666	1484.0	8.6	1.5
	20.035*	1406.7	8.5	2.2
0.163 8	31.360	1077.2	4.4	2.4
	27.123	1096.2	2.9	2.1
0.087 27	16.104	908.3	0.1	1.6
	20.196	883.8	2.1	1.3
0.038 09	7.420	714.3	4.5	3.6
	7.857	709.1	4.0	3.5
0.001 798^{c}	4.347	—	—	—
0.001 775	8.845	83.0	12.2	7.0
0.001 711	8.277	71.2	−1.1	6.8
0.001 403	6.802	71.4	5.0	5.5
0.001 554	7.690	61.7	−5.9	6.0
0.001 488	7.333	67.9	1.2	5.3
0.001 723	8.300	76.1	3.3	6.1
0.002 026	9.967	75.4	−0.5	6.2
0.002 114	10.550	71.1	−4.8	5.8
0.003 229	15.602	91.4	−1.8	6.8
0.003 325	16.281	94.8	2.1	6.9
0.003 628	17.506	101.5	4.0	6.8
0.003 677	18.114	92.4	−3.3	6.1
0.003 753	18.533	96.9	0.8	6.1
0.003 954	19.501	101.3	3.1	5.2
0.004 053	19.687	99.6	−1.3	5.3
0.003 913	19.325	96.2	−1.4	4.5
0.003 983	19.785	100.8	3.3	4.5
0.004 309	21.050	105.1	2.6	4.3
0.004 310	21.391	104.4	3.8	4.3
0.004 614	23.184	99.2	−2.3	4.1
0.003 216	16.008	88.3	−1.4	2.6
0.002 134	10.420	73.4	−4.9	2.4
0.002 003	9.666	77.4	0.1	2.6
Ytterbium Chloride				
4.003	10.189	8172.3	−1.0	5.1
	21.298*	8091.9	−1.9	7.4
3.515	11.465	7114.8	5.4	5.6
	10.903	—	—	—
3.204	13.126	6445.2	5.0	4.9
	25.412*	6359.7	−3.0	6.6
2.881	17.573	5743.6	−6.2	6.0
	35.665*	5651.0	−5.1	8.5
2.558	18.131	5109.8	−7.0	5.6
	37.357*	5019.5	−0.1	7.9
2.176	16.999	4426.0	2.2	4.4
	33.028*	4336.0	−1.6	5.9
1.920	17.783	3971.0	−6.3	4.9
	17.986	3983.7	7.7	5.0
1.667	23.522	3533.0	4.5	5.0
	49.886*	3417.9	1.2	7.3
1.445	26.595	3168.5	4.3	4.9
	52.476*	3060.1	0.0	6.6
1.206	25.756	2807.0	0.0	4.3
	52.766*	2692.8	−4.7	6.0
1.005	31.315	2482.1	−0.2	4.5
	63.028*	2363.6	−4.7	6.1
0.794 4	32.810	2165.0	1.1	4.1
	65.545*	2047.2	−2.4	5.5
0.656 7	39.753	1927.7	0.7	5.3
0.497 5	39.363	1679.2	2.0	4.6
0.387 5	39.200	—	—	—
1.478	23.455	3219.4	1.6	4.5
	47.569*	3113.4	0.5	6.2
	23.678	3218.3	1.7	4.5
	48.247*	3111.2	0.7	6.3

Table I. Continued

m_i	$10^4 m_f$	$-\Delta H_{i,f}$, cal mol^{-1}	Exptl − calcd (cal mol^{-1})	σ, cal mol^{-1}
1.215	19.643	2847.9	2.5	3.3
	39.263*	2750.9	1.6	4.5
	19.342	2847.3	0.1	3.3
	39.577*	2747.0	−1.1	4.6
1.002	31.282	2468.6	−2.7	4.7
	67.519*	2339.5	−3.9	6.8
	37.835	2440.7	−2.1	6.3
	21.604	2521.0	−0.3	3.2
	43.283*	2418.7	−2.7	4.4
	21.734	2521.0	0.5	3.2
	43.983*	2418.5	−0.3	4.5
0.796 3	22.487	2212.7	−2.5	3.0
	47.005*	2098.7	−8.1	4.2
	23.697	2195.5	−13.0	3.6
	21.381	2222.5	0.9	3.0
	47.527*	2103.3	−1.6	4.4
	22.146	—	—	—
	46.854*	2106.1	−1.2	4.2
0.648 7	23.775	1986.6	−1.1	2.8
	48.637*	1877.0	−3.8	3.9
	22.877	1986.6	−6.1	2.8
	49.112*	1871.5	−7.5	4.0
0.503 6	19.936	1792.0	8.0	2.2
	42.732*	1681.2	4.8	3.1
	17.901	1795.4	−1.5	1.9
	36.796*	1696.0	−3.9	2.7
0.432 4	31.170	1607.5	−0.3	3.0
	64.899*	1484.7	−2.2	4.1
	28.441	—	—	—
	58.829*	1500.0	−4.8	3.7
0.251 9	24.187	1318.0	8.3	1.3
	28.037	1291.8	2.1	2.6
	33.408	1270.8	6.3	3.0
0.162 5	30.858	1064.6	−2.3	2.3
	27.594	1081.1	−1.5	2.1
	33.501	1044.7	−10.2	2.5
	24.641	1089.0	−9.0	1.9
	17.995	1137.4	0.3	1.5
	18.241	1141.4	5.9	1.5
0.002 130[c]	10.189	80.4	0.9	9.0
0.002 541	13.126	85.5	8.0	8.2
0.003 566	17.573	92.6	−1.1	10.4
0.003 736	18.131	90.3	−6.9	9.7
0.003 303	16.999	90.0	3.8	7.3
0.004 989	23.522	115.1	3.3	8.9
0.005 248	26.595	108.4	4.3	8.2
0.005 277	25.756	114.2	4.8	7.3
0.006 303	31.315	118.5	4.5	7.6
0.006 555	32.810	117.8	3.4	6.9
Lutetium Chloride				
4.128	7.552	—	—	—
	15.437*	8297.7	−11.7	5.5
	6.970	8362.3	−21.8	4.0
3.913	7.404	7927.2	9.5	4.1
	7.258	7949.7	30.4	4.0
3.307	10.043	6622.8	10.3	4.2
	21.800*	6537.4	9.2	6.3
	9.622	6621.2	4.8	3.8
	19.519*	6549.3	7.4	5.4
3.086	8.815	6162.6	−11.1	3.3
	18.037*	6087.5	−13.2	4.7
	9.413	6176.6	8.8	3.6
	19.981*	6095.5	7.0	5.3
2.917	8.032	5839.2	−5.8	2.9
	16.386*	5765.3	−9.9	4.1
	8.970	5821.7	−13.8	3.2
	18.542*	5748.4	−12.5	4.6
2.569	9.437	5167.1	4.1	3.1
	20.693*	5069.4	−10.2	4.8
	10.963	5154.8	5.7	3.9
2.249	11.269	4573.1	7.7	3.6
	11.451	4561.7	−2.2	3.2
	23.484*	4480.7	−1.9	4.5
1.999	12.631	4139.7	16.1	3.7
	15.054	—	—	—
	30.658*	4025.0	9.4	5.2
1.719	23.194	3598.4	3.1	5.0
	47.679*	3491.9	3.4	7.0
	22.043	3606.9	5.0	4.7
	44.436*	3502.1	1.9	6.5
0.090 44	14.501	921.4	−8.1	1.9
	12.859	940.0	−2.1	2.2
0.041 02	5.726	745.1	−5.2	3.8
	7.263	720.8	−11.2	3.6
0.011 19	1.899	499.4	25.6	4.5
	2.161	464.7	−3.2	4.4
0.002 180[c]	10.043	85.4	1.2	7.6
0.001 952	9.622	71.9	−2.6	6.7
0.001 804	8.815	75.0	2.1	5.8
0.001 998	9.413	81.1	1.8	6.4
0.001 639	8.032	73.9	4.1	5.0
0.001 854	8.970	73.3	−1.3	5.6
0.002 069	9.437	97.7	14.3	5.7
0.002 348	11.451	81.0	−0.3	5.5
0.004 768	23.194	106.5	−0.3	8.6
0.004 444	22.043	104.8	3.1	8.0
0.004 757	23.455	106.1	1.1	7.6
0.004 825	23.678	107.1	1.0	7.7
0.003 926	19.643	97.0	1.0	5.6
0.003 958	19.342	100.3	1.2	5.7
0.006 752	31.282	129.1	1.2	8.2
0.004 328	21.604	102.2	2.4	5.4
0.004 398	21.734	102.5	0.8	5.5
0.004 700	22.487	114.0	5.6	5.2
0.004 753	21.381	119.1	2.5	5.3
0.004 864	23.775	109.6	2.7	4.8
0.004 911	22.877	115.0	1.5	4.8
0.004 273	19.936	110.9	3.1	3.8
0.003 680	17.901	99.3	2.3	3.3
0.006 490	31.170	122.9	1.9	5.0

[a] Dilutions made into very dilute HCl (pH 4.4). [b] For a starred sample $f = 3$ and its corresponding $f = 2$ value (unstarred) is given immediately above. [c] For each salt, all entries above this point are $\Delta H_{1,2}$ or $\Delta H_{1,3}$ values, the rest are $\Delta H_{2,3}$ values.

The order of the ϕ_L curves in dilute solutions for the chlorides, perchlorates, and nitrates are in agreement with a general trend in that ϕ_L decreases with increasing anion size. The lower ϕ_L values of the nitrates, particularly near $Sm(NO_3)_3$, are due to nitrate complex formation as discussed in the nitrate paper (*30*), where it was shown that the largest amount of complex formation occurs near $Sm(NO_3)_3$ in dilute solutions. Complex formation is also responsible for the eventual drop of all the nitrates below the respective perchlorates at higher concentrations. The $Sm(NO_3)_3$ ϕ_L curve drops below $Sm(ClO_4)_3$ at 0.04 *m* while the others cross at higher concentration. This is in agreement with the degree of complex formation for the nitrates. Curves similar to Figures 3, 4, and 5 for Pr, Nd, Gd, Dy, and Er, salts for which data on the three anions are available, show behavior intermediate to those given for La, Sm, and Lu. The ϕ_L curves of all the rare earth chlorides are quite similar as was the case for the perchlorates (*31*), while the nitrate curves showed a much larger spread with concentration (*30*). The L_2 curves for four chlorides

Table II. Heats of Solution of Some Rare Earth Chloride Hydrates at 25 °C

Hydrate	$10^4\ m_f$	$-\Delta H_{x,f}$, cal mol^{-1}	$\phi_L(m_f)$, cal mol^{-1}		$\bar{L}^{\cdot}$, cal mol^{-1}
$LaCl_3 \cdot 7H_2O$	11.580	6 476.9	217.8		6 694.7
	27.857*[a]	6 363.3	322.7		6 686.0
	13.898	6 461.6	236.7		6 698.4
	27.963*	6 371.2	323.2		6 694.4
				Av	6 693 ± 5
$PrCl_3 \cdot 7H_2O$	15.984	6 761.2	248.0		7 009.3
	34.328*	6 653.0	346.3		6 999.3
	16.744	6 753.4	253.2		7 006.7
	34.469*	6 657.0	346.9		7 003.9
				Av	7 005 ± 4
$NdCl_3 \cdot 6H_2O$	9.296	8 965.3	191.9		9 157.2
	12.503	8 900.4	219.4		9 119.8
	28.058*	8 806.6	312.8		9 119.4
				Av	9 132 ± 18
$SmCl_3 \cdot 6H_2O$	7.236	8 430.1	172.7		8 602.7
	15.896*	8 366.9	246.7		8 613.7
	7.355	8 441.9	174.0		8 615.9
	16.606*	8 367.0	251.6		8 618.6
				Av	8 613 ± 6
$EuCl_3 \cdot 6H_2O$	13.557	8 488.8	231.4		8 720.1
	28.175*	8 387.7	320.1		8 707.8
				Av	8 714 ± 6
$GdCl_3 \cdot 6H_2O$	7.795	8 949.5	179.9		9 129.4
	19.141*	8 843.2	270.6		9 113.8
	9.666	8 921.6	198.6		9 120.2
	19.901*	8 835.1	275.3		9 110.4
				Av	9 119 ± 7
$TbCl_3 \cdot 6H_2O$	10.234	9 394.3	204.7		9 599.0
	20.412*	9 280.8	279.9		9 560.6
	9.211	9 348.8	195.0		9 543.8
	17.834*	9 257.9	263.5		9 521.3
	9.891	9 323.1	201.5		9 524.6
	20.044*	9 262.6	277.6		9 540.2
	13.469	9 338.8	232.1		9 570.9
	29.138*	9 268.2	327.5		9 595.7
	11.323	9 309.1	214.4		9 523.6
	27.030*	9 242.1	316.9		9 559.0
				Av	9 554 ± 27
$DyCl_3 \cdot 6H_2O$	9.443	9 788.7	199.0		9 987.7
	19.598*	9 691.8	277.7		9 969.5
	9.060	9 773.1	195.2		9 968.3
	19.342*	9 690.3	276.0		9 966.4
				Av	9 973 ± 9
$HoCl_3 \cdot 6H_2O$	9.753	10 232.3	201.5		10 433.8
	27.868*	10 101.2	323.3		10 424.5
	9.321	10 185.9	197.3		10 383.2
	19.999*	10 134.9	279.2		10 414.1
	12.110	10 192.5	222.5		10 415.0
	23.232*	10 129.1	298.4		10 427.5
	9.223	10 211.9	196.3		10 408.2
	17.314*	10 163.5	261.7		10 425.2
				Av	10 416 ± 15
$ErCl_3 \cdot 6H_2O$	6.436	10 578.6	164.3		10 742.9
$TmCl_3 \cdot 6H_2O$	9.784	10 922.2	199.5		11 121.7
$YbCl_3 \cdot 6H_2O$	6.595	11 366.4	165.9		11 532.3
	14.205*	11 265.5	235.6		11 501.1
	6.959	—	—		—
	14.319*	11 274.6	236.5		11 511.1
				Av	11 515 ± 11
$LuCl_3 \cdot 6H_2O$	7.728	11 675.3	178.9		11 854.2
	18.801	11 607.5	267.9		11 875.4
	5.551	11 696.0	153.4		11 849.5
				Av	11 860 ± 11

[a] For a starred sample $f = 3$ and its corresponding $f = 2$ value (unstarred) is given immediately above.

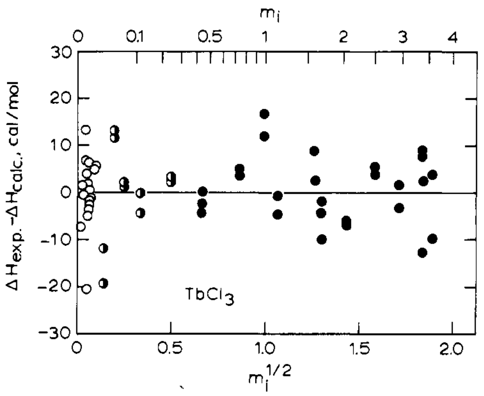


Figure 1. Comparison of experimental and calculated ΔH for $TbCl_3$: solid circles, $\Delta H_{1,2}$ and $\Delta H_{1,3}$, this work; half-filled circles, $\Delta H_{1,2}$ and $\Delta H_{1,3}$, Spedding, Csejka, and DeKock (*28*); open circles, $\Delta H_{3,2}$, this work and Spedding, Csejka, and DeKock (*28*).

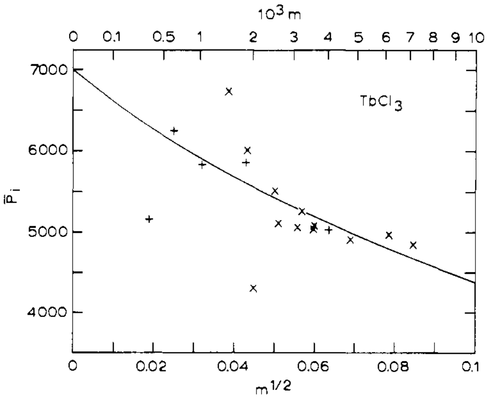


Figure 2. $\bar{P}_i$ for $TbCl_3$; plus, Spedding, Csejka, and DeKock (*28*); cross, this research; line, from eq 7.

are shown in Figure 6. The rest of the chlorides fall between $TbCl_3$ and $NdCl_3$. The $\bar{L}_1$ curves for three rare earth chlorides, perchlorates, and nitrates are compared in Figure 7. Clearly, the effect on the solvent by the chlorides and perchlorates is different from that of the nitrates.

In order to compare differences between the several rare earth chlorides, the ϕ_L, $\bar{L}_2$, and $\bar{L}_1$ values are shown as a function of rare earth ionic radius at several even concentrations in Figures 8, 9, and 10. The two-series effect in perchlorate solutions and in dilute nitrate solutions also appears in the rare earth chloride solutions. At a given concentration, ϕ_L decreases for the light rare earth chlorides to about $NdCl_3$, then increases to somewhere near $TbCl_3$, and again decreases for the rest of the heavy rare earth chlorides. It has been suggested that the coordination in the first cation hydration sphere decreases between Nd and Tb, where the light, larger rare earths have the higher, and the heavy, smaller rare earths have the lower water coordination (*33*). The rare earth ions between Nd and Tb would have mixtures of the two coordinations. Differences in the heats of hydration of the two coordinated forms and the effect on hydration beyond the first coordination sphere, as a function of concentration, are thought to be responsible for the displacement of ϕ_L in the middle of the rare earth series. Similar anomalies in the partial molal volumes (*35*), expansibilities (*13*), heat capacities (*38*), activities (*39*), conductances (*34*), and viscosities (*40*) have been correlated with this model.

As mentioned earlier, ϕ_L decreases with increasing anion size (if allowance is made for nitrate complex formation) in agreement with trends found for other strong electrolyte solutions. However, opposite the trend expected, ϕ_L increases with increasing rare

Table III. Parameters for Equations 6 and 7

Salt[a]	p_2 A_2	p_3 A_3	p_4 A_4	p_5 A_5	p_6 A_6
$LaCl_3$	1.00	1.50	1.75	2.00	2.75
	−18851.9306	56881.9234	−66921.7907	25185.78432	−700.23677
$PrCl_3$	1.00	1.25	1.75	2.25	2.50
	−25828.7453	31450.0882	−15249.2703	7777.34511	−2633.94188
$NdCl_3$	1.00	1.25	1.50	1.75	2.25
	−31713.2644	58452.1912	−45251.2878	14585.94568	−581.33918
$SmCl_3$	1.00	1.25	1.75	2.25	2.50
	−26728.8051	33919.6472	−17962.2252	9904.52418	−3498.29178
$EuCl_3$	1.00	1.25	1.75	2.25	2.50
	−24928.1020	30523.8496	−14973.3525	7860.25313	−2724.85141
$GdCl_3$	1.00	1.25	1.75	2.25	2.50
	−24509.6976	29804.0854	−14242.9582	7309.40773	−2509.29592
$TbCl_3$	1.00	1.25	1.75	2.25	2.50
	−23236.0089	26966.4642	−11268.9175	5068.04202	−1620.50293
$DyCl_3$	1.00	1.50	1.75	2.00	2.75
	−18103.0608	55337.3144	−65298.4944	24686.18650	−700.87878
$HoCl_3$	1.00	1.50	1.75	2.00	2.75
	−18734.6295	58919.0500	−70253.7518	26715.43185	−757.19460
$ErCl_3$	1.00	1.25	1.75	2.25	2.50
	−25245.0667	31254.9820	−15471.4556	8199.42200	−2865.06067
$TmCl_3$	1.00	1.25	1.75	2.25	2.50
	−24810.8966	30331.2598	−14683.1379	7662.19592	−2659.03415
$YbCl_3$	1.00	1.25	1.75	2.25	2.50
	−25672.0766	31961.3106	−16003.8184	8506.16918	−2972.90038
$LuCl_3$	1.00	1.25	1.75	2.25	2.50
	−24936.2600	30531.9869	−14832.5564	7731.35861	−2681.23967

[a] $p_1 = 0.50$, $A_1 = 6990.00$ for all salts.

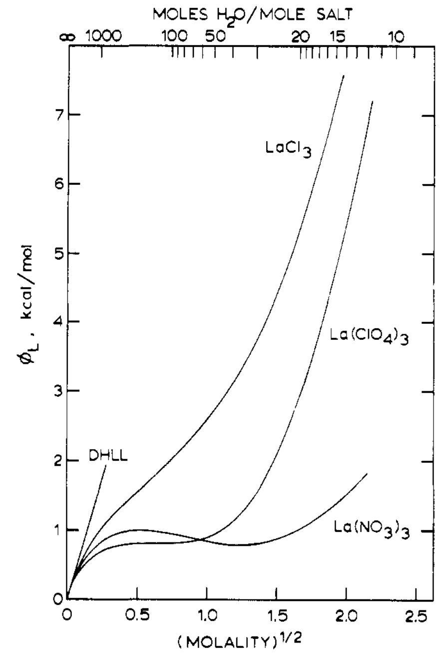


Figure 3. Relative apparent molal enthalpy of aqueous lanthanum chloride, perchlorate, and nitrate solutions at 25 °C, from eq 7; DHLL, Debye-Hückel limiting law.

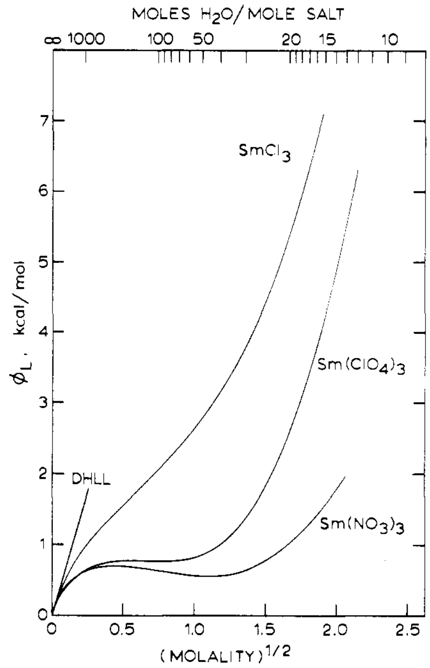


Figure 4. Relative apparent molal enthalpy of aqueous samarium chloride, perchlorate, and nitrate solutions at 25 °C, from eq 7; DHLL, Debye-Hückel limiting law.

earth cation size (for a given hydration series) in the chlorides reported here and the perchlorates and nitrates presented in earlier papers. This might be understood if the total hydrated cation radius plays a dominant role rather than the inner sphere cationic radius. It is known that the effective hydrated radius increases from La to Nd and Tb to Lu as shown by increasing viscosities (*40*) and decreasing conductances (*34*).

Most of the rare earth chloride complexation studies (*1, 4–6, 9, 10, 18, 20–22, 24, 26*) indicate that outer sphere chloride complexes are formed by an ionic strength of 1 M. Furthermore, the amount of inner sphere chloride complex formation is small (*3–6, 9, 18, 24*), if it is present at all. The persistence of the two-series effect, in the heat properties to high concentrations for the rare earth chlorides, indicates that the first hydration sphere of the cation remains largely intact to high concentrations. This is in agreement with the stability constant studies mentioned above. In contrast, the two-series effect disappears in the rare earth nitrates (*30*) where inner sphere nitrate com-

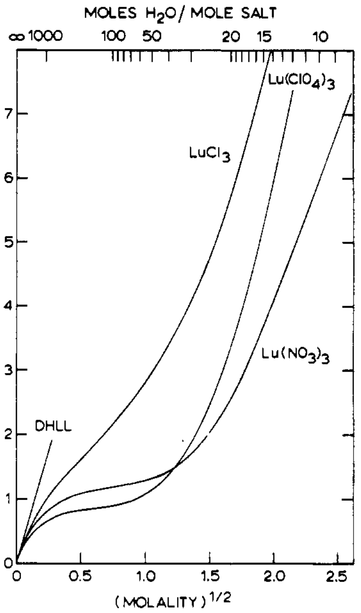


Figure 5. Relative apparent molal enthalpy of aqueous lutetium chloride, perchlorate, and nitrate solutions at 25 °C, from eq 7; DHLL, Debye–Hückel limiting law.

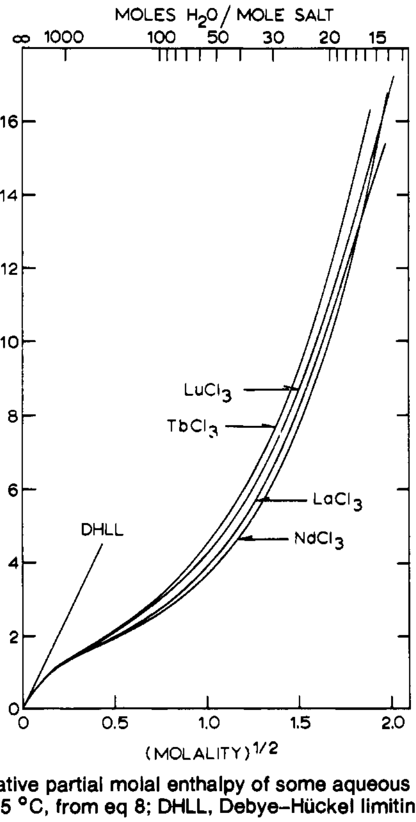


Figure 6. Relative partial molal enthalpy of some aqueous rare earth chlorides at 25 °C, from eq 8; DHLL, Debye–Hückel limiting law.

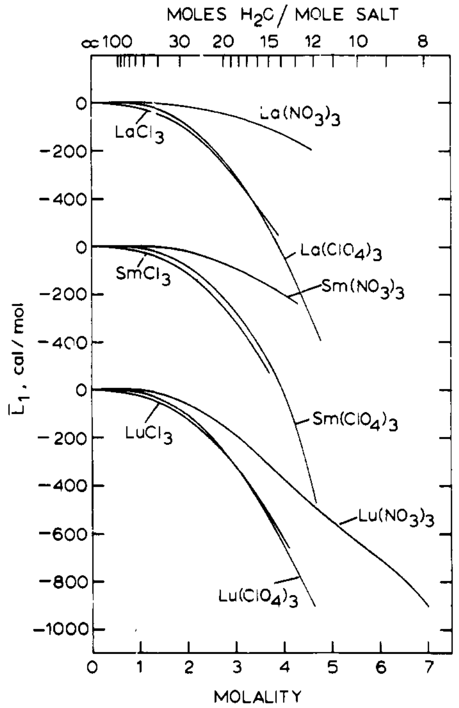


Figure 7. Relative partial molal enthalpy of the solvent in some aqueous rare earth chloride, perchlorate, and nitrate solutions at 25 °C, from eq 9.

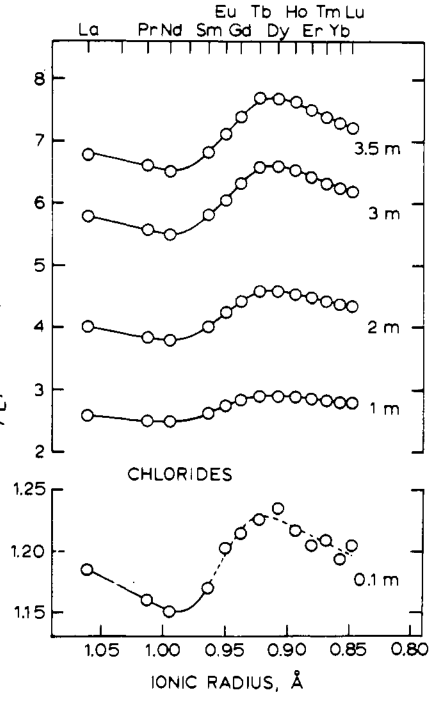


Figure 8. Relative apparent molal enthalpy of some aqueous rare earth chloride solutions at 25 °C, from eq 7.

plexation is known to occur. Furthermore, although most of the equilibrium constants reported in the literature for the chloride complexes are only slightly smaller than those for the nitrates, the heat of formation of the chloride complex is smaller than the heat of formation of the nitrate complex by an order of magnitude (*5*). This accounts for the fact that the ϕ_L curves of the chlorides (Figures 3–5) are lowered to a much smaller extent than the ϕ_L curves of the nitrates.

The heats of solution for 13 rare earth chloride hydrates, six rare earth nitrate hydrates, and four rare earth perchlorate hydrates are shown in Figure 11. $LaCl_3{\cdot}7H_2O$ and $PrCl_3{\cdot}7H_2O$ are nine-coordinated with two chlorides and seven waters in the first coordination sphere, while the rest of the chloride hydrates are eight-coordinated with two chlorides and six waters in the first coordination sphere (*2, 11, 19, 41*). From the discussion above we believe that upon dissolution of the rare earth chloride hydrates, the two chlorides in the first hydration sphere are displaced by water molecules in the solution. In Figure 11 we have

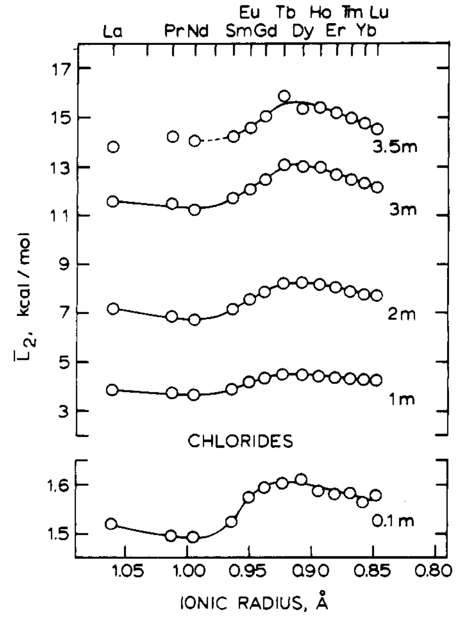


Figure 9. Relative partial molal enthalpy of some aqueous rare earth chloride solutions at 25 °C, from eq 8.

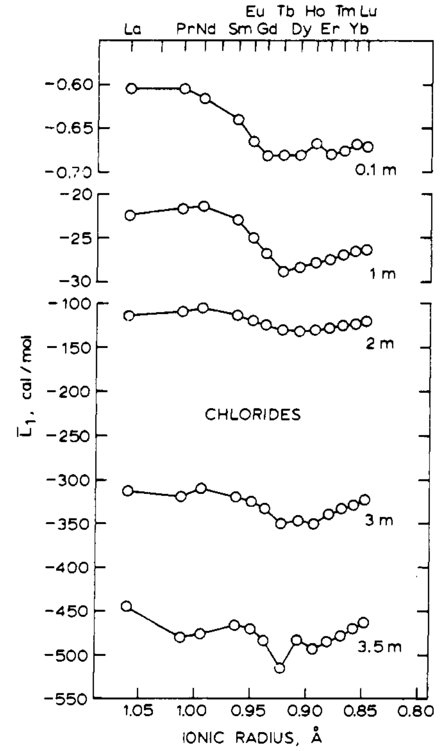


Figure 10. Relative partial molal enthalpy of the solvent in some aqueous rare earth chloride solutions at 25 °C, from eq 9.

plotted the heat of the solution of the rare earth hexahydrates to form a 3.5 *m* solution (solid circles), and the heat of solution in forming saturated solutions (crosses). Although these 11 rare earth chloride hexahydrates are isostructural (*11*), in both the heats of forming a 3.5 *m* and saturated solutions, there is an upturn from Tb to Nd. This may reflect the formation of some of the higher inner sphere water coordination for these ions, while Tb to Lu form solely the lower coordination in the solution phase.

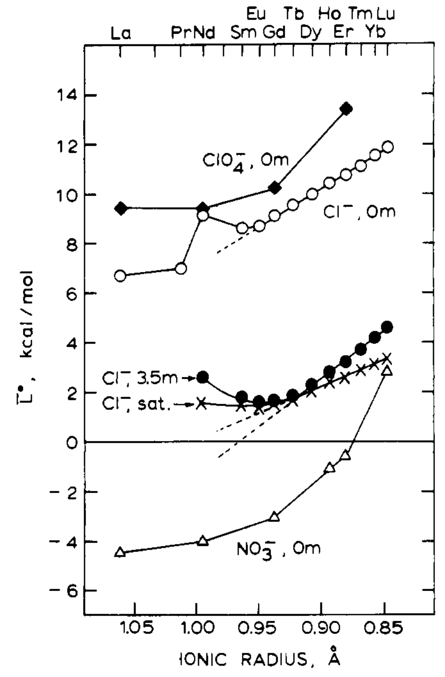


Figure 11. Relative molal enthalpies of some rare earth chloride, perchlorate, and nitrate hydrates at 25 °C; diamonds, perchlorate octahydrates; open circles, chloride hydrates; triangles, nitrate hydrates. The (negative) heats of solution in forming a 3.5 *m* solution (filled circles) and the (negative) heats of solution in forming a saturated solution (crosses) from the rare earth chloride hexahydrates are also shown.

Of the nitrate hydrates for which heats of solution were measured in this laboratory, the nitrates of La, Nd, Gd, Ho, and Er are hexahydrates, while lutetium nitrate is a pentahydrate (*30*). In $Pr(NO_3)_3{\cdot}6H_2O$ the praseodymium ion is ten-coordinated with three bidentate nitrate ions and four waters in the first coordination sphere (*8, 25, 42*). From the primitive cell dimensions, the La, Ce, Pr, and Sm nitrate hexahydrates appear to be isostructural (*8, 16, 17, 25, 42*). The four perchlorates examined are octahydrates (*31*). We are not aware of any structural information on the rare earth perchlorate hydrates.

Acknowledgment

The authors thank the Ames Laboratory Rare Earth Separation Group for furnishing the oxides. They also thank J. A. Rard for helpful suggestions concerning this work, and J. L. Derer for doing preliminary calculations.

Literature Cited

(1) Bansal, B. M. L., Patil, S. K., Sharma, H. D., *J. Inorg. Nucl. Chem.*, **26**, 993 (1963).
(2) Bel'skii, N. K., Struchkov, Yu. T., *Sov. Phys.-Crystallogr.* (*Engl. Trans.*), **10**, 15 (1965).
(3) Choppin, G. R., Bertha, S. L., *J. Inorg. Nucl. Chem.*, **35**, 1309 (1973).
(4) Choppin, G. R., Henrie, D. E., Buijs, K., *Inorg. Chem.*, **5**, 1743 (1966).
(5) Choppin, G. R., Strazik, W. F., *Inorg. Chem.*, **4**, 1250 (1965).
(6) Choppin, G. R., Unrein, P. I., *J. Inorg. Nucl. Chem.*, **25**, 387 (1963).
(7) Derer, J. L., Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1974.
(8) Fuller, C. C., Jacobson, R. A., submitted to *Cryst. Struct. Commun.*
(9) Garnsey, R., Ebdon, D. W., *J. Am. Chem. Soc.*, **91**, 50 (1969).
(10) Goto, T., Smutz, M., *J. Inorg. Nucl. Chem.*, **27**, 663 (1965).
(11) Graeber, E. J., Conrad, G. H., Duliere, S. F., *Acta Crystallogr.*, **21**, 1012 (1966).
(12) Gucker, F. T., Jr., Pickard, H. B., Planck, R. W., *J. Am. Chem. Soc.*, **61**, 459 (1939).
(13) Habenschuss, A., Spedding, F. H., *J. Chem. Eng. Data*, **21**, 95 (1976).
(14) Hepler, L. G., Woolley, E. M., "Water, a Comprehensive Treatise", Vol. 3, F. Franks, Ed., Plenum Press, New York-London, 1973, p 149.
(15) Hinchey, R. J., Cobble, J. W., *Inorg. Chem.*, **9**, 917 (1970).
(16) Iveronova, V. I., Tarasova, V. P., Umanskii, M. M., *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **15**, 164 (1951).
(17) Iveronova, V. I., Tarasova, V. P., Zolina, Z. K., Marsakhin, G. V., Sukhodreva, I. M., *Zh. Fiz. Khim.*, **29**, 314 (1955).
(18) Kozachenko, N. N., Batyaev, I. M., *Russ. J. Inorg. Chem.*, **16** (1), 66 (1971).
(19) Marezio, M., Plettinger, H. A., Zachariasen, W. H., *Acta Crystallogr.*, **14**, 234 (1961).

(20) Moulin, N., Hussonnois, M., Brillard, L., Guillaumont, R., *J. Inorg. Nucl. Chem.*, **37**, 2521 (1975).
(21) Nakamura, K., Kawamura, K., *Bull. Chem. Soc. Jpn.*, **44**, 330 (1971).
(22) Peppard, D. F., Mason, G. W., Hucher, I., *J. Inorg. Nucl. Chem.*, **24**, 881 (1962).
(23) Rard, J. A., Spedding, F. H., *J. Phys. Chem.*, **79**, 257 (1975).
(24) Reuben, J., Fiat, D., *J. Chem. Phys.*, **51**, 4909 (1969).
(25) Rumanova, I. M., Volodina, G. F., Belov, N. V., *Sov. Phys.-Crystallogr.*, **9**, 545 (1965).
(26) Sayre, E. V., Miller, D. G., Freed, S., *J. Chem. Phys.*, **26**, 109 (1957).
(27) Spedding, F. H., Baker, J. L., Walters, J. P., *J. Chem. Eng. Data*, **20**, 189 (1975).
(28) Spedding, F. H., Csejka, D. A., DeKock, C. W., *J. Phys. Chem.*, **70**, 2423 (1966).
(29) Spedding, F. H., Cullen, P. F., Habenschuss, A., *J. Phys. Chem.*, **78**, 1106 (1974).
(30) Spedding, F. H., Derer, J. L., Mohs, M. A., Rard, J. A., *J. Chem. Eng. Data*, **21**, 474 (1976).
(31) Spedding, F. H., Mohs, M. A., Derer, J. L., Habenschuss, A., *J. Chem. Eng. Data*, submitted, 1976.
(32) Spedding, F. H., Naumann, A. W., Eberts, R. E., *J. Am. Chem. Soc.*, **81**, 23 (1959).
(33) Spedding, F. H., Pikal, M. J., Ayers, B. O., *J. Phys. Chem.*, **70**, 2440 (1966).
(34) Spedding, F. H., Rard, J. A., Saeger, V. W., *J. Chem. Eng. Data*, **19**, 373 (1974).
(35) Spedding, F. H., Saeger, V. W., Gray, K. A., Boneau, P. K., Brown, M. A., DeKock, C. W., Baker, J. L., Shiers, L. E., Weber, H. O., Habenschuss, A., *J. Chem. Eng. Data*, **20**, 72 (1975).
(36) Spedding, F. H., Shiers, I. E., Brown, M. A., Baker, J. L., Gutierrez, L., McDowell, L. S., Habenschuss, A., *J. Phys. Chem.*, **79**, 1087 (1975).
(37) Spedding, F. H., Shiers, L. E., Rard, J. A., *J. Chem. Eng. Data*, **20**, 88 (1975).
(38) Spedding, F. H., Walters, J. P., Baker, J. L., *J. Chem. Eng. Data*, **20**, 438 (1975).
(39) Spedding, F. H., Weber, H. O., Saeger, V. W., Petheram, H. H., Rard, J. A., Habenschuss, A., *J. Chem. Eng. Data*, **21**, 341 (1976).
(40) Spedding, F. H., Witte, D., Shiers, L. E., Rard, J. A., *J. Chem. Eng. Data*, **19**, 369 (1974).
(41) Urgo, J. V., unpublished Ph.D. Thesis, Iowa State University, Ames, Iowa, 1967.
(42) Volodina, G. F., Rumanova, I. M., Belov, N. V., *Sov. Phys.-Crystallogr.*, **6**, 741 (1962).
(43) Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., *Natl. Bur. Stand.* (*U.S.*) *Tech. Note*, **No. 270-(1-6)** (1968–1971).

Received for review May 3, 1976. Accepted July 31, 1976. This report was prepared for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82, and is based, in part, on the Ph.D. dissertations of C. W. DeKock (1965) and G. W. Pepple (1967), submitted to the Graduate Faculty of Iowa State University, Ames, Iowa 50011.

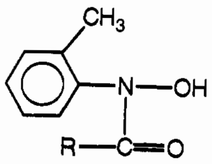
Supplementary Material Available: Tables IV, V, and VI, listings of the ϕ_L, $\bar{L}_2$, and L_1 data for the rare earth chlorides, perchlorates, and nitrates at even concentrations, are available (23 pages). Ordering information is given on any current masthead page.

Synthesis of *N*-Arylhydroxamic Acids

Yadvendra K. Agrawal*
Department of Chemistry, Govt. Science College, Rewa (M.P.), India

Preparation and properties of ten new *N*-arylhydroxamic acids derived from *O*-tolylhydroxylamine are described. These acids are white crystalline solids and characterized by elemental analysis and infrared spectra.

In the previous communication the preparation and properties of 25 hydroxamic acids derived from *p*- and *m*-tolylhydroxylamine have been described (*1, 2*). Further work on ten *N*-arylhydroxamic acids derived from substituted benzoic acid with the general formula (I) are reported for the first time



I

where R is substituted benzoic acid derivatives.

The procedure based on the Schotten and Baumann reaction was used for the preparation of these *N*-arylhydroxamic acids. Thus freshly prepared *N*-*o*-tolylhydroxylamine and vacuum distilled acid chloride in equimolar proportions are reacted at low temperature in diethyl ether containing an aqueous suspension of sodium bicarbonate. The *N*-arylhydroxamic acids so obtained are purified by crystallization from a mixture of benzene and petroleum ether.

Discussion

The physical properties of *N*-arylhydroxamic acids are given in Table I. All the hydroxamic acids are white crystalline solids except the iodo and nitro derivatives which are light pink and yellow, respectively. They are sparingly soluble in water but readily soluble in benzene, ethyl alcohol, dioxane, diethyl ether, and chloroform.

The infrared spectra of the synthesized hydroxamic acids were determined primarily for their characterization. In the infrared spectra only those bonds which are associated with the hydroxamic acid functional group, -N(OH)-C═O have been assigned. The presence of the (O–H) stretching band is assigned in the region of 3200 cm^{-1} and conforms with the reported value (*1–6*). The lower shift of (O–H) was due to the intramolecular hydrogen bonding of the type -OH···C═O. The (C═O) and (N—O) bands are assigned at about 1620 and 920 cm^{-1}, respectively.

Experimental Section

Infrared Spectra. Infrared spectra were recorded in the 2–15 μ region on a Perkin-Elmer Model 137 or 221 spectrophotometer equipped with sodium chloride optics and calibrated by standard methods. *N*-Arylhydroxamic acids were dried under vacuum over P_2O_5 and examined as KBr pellets.

Acid Chlorides. These were prepared by the action of thionyl chloride on the corresponding benzoic acids. The boiling points and yields of the acid chlorides, thus produced, were in agreement with the values given in literature (*7*).

Procedure. A typical procedure for *N*-*o*-tolyl-*p*-fluorobenzohydroxamic acid is described here.

Into a 500-ml, three-necked flask, equipped with stirrer, dropping funnel, and thermometer, 100 ml of diethyl ether, 12.3 g (0.1 mol) of freshly crystallized *O*-tolylhydroxylamine, and a

---

* Address correspondence to this author at Health Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085, India.