Heats of Dilution of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 1. Rare Earth Perchlorates

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The heats of dilution of aqueous $La(ClO_4)_3$, $Pr(ClO_4)_3$, $Nd(ClO_4)_3$, $Sm(ClO_4)_3$, $Gd(ClO_4)_3$, $Dy(ClO_4)_3$, $Er(ClO_4)_3$, and $Lu(ClO_4)_3$ solutions have been determined from approximately 0.001 *m* to saturation at 25 °C. The integral heats of solution of $La(ClO_4)_3 \cdot 8H_2O$, $Nd(ClO_4)_3 \cdot 8H_2O$, $Gd(ClO_4)_3 \cdot 8H_2O$, and $Er(ClO_4)_3 \cdot 8H_2O$ in water at 25 °C have also been measured. The heat of dilution data are represented by empirical polynomial equations, and relative apparent and partial molal heat contents are calculated. The heat content data are correlated with the inner sphere water coordination numbers of the rare earth cations.

This work was undertaken as part of an extensive program to gain a better understanding of rare earth electrolyte solutions through the measurement of their thermodynamic and transport properties (*4, 8, 10, 16, 18*). Heats of dilution provide a measure of the energy changes involved in complex formation, hydration, modification of the solvent by the hydrated ions, and the electrical work between different solution states. The heats of dilution of a number of rare earth chlorides and nitrates have been measured up to 0.2 *m* (*11, 13*). These heats of dilution were shown to conform to the Debye–Hückel limiting law at concentrations below 0.006 *m*. At higher concentrations the heat data for the chlorides showed a two-series trend across the rare earth series which was correlated with dilute partial molal volume data of the rare earth chlorides (*12*). The two series trends have been interpreted as reflecting a difference in the inner sphere water coordination between the light and heavy rare earth cations (*14*). Heats of dilution of aqueous $La(ClO_4)_3$ have recently been reported by Vanderzee and Nutter (*19*). Here we report heat of dilution measurements for eight rare earth perchlorate solutions from 0.001 *m* to saturation at 25 °C.

Experimental Section

Apparatus. The adiabatically jacketed differential calorimeter used in this work has been previously described (*11, 13*). Although several modifications have been made since then (*3, 7*), the essential characteristics of the calorimeter remain unchanged. The sample holders previously described (*11*) were replaced by thin-walled, annealed Pyrex bulbs (*2*) which were broken by lowering them against pointed stainless steel rods.

To monitor the accuracy of the calorimeter, the heat of neutralization of HCl with NaOH at an ionic strength of 0.003 was determined. From a total of 28 neutralizations an average value of -13.338 ± 0.020 kcal mol^{-1} was obtained at infinite dilution. This is in good agreement with -13.34 kcal mol^{-1} recommended by Hepler and Woolley (*5*).

Materials. The solutions were prepared from the rare earth oxides and perchloric acid. The oxides were purified by ion-exchange methods by the Rare Earth Separation Group of the Ames Laboratory. Total rare earth impurities were less than 0.1% by weight, and total other impurities were also less than 0.1% by weight. The stock solutions were adjusted to the equivalence pH to ensure a 1:3 ratio of rare earth ions to perchlorate ions. The stock solutions, secondary stock solutions, and saturated solutions were analyzed by gravimetric sulfate (*14*) and EDTA (*12*) methods. The concentrations of the solutions were known to 0.1% in terms of molality. The dilutions were prepared by weight from the stock solutions and conductivity water having a specific conductance of less than 1×10^{-6} mho cm^{-1}, all weights being corrected to vacuum. Detailed descriptions of the preparation and analyses of the solutions can be found in ref 3.

Hydrated crystals were grown from saturated solutions of lanthanum, neodymium, and gadolinium perchlorates at 25 °C. The crystals were dried over magnesium perchlorate until the stoichiometric equilibrium of the hydrate was reached. The rare earth content was determined by EDTA titration so that the rare earth content was known to 0.1%. In every case the crystals were the octahydrate to within 0.06 of a water molecule.

Growth of suitable hydrate crystals from the saturated solution of erbium perchlorate was unsatisfactory. For this reason the hydrated crystals obtained for erbium perchlorate were grown from a solution of $Er(ClO_4)_3$ containing an excess of perchloric acid. Data from the $Ce(ClO_4)_3$–$HClO_4$–H_2O phase system (*25*) indicated that the pure $8H_2O$ hydrate would precipitate out without being contaminated with acid perchlorate, and analysis of the hydrate obtained from the mixture used indicated that the pure octahydrate was obtained. The ratio of $Er(ClO_4)_3$–$HClO_4$–H_2O, in percent by weight, in the mixture was 35.2:24.7:35.2. The crystals grown from this mixture were washed with chloroform and dried under vacuum until they reached the octahydrate composition. The crystals were analyzed as described above.

Procedure. One (10 to 20 mL) or two (4 to 10 mL) sample bulbs were suspended in each calorimeter container and enough conductivity water was weighed into each container to give a total liquid content of 900 g.

When a sample of molality m_1, containing n' moles of rare earth, was diluted into water to give a solution of molality m_2, a quantity of heat q' was evolved. When the second sample of molality m_1, containing n'' moles of rare earth, was diluted into the solution of molality m_2 to give a solution of molality m_3, a quantity of heat q'' was evolved. The relative apparent molal heat content is related to the evolved heat by the expressions

$$q' = n'[\phi_L(m_2) - \phi_L(m_1)] \qquad (1)$$

$$q'' = (n' + n'')\phi_L(m_3) - n''\phi_L(m_1) - n'\phi_L(m_2) \qquad (2)$$

where $\phi_L(m_i)$ is the relative apparent molal heat content at concentration m_i. In general, two samples could be diluted in one run at high concentrations (q' and q''), while the large size of the sample bulb for dilute solutions allowed only one dilution per run (q').

Similarly, two samples of the crystal hydrates were used to obtain the heats of solution. Dissolving the first sample containing n' moles of rare earth octahydrate gave a solution of molality m_2 with q' calories of heat being evolved. The second sample containing n'' moles of the rare earth hydrate, dissolved into this solution of molality m_2 gave a solution of molality m_3, evolving q'' calories of heat. The heat of solution to infinite dilution, $-\bar{L}^{\cdot}$, is related to the heats evolved by

$$q' = n'[\phi_L(m_2) - \bar{L}^{\cdot}] \qquad (3)$$

$$q'' = (n' + n'')\phi_L(m_3) - n'\phi_L(m_2) - n''\bar{L}^{\cdot} \qquad (4)$$

Since the vapor pressure of water over rare earth perchlorate solutions decreases with concentration, water will evaporate into the empty volume of a sample bulb when a partially filled bulb is broken. The measured heat quantities were corrected for this effect, as well as for the heat of breaking the glass bulbs, and for daily variations in the ratio of the heat capacities of the two calorimeter containers. All heat of dilution and heat of solution measurements were made at 25.00 ± 0.02 °C and the defined thermochemical calorie, 4.1840 absolute J, was used throughout this work.

Calculations and Results

Heats of Dilution and Heats of Solution. The integral heats of dilution, $\Delta H_{i,f}$, are given by

$$\Delta H_{1,2} = \phi_L(m_2) - \phi_L(m_1) = q'/n' \qquad (5)$$

$$\Delta H_{1,3} = \phi_L(m_3) - \phi_L(m_1) = (q' + q'')/(n' + n'') \qquad (6)$$

Similarly, the integral heats of solution, $\Delta H_{x,f}$, are given by

$$\Delta H_{x,2} = \phi_L(m_2) - \bar{L}^{\cdot} = q'/n' \qquad (7)$$

$$\Delta H_{x,3} = \phi_L(m_3) - \bar{L}^{\cdot} = (q' + q'')/(n' + n'') \qquad (8)$$

The experimental heats of dilution and solution are given in Tables I and II, respectively. The first set of entries for each salt in Table I refers to dilution of the saturated solution. For those groups of dilutions having the same initial concentration, m_i, the initial concentration is listed only once. For the final concentrations of each dilution or solution, m_f, an asterisk denotes sample dilution processes corresponding to eq 2 and 6, and 4 and 8, where $m_f = m_3$. These samples were diluted into the solution resulting from the dilution of the immediately preceding sample, $m_f = m_2$, corresponding to eq 1 and 5, and 3 and 7.

For the heats of dilution the dilution scheme was designed so that the final concentrations, m_2 and m_3, covered the very dilute concentration range, <0.01 *m*, while the initial concentration, m_1, systematically covered the range from saturation to 0.01 *m*. The $\Delta H_{1,2}$ and $\Delta H_{1,3}$ values were combined to give heats of dilution in the dilute range

$$\Delta H_{3,2} = \Delta H_{1,2} - \Delta H_{1,3} = \phi_L(m_2) - \phi_L(m_3) \qquad (9)$$

The $\Delta H_{3,2}$ values and the corresponding m_i and m_f values are listed immediately following the $\Delta H_{1,2}$ and $\Delta H_{1,3}$ data in Table I.

Initially the heats of dilution were analyzed by the "short chord-long chord" method of Young and co-workers (*22-24*) and its modification (*9, 21*). In this method (see ref 11, for example) the $\Delta H_{3,2}$, the "short chords", are used to extrapolate to infinite dilution with the aid of the Debye-Hückel limiting slope by means of a $\bar{P}_i$ plot,

$$\frac{\partial \phi_L}{\partial m^{1/2}} \cong \bar{P}_i = \frac{\Delta H_{3,2}}{m_2^{1/2} - m_3^{1/2}} = A + Bm^{1/2} + Cm + \ldots \qquad (10)$$

where A is the limiting slope and $m^{1/2} = 1/2(m_2^{1/2} + m_3^{1/2})$. Integration of eq 10 gives ϕ_L up to 0.01 *m*, and ϕ_L from 0.01 *m* to saturation can be calculated from eq 5 and 6.

In our attempts to subsequently fit all of the ϕ_L values over the whole concentration range within experimental precision, including the correct limiting behavior, we found that for the rare earth perchlorates this is possible with polynomials of the kind

$$\phi_L = \sum_{j=1}^{7} A_j m^{p_j} \qquad (11)$$

where A_1 is the Debye-Hückel limiting slope with $p_1 = 1/2$, and the other p_j are certain multiples of ¼ in the range ¾ to 16/4. This suggested the possibility of fitting the $\Delta H_{i,f}$ values directly, omitting the more elaborate $\bar{P}_i$ analysis.

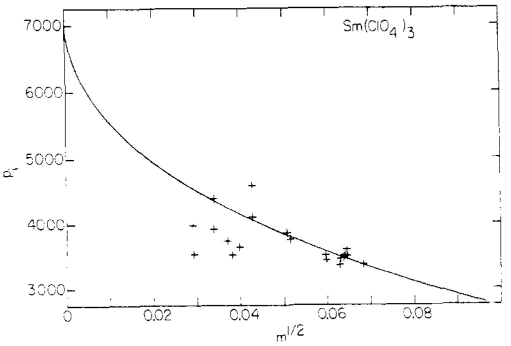

Figure 1. $\bar{P}_i$ plot for Sm(ClO$_4$)$_3$: plus, $\Delta H_{3,2}/(m_2^{1/2} - m_3^{1/2})$; line, $(d\phi_L/dm^{1/2})$ from eq 11.

If we assume that a single ϕ_L equation can represent all of the concentration range, then from eq 5, 6, and 9 we have

$$\Delta H_{i,f} = \phi_L(m_f) - \phi_L(m_i) \qquad (12)$$

and from eq 11

$$\Delta H_{i,f} = \sum_{j=1}^{7} A_j(m_f^{p_j} - m_i^{p_j}) \qquad (13)$$

The A_j can be determined by least-squares methods. Then, by setting $m_i = 0$, eq 13 reduces to eq 11. The ϕ_L values calculated from this ΔH fit agreed with the ϕ_L values obtained by the $\bar{P}_i$ analysis to within the experimental precision of the data.

The main strength of the $\bar{P}_i$ treatment is that the extrapolation to zero concentration depends mostly on the data near where the limiting law should hold, and is not hindered by depending on data at higher concentrations. For this reason it is very important in our present treatment that the equation chosen is capable of fitting the $\Delta H_{3,2}$ data in the dilute region accurately. In Figure 1 we show $\bar{P}_i$ data for Sm(ClO$_4$)$_3$ based on the $\Delta H_{3,2}$ values, together with $(d\phi_L/dm^{1/2})$ calculated from our ΔH fit based on all the data. It can be seen that the fit is acceptable. The coefficients, A_j, and powers, p_j, to be used with eq 11 and 13 are given in Table III. The differences between the experimental $\Delta H_{i,f}$ and those calculated from eq 13 are given in the fourth column in Table I, and are plotted for Sm(ClO$_4$)$_3$ in Figure 2 vs. $m_i^{1/2}$.

The particular powers, p_j, in eq 13 for each salt were chosen in the following way. First, it was determined that, in general, powers in multiples of $m^{1/4}$ gave better fits than powers in multiples of m, $m^{1/2}$, $m^{1/3}$, $m^{1/6}$, $m^{1/8}$, or $m^{1/16}$. In this and the following, the criterion for goodness of fit was the reduced χ^2 statistic (*1*). Second, best fits were obtained with $p_1 = ½$, the

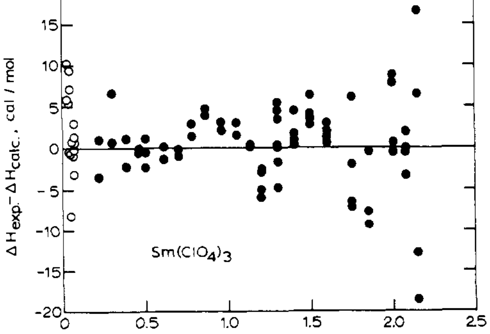

Figure 2. Comparison between experimental and calculated ΔH from eq 13 for Sm(ClO$_4$)$_3$: solid circles, $\Delta H_{1,2}$ and $\Delta H_{1,3}$; open circles, $\Delta H_{3,2}$.

Table I. Heats of Dilution of Some Aqueous Rare Earth Perchlorate 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 Perchlorate			
4.791	8.9700	7089.5	11.4	3.8
	18.020*^{a}	7036.2	5.3	4.7
	8.9401	7093.3	7.8	3.8
	17.944*	7037.8	4.1	4.7
4.465	7.2469	6347.7	−9.2	2.8
	14.592*	6294.4	−11.3	3.4
	7.4093	6350.9	−14.0	2.8
	14.334*	6301.1	−16.4	3.4
4.093	10.074	5449.5	15.8	4.0
	23.377*	5368.1	21.1	4.9
	14.311	5407.4	28.7	4.0
	26.245*	5353.2	23.9	4.9
3.581	24.423	4260.7	14.6	6.0
	47.169*	4186.9	13.8	7.4
	27.458	4243.8	19.1	6.0
	50.112*	4179.1	14.1	7.4
3.255	12.117	3676.4	−3.8	2.7
	24.000*	3616.5	−7.8	3.3
	11.343	3678.9	−0.8	2.7
	24.572*	3610.2	−3.9	3.3
2.902	17.783	2959.6	−3.2	2.9
	33.432*	2893.2	−2.4	3.5
	15.817	2972.5	−5.3	2.9
	32.376*	2903.1	−8.7	3.5
2.565	18.481	2356.9	−3.8	2.6
	37.970*	2279.0	−2.5	3.2
	18.602	2356.3	−3.9	2.6
	36.784*	2286.2	−6.0	3.2
2.238	38.341	1747.0	8.3	2.8
	18.680	1826.1	5.9	3.2
	30.085	1779.1	3.7	2.7
	58.921*	1700.7	1.9	3.4
	29.398	1782.3	3.1	2.7
	60.746*	1696.8	1.9	3.4
1.982	27.092	1432.3	6.4	2.3
	53.597*	1355.3	3.8	2.8
	27.217	1438.0	0.2	2.3
1.733	31.697	1123.5	3.2	2.0
	64.096*	1041.2	0.2	2.1
	31.517	—	—	—
	63.952*	1040.0	1.7	2.6
1.465	43.705	837.3	−2.6	2.1
	90.611*	744.3	−3.9	2.6
	39.854	847.0	−1.3	2.1
	93.954*	738.9	−3.5	2.6
1.176	34.281	670.0	−2.5	1.7
	34.258	667.0	0.5	1.7
1.005	41.165	571.0	−1.2	1.7
	40.322	573.0	−0.7	1.7
0.816 7	33.143	545.0	−1.8	1.3
	32.994	544.0	−0.3	1.3
0.644 8	33.212	521.0	0.6	1.3
	32.160	524.0	1.3	1.3
0.493 9	29.441	529.0	1.9	1.6
	26.173	538.0	5.6	1.6
0.350 4	26.235	546.0	−2.7	1.8
	23.571	556.0	−1.5	1.8
0.250 0	16.346	588.0	−4.4	2.7
	16.233	586.0	−1.8	2.7
0.161 1	11.635	594.0	−3.6	3.2
	11.263	599.0	−5.9	3.2
	12.348	585.0	0.5	3.2
0.089 12	7.9919	562.0	4.8	3.7
	7.9750	560.0	6.9	3.7
0.039 91	3.3636	522.0	−0.7	10.0
	3.1684	526.0	−1.6	10.0
0.010 27	0.8214	378.0	5.7	10.0
0.001 794	8.940^b	55.5	3.7	5.1
0.001 802	8.970	53.3	6.0	5.1
0.001 433	7.409	49.8	2.5	3.7
0.001 459	7.247	53.3	2.1	3.7
0.002 625	14.311	54.2	4.8	5.4
0.002 338	10.074	81.4	−5.2	5.4
0.005 011	27.458	64.7	5.0	8.2
0.004 717	24.423	73.8	0.9	8.2
0.002 457	11.343	68.7	3.1	3.6
0.002 400	12.117	59.9	4.0	3.6
0.003 238	15.817	69.4	3.5	3.9
0.003 343	17.783	66.4	−0.8	3.9
0.003 678	18.602	70.1	2.1	3.5
0.003 797	18.481	77.9	−1.3	3.5
0.006 075	29.398	85.5	1.2	3.7
0.005 892	30.085	78.4	1.8	3.7
0.005 360	27.092	77.0	2.6	3.1
0.006 410	31.697	82.3	3.0	2.4
0.009 395	39.854	108.1	2.2	2.8
0.009 061	43.705	93.0	1.4	2.8
	Praseodymium Perchlorate			
4.695	4.3586	6622.3	3.4	1.7
	8.3484*	6594.0	−6.0	2.4
	4.0220	6625.6	4.1	1.6
	7.8535*	6601.0	−9.1	2.3
4.255	5.3322	5488.4	0.6	1.8
	10.604*	5450.8	−5.2	2.5
	5.5215	5483.5	3.5	1.8
	10.793*	5448.1	−3.8	2.5
3.862	6.6604	—	—	—
	13.047*	4550.8	5.5	2.1
	6.1428	4606.5	0.6	1.8
	12.419*	4567.1	−7.0	2.5
	7.1657	—	—	—
	14.268*	4544.0	5.3	2.3
	7.1976	4595.0	2.5	2.0
	14.370*	4544.3	4.5	2.8
3.398	6.7974	3666.3	−3.4	1.7
	15.531*	3612.2	−7.8	2.7
	8.5256	—	—	—
	17.094*	3603.8	−7.3	2.2
2.930	12.332	2751.7	0.8	2.0
	23.274*	2700.7	−1.6	2.6
	11.859	2756.5	−1.0	2.0
	24.636*	2698.7	−5.0	2.9
2.508	15.362	2022.1	4.8	1.9
	31.492*	1956.7	4.5	2.7
	15.665	2016.5	8.9	1.9
	31.267*	1956.9	5.0	2.6
2.150	18.208	1491.4	−1.8	1.7
	38.917*	1413.5	2.3	2.4
	17.525	1496.4	−3.5	1.7
	38.164*	1420.6	−2.7	2.4
1.966	25.514	1227.4	−0.4	1.9
	54.304*	1143.5	2.6	2.7
	24.422	1230.6	0.6	1.9
	52.341*	1146.4	4.1	2.6
1.773	32.347	991.8	−2.3	1.9
	67.934*	904.9	0.2	2.6
	31.656	996.6	−4.8	1.9
	68.556*	906.6	−2.7	2.7
1.521	44.733	726.8	0.5	1.8
	86.942*	647.2	−0.9	2.3
	41.083	729.9	6.9	1.8
	87.263*	646.3	−0.5	2.4
1.305	36.255	610.7	−5.2	1.3
	74.613*	522.2	−1.0	1.7
	36.232	606.4	−0.8	1.3
	74.013*	526.1	−3.9	1.7

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}
1.119	49.791	483.3	−0.8	1.3
	100.293*	396.0	−1.2	1.7
	51.468	473.7	5.0	1.3
	102.515*	387.9	4.0	1.7
0.952 9	38.593	461.3	0.0	1.3
	76.345*	381.0	−0.3	2.6
	37.905	463.2	0.0	1.3
	76.020*	384.6	−3.3	2.5
0.709 6	58.126	380.3	5.8	1.6
	58.280	379.3	6.4	1.6
0.504 2	47.716	422.8	−4.8	1.5
	45.822	424.6	−2.0	1.4
	44.984	429.2	−4.5	1.4
0.382 0	32.523	474.1	−1.3	1.5
	33.342	468.1	2.1	1.4
0.256 4	31.696	484.3	0.8	1.5
	31.653	482.4	2.9	1.5
0.160 8	20.866	516.3	−1.1	2.4
	20.794	512.5	3.0	2.4
0.099 76	14.491	517.5	−5.0	3.1
	14.664	512.3	−0.7	3.1
0.041 74	6.7044	470.1	−6.7	4.0
	6.7086	470.2	−6.9	4.0
0.000 835	4.359^b	28.3	9.4	2.6
0.000 785	4.022	24.6	13.2	2.4
0.001 060	5.332	37.7	5.7	2.7
0.001 079	5.521	35.3	7.4	2.7
0.001 242	6.143	39.3	7.7	2.7
0.001 437	7.198	50.7	−1.9	3.1
0.001 553	6.797	54.2	4.3	2.8
0.002 327	12.332	51.0	2.5	2.9
0.002 464	11.859	57.8	3.9	3.2
0.003 149	15.362	65.4	0.4	2.9
0.003 127	15.665	59.6	3.9	2.8
0.003 892	18.208	77.9	−4.1	2.6
0.003 816	17.525	75.7	−0.7	2.6
0.005 430	25.514	83.8	−2.9	2.9
0.005 234	24.422	84.2	−3.5	2.8
0.006 793	32.347	86.9	−2.4	2.9
0.006 856	31.656	90.1	−2.3	2.9
0.008 694	44.733	79.6	1.4	2.5
0.008 726	41.083	83.6	7.4	2.6
0.007 461	36.255	88.5	−4.2	1.8
0.007 401	36.232	80.3	3.1	1.8
0.010 03	49.791	87.3	0.4	1.9
0.010 25	51.468	85.7	1.1	1.9
0.007 634	38.593	80.3	0.2	2.7
0.007 602	37.905	78.6	3.3	2.6
	Neodymium Perchlorate			
4.685	8.6025	6383.0	−1.5	3.6
	18.182*	6320.7	3.8	4.5
	11.785	6343.7	15.6	3.6
	20.232*	6300.2	14.9	4.5
4.509	8.7261	5937.4	−12.0	3.1
	17.523*	5884.4	−11.9	3.8
	8.9760	5932.4	−8.9	3.1
	17.464*	5883.6	−10.9	3.8
4.075	14.969	4869.2	9.2	4.2
	29.823*	4803.4	12.3	5.2
	14.977	4864.9	13.4	4.2
	29.052*	4809.5	8.8	5.2
3.625	17.073	3926.5	7.2	4.0
	34.492*	3859.0	7.9	4.9
	17.548	3921.5	9.9	4.0
	34.094*	3858.6	9.6	4.9
3.223	15.896	3174.3	−6.3	2.8
	30.437*	3110.9	−2.7	3.5
	14.062	3193.0	−15.1	3.3
2.879	14.130	2563.9	−2.4	2.2
	28.580*	2499.6	−1.1	2.7
	13.242	2573.3	−6.7	2.2
	27.889*	2503.9	−3.0	2.7
2.603	18.992	2074.4	4.2	2.5
	41.204*	1996.6	5.2	3.0
	19.705	2072.9	2.5	2.5
	40.437*	1998.7	5.2	3.0
2.254	20.784	1550.5	0.7	1.8
	40.183*	1480.0	5.2	2.3
	20.268	1556.0	−2.5	1.8
	39.640*	1485.8	0.9	2.3
1.964	27.626	1154.1	2.6	2.0
	58.706*	1069.2	4.6	2.4
	29.452	1147.2	3.1	2.0
	59.737*	1066.2	5.4	2.4
1.670	33.339	841.8	−5.3	1.7
	71.978*	750.3	−3.0	2.1
	35.117	834.8	−3.8	1.7
	72.642*	748.4	−2.2	2.1
1.444	52.722	609.9	−1.2	1.7
	102.941*	524.3	−0.7	2.1
	52.722	607.5	1.2	1.7
	107.952*	517.3	−0.2	2.1
1.227	49.323	490.0	4.2	1.7
	47.748	499.0	−1.0	1.7
1.005	38.963	445.0	−1.1	1.3
	41.216	437.0	0.7	1.3
0.794 5	46.717	392.0	1.3	1.4
	50.937	382.0	1.3	1.4
0.639 0	32.856	431.0	1.8	1.6
	34.928	428.0	−1.6	1.6
0.476 3	27.731	473.0	−5.8	2.0
	26.564	474.0	−2.6	2.0
0.360 6	23.387	501.0	−0.4	2.2
	24.030	495.0	3.1	2.2
0.249 6	15.117	549.0	1.7	2.9
	16.185	542.0	3.1	2.9
0.159 9	11.149	569.0	−2.1	3.4
	10.890	568.0	0.7	3.4
0.100 4	6.4161	563.0	9.3	3.9
	6.7808	562.0	7.0	3.9
0.042 21	3.6328	517.0	−16.0	10.0
	3.1082	497.0	11.2	10.0
0.010 50	0.6947	416.0	−56.6	10.0
	0.7110	406.0	−47.1	10.0
0.002 023	11.785^b	43.5	0.8	4.9
0.001 818	8.602	62.3	−5.3	4.9
0.001 746	8.976	48.8	1.9	4.2
0.001 752	8.726	53.0	−0.1	4.2
0.002 905	14.977	55.4	4.6	5.7
0.002 982	14.969	65.8	−3.1	5.7
0.003 409	17.548	62.9	0.3	5.4
0.003 449	17.073	67.5	−0.7	5.4
0.003 044	15.896	63.4	−3.6	3.8
0.002 789	13.242	69.4	−3.7	2.9
0.002 858	14.130	64.3	−1.3	2.9
0.004 044	19.705	74.2	−2.7	3.4
0.004 120	18.992	77.8	−1.0	3.4
0.003 964	20.268	70.2	−3.4	2.5
0.004 018	20.784	70.5	−4.5	2.5
0.005 974	29.452	81.0	−2.3	2.6
0.005 871	27.626	84.9	−1.9	2.6
0.007 264	35.117	86.4	−1.5	2.3
0.007 198	33.339	91.5	−2.3	2.3
0.010 80	52.722	90.2	1.4	2.3
0.010 29	52.722	85.6	−0.5	2.3

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}
	Samarium Perchlorate			
4.640	5.8309	6275.6	16.6	2.2
	11.675*	6240.2	6.5	3.1
	5.6833	6306.4	−12.8	2.2
	11.562*	6266.0	−18.6	3.2
4.324	7.6591	5478.4	−0.5	2.6
	16.190*	5423.2	−0.1	3.9
	7.6784	5475.7	2.0	2.6
	15.851*	5428.2	−3.3	3.8
4.006	8.9919	4748.3	7.9	2.7
	19.360*	4695.9	0.8	4.1
	9.8104	4741.4	8.8	2.8
	20.158*	4693.6	−0.5	4.1
3.433	11.142	—	—	—
	22.168*	3555.4	−9.3	2.7
	10.706	3606.2	−0.5	2.4
	21.936*	3554.8	−7.7	3.4
3.051	12.445	2913.6	−7.2	2.2
	25.233*	2852.2	−6.5	3.1
	12.282	2909.5	−2.1	2.2
	25.487*	2838.6	6.1	3.2
2.560	18.103	2072.6	3.0	2.3
	36.291*	2006.2	2.2	3.1
	17.368	2078.6	0.6	2.2
	35.564*	2009.2	1.4	3.1
2.244	24.360	1596.7	4.2	2.3
	48.619*	1525.1	2.9	3.1
	24.435	1594.2	6.4	2.3
	49.134*	1523.3	3.4	3.2
1.942	27.329	1221.6	0.9	2.0
	54.538*	1146.9	0.4	2.6
	27.060	1218.9	4.6	2.0
	54.352*	1146.0	1.7	2.6
1.693	28.296	974.6	−4.9	1.6
	57.129*	894.0	−1.7	2.2
	28.517	964.4	4.5	1.6
	57.302*	886.4	5.5	2.2
	31.239	956.2	3.5	2.1
	31.853	957.7	0.0	1.8
	64.108*	878.0	0.2	2.4
1.444	28.074	780.6	−6.0	1.3
	56.148*	703.6	−5.1	1.7
	27.886	778.2	−2.9	1.3
	55.836*	702.1	−2.9	1.7
1.286	50.548	615.7	0.2	2.2
	50.595	615.4	0.4	2.2
1.107	53.342	526.0	3.2	2.0
	55.428	523.0	1.6	2.1
0.922 6	74.409	431.6	3.1	2.3
	75.341	431.0	2.1	2.3
0.747 4	75.504	403.3	4.0	2.2
	77.632	398.9	4.8	2.2
0.611 6	71.874	406.4	1.4	2.1
	70.637	407.2	2.8	2.1
0.498 1	56.991	439.8	−1.1	1.8
0.498 1	57.219	438.5	−0.3	1.8
0.375 2	47.588	465.2	0.2	1.6
	51.519	457.5	−1.4	1.7
0.249 7	32.099	508.8	−0.6	1.2
	26.838	528.7	−2.5	1.7
	28.641	518.6	1.2	1.6
0.211 9	28.533	516.5	−0.7	1.6
	30.518	509.1	−0.1	1.4
0.143 6	22.164	521.5	−2.2	2.2
	23.648	512.1	1.2	2.1
0.092 45	15.723	509.0	0.7	3.0
	16.001	501.6	6.7	3.0
0.048 85	8.4845	475.3	1.1	3.8
	8.4092	480.4	−3.4	3.8
0.001 168	5.831[b]	35.4	10.1	3.4
0.001 156	5.683	40.5	5.8	3.4
0.001 619	7.659	55.2	−0.4	4.2
0.001 585	7.678	47.5	5.3	4.0
0.001 936	8.992	52.4	7.2	4.3
0.002 016	9.810	47.8	9.4	4.4
0.002 194	10.706	51.5	7.2	3.7
0.002 523	12.445	61.4	−0.7	3.4
0.002 549	12.282	70.9	−8.2	3.4
0.003 629	18.103	66.4	0.8	3.4
0.003 556	17.368	69.4	−0.8	3.3
0.004 862	24.360	71.6	1.3	3.4
0.004 913	24.435	70.9	2.9	3.4
0.005 454	27.329	74.7	0.6	2.9
0.005 435	27.060	72.9	2.9	2.9
0.005 713	28.296	80.6	−3.2	2.4
0.005 730	28.517	78.0	−1.0	2.4
0.006 411	31.853	79.7	−0.2	2.6
0.005 615	28.074	77.1	−1.0	1.9
0.005 584	27.886	76.1	0.0	1.8
	Gadolinium Perchlorate			
4.611	8.4681	6799.0	2.1	4.0
	8.3175	6807.0	−4.7	4.0
4.205	6.9064	5852.2	4.0	2.4
	13.631*	5802.1	5.7	3.0
	6.8225	5862.0	−5.1	2.8
3.827	7.9580	5035.6	1.0	2.5
	16.176*	4980.8	2.4	3.0
	8.0826	5040.6	−5.0	2.5
	16.257*	4982.9	−0.1	3.0
3.499	12.180	4352.0	−6.1	3.6
	12.180	4351.9	−6.0	3.1
	23.668*	4289.1	−0.9	3.8
3.104	17.682	3559.6	3.8	3.5
	33.513	3496.6	4.2	4.3
	17.497	3557.7	6.7	3.5
	33.443*	3495.4	5.6	4.3
2.891	14.723	3200.0	−5.7	4.1
	14.608	3197.2	−2.2	3.5
	27.720*	3139.7	−3.7	4.3
2.389	21.013	2324.1	4.0	2.8
	41.409*	2249.4	8.0	3.4
2.074	24.621	1849.3	5.7	2.7
	49.365*	1775.1	3.7	3.3
	24.552	1853.2	2.1	2.7
	49.351*	1774.2	4.6	3.3
1.823	29.724	1523.4	−6.7	2.5
	58.049*	1445.6	−6.1	3.1
	29.692	1522.4	−5.6	2.5
	57.866*	1444.1	−4.2	3.1
1.556	14.846	1299.5	−6.5	1.7
	24.275*	1258.1	−9.4	2.1
	14.907	1293.4	−0.7	1.7
	24.433*	1251.9	−3.9	2.1
	38.900	1198.1	0.9	1.7
	74.667*	1115.2	3.0	2.1
	39.075	1194.7	3.8	1.7
	74.822*	1113.9	4.1	2.1
1.320	42.107	981.9	0.6	2.0
	89.302*	884.2	2.1	2.4
	41.977	—	—	—
	89.246*	884.5	1.9	2.1
	21.884	1052.3	−1.0	2.0
	32.422*	1015.4	−3.8	2.4
1.081	20.702	894.8	−1.0	1.3
	32.138*	850.6	−0.7	1.6
	20.967	892.8	−0.2	1.3
	31.956*	852.9	−2.4	1.6
	43.957	809.0	5.8	1.5
	43.957	812.0	2.8	1.5
0.918 2	56.010	694.0	7.7	2.2
	56.355	696.0	5.0	2.2
	30.669	767.0	4.1	2.2
	30.980	768.0	2.1	2.2

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}
0.733 0	30.492	696.0	5.4	1.5
	30.437	703.0	−1.4	1.5
	25.261	717.0	3.7	1.5
	24.800	732.0	−9.5	1.5
0.552 5	38.465	629.0	0.5	1.5
	38.490	632.0	−2.6	1.5
	24.315	680.0	−2.2	1.5
	24.384	677.0	0.5	1.5
0.425 6	47.665	580.0	0.4	1.7
	47.790	582.0	−1.9	1.7
	32.558	625.0	−1.3	1.7
	32.627	625.0	−1.6	1.7
0.327 5	38.143	589.0	−0.9	1.5
	38.155	589.0	−0.9	1.5
	27.552	621.0	1.9	1.5
	27.426	625.0	−1.6	1.5
0.198 2	28.228	578.0	4.9	1.3
	30.305	580.0	−4.4	1.3
	28.633	582.0	−0.5	1.3
0.113 2	14.784	582.0	1.7	2.8
	15.265	570.0	11.0	2.8
	15.571	575.0	4.4	2.8
0.059 15	8.3290	526.0	10.1	3.7
	8.3810	535.0	0.7	3.7
	8.6671	525.0	8.4	3.7
0.001 363	6.906^b	50.1	−1.8	3.3
0.001 626	8.083	57.7	−4.9	3.3
0.001 618	7.958	54.8	−1.4	3.3
0.002 367	12.180	62.8	−5.1	4.2
0.002 772	14.608	57.5	1.5	4.8
0.003 344	17.497	62.3	1.0	4.8
0.003 351	17.682	63.0	−0.4	4.8
0.004 141	21.013	74.7	−4.1	3.8
0.004 935	24.552	79.0	−2.5	3.6
0.004 936	24.621	74.2	2.0	3.6
0.005 787	29.692	78.3	−1.4	3.4
0.005 805	29.724	77.8	−0.6	3.4
0.007 482	39.075	80.8	−0.3	2.3
0.007 467	38.900	82.9	−2.2	2.3
0.002 443	14.907	41.5	3.1	2.3
0.002 428	14.846	41.4	3.0	2.3
0 003 242	21.884	36.9	2.7	2.7
0.008 930	42.107	97.7	−1.5	2.7
0.003 196	20.967	39.9	2.2	1.8
0.003 214	20.702	44.2	−0.3	1.8
Dysprosium Perchlorate				
4.602	5.2175	7404.8	14.1	2.4
	10.478*	7374.7	0.6	3.3
	5.4583	—	—	—
	10.659*	7393.0	−19.0	2.7
4.317	5.6414	6747.9	−0.2	2.3
	11.280*	6709.6	−6.5	3.3
4.044	5.9287	6111.8	7.8	2.2
	11.799*	6077.4	−2.9	3.1
	6.0749	6114.2	4.0	2.3
	12.087*	6077.1	−4.4	3.2
3.537	6.3788	4991.2	−3.9	1.9
	6.2727	4991.7	−3.4	1.9
2.869	10.398	3567.7	7.9	2.2
	20.128*	3519.9	3.0	3.0
	9.6409	3582.9	−2.0	2.1
	19.186*	3534.2	−7.1	2.9
2.561	13.498	2980.8	−1.7	2.4
	26.606*	2921.4	−1.7	3.3
	13.508	2975.0	4.1	2.4
	27.039*	2914.8	3.3	3.4
2.303	16.039	2513.4	3.1	2.4
	32.242*	2448.1	3.5	3.4
	16.232	2516.3	−0.7	2.5
	32.599*	2450.9	−0.4	3.4
2.086	19.316	2152.3	0.5	2.5
	38.258*	2086.7	−1.1	3.4
	18.638	2156.1	−0.1	2.4
	37.514*	2088.4	−0.7	3.3
1.792	19.400	1728.7	0.8	2.0
	39.588*	1656.9	2.0	2.8
	19.070	1731.0	0.0	2.0
	38.574*	1662.6	−0.9	2.8
1.680	22.096	1572.5	1.7	2.1
	44.459*	1499.2	3.1	2.8
	21.991	1579.4	−4.8	2.1
	43.943*	1506.6	−2.9	2.8
1.456	22.059	1317.5	−1.6	1.7
	21.831	1321.6	−4.7	1.8
	45.171*	1242.1	0.0	2.4
1.190	23.448	1061.9	−1.9	1.5
	46.767*	987.7	0.2	2.0
	23.619	1060.3	−1.0	1.5
	47.036*	989.6	−2.4	2.0
1.069	26.485	952.7	2.2	1.5
	52.545*	879.7	1.0	2.0
	26.601	956.4	−2.0	1.5
	54.491*	875.9	0.5	2.1
0.923 9	26.664	862.4	−1.8	1.4
	54.708*	781.1	1.2	1.8
	26.269	854.6	7.4	1.4
	54.371*	773.8	9.2	1.8
0.745 8	38.423	733.2	0.1	1.6
	76.227*	647.6	3.6	2.1
	37.128	740.2	−3.1	1.6
	75.236*	656.6	−3.7	2.1
0.588 5	40.862	671.9	−3.0	2.0
	40.237	674.7	−4.0	2.0
0.509 0	53.171	611.6	4.0	2.3
	53.369	616.4	−1.3	2.4
	34.727	665.4	−1.8	1.7
	37.908	656.3	−2.1	1.8
0.402 1	41.910	617.5	−1.8	1.9
	46.014	603.9	1.2	2.0
0.244 1	31.310	599.5	0.6	1.4
	32.842	596.7	−1.5	1.5
0.163 2	23.187	586.4	0.1	1.8
	24.461	577.7	3.7	1.7
0.104 5	16.709	556.2	1.7	2.7
	16.799	555.5	2.0	2.7
0.040 46	6.6273	484.5	−5.8	4.0
	6.5234	483.1	−3.5	4.0
0.001 048	5.218^b	30.1	13.6	3.6
0.001 128	5.641	38.3	6.4	3.5
0.001 180	5.929	34.4	10.7	3.3
0.001 209	6.075	37.1	8.4	3.4
0.002 013	10.398	47.8	5.0	3.2
0.001 919	9.641	48.6	5.2	3.2
0.002 661	13.498	59.5	−0.1	3.6
0.002 704	13.508	60.1	0.9	3.6
0.003 224	16.039	65.3	−0.4	3.6
0.003 260	16.232	65.4	−0.3	3.7
0.003 826	19.316	65.7	1.5	3.6
0.003 751	18.638	67.8	0.4	3.6
0.003 959	19.400	71.9	−1.3	3.1
0.003 857	19.070	68.4	0.9	3.0
0.004 446	22.096	73.2	−1.3	3.1
0.004 394	21.991	72.8	−1.8	3.1
0.004 517	21.831	79.5	−4.7	2.6
0.004 677	23.448	74.2	−2.1	2.2
0.004 704	23.619	70.7	1.4	2.2
0.005 255	26.485	72.9	1.2	2.2
0.005 449	26.601	80.5	−2.4	2.2
0.005 471	26.664	81.3	−3.0	2.0
0.005 437	26.269	80.8	−1.8	2.0
0.007 623	38.423	85.7	−3.6	2.3
0.007 524	37.128	83.6	0.5	2.3

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}
		Erbium Perchlorate		
4.627	8.8685	7399.3	0.1	3.0
	17.514*	7338.0	10.2	3.6
	8.3348	7400.0	3.5	3.0
	17.156*	7350.0	−0.1	3.6
4.215	15.817	6396.4	−4.7	4.8
	32.274*	6323.8	2.3	5.9
	10.824	6431.7	−11.0	4.8
	21.716*	6372.1	−7.7	5.9
	10.883	6435.2	−14.9	4.8
	23.098*	6367.8	−9.1	5.9
	10.272	6446.0	−21.6	5.6
3.413	8.6966	4648.9	−3.0	2.6
	18.207*	4579.9	10.2	3.1
	8.6554	4651.2	−5.0	2.6
	18.284*	4575.6	14.1	3.1
3.086	9.3086	3963.2	−4.5	2.9
	20.458*	3880.7	16.6	3.5
	9.1930	3956.2	3.4	2.9
	19.272*	3890.6	11.9	3.5
	9.2294	3965.0	−5.7	3.3
	14.493	3929.4	−3.2	2.9
	28.794*	3865.8	−0.7	3.5
	14.432	3925.3	1.3	2.9
	29.074*	3867.6	−3.5	3.5
2.676	16.540	3113.7	0.9	3.1
	33.397*	3043.8	5.4	3.8
	16.557	3117.7	−3.1	3.1
	33.281*	3052.0	−2.5	3.8
2.358	36.518	2468.5	3.8	4.8
	68.145*	2392.9	6.9	5.9
	36.724	2469.6	2.1	4.8
	68.096*	2391.8	8.1	5.9
2.033	39.930	1957.2	−14.4	4.4
	78.925*	1874.7	−13.5	5.4
	40.196	1959.4	−17.3	4.4
	78.997*	1875.2	−14.1	5.4
1.700	32.501	1508.3	−0.7	2.9
	67.191*	1425.9	−1.2	3.5
	32.753	1508.3	−1.5	2.9
	67.273*	1418.7	5.9	3.5
1.498	44.409	1243.5	−4.0	3.2
	92.641*	1149.5	−1.0	3.9
	44.316	1244.3	−4.5	3.2
	91.968*	1149.0	0.5	3.9
1.227	53.978	—	—	—
	114.426*	867.7	−6.6	3.3
	53.802	956.7	2.3	3.0
	115.434*	854.4	5.5	3.7
	53.978	961.6	−2.9	3.0
	114.105*	860.6	0.9	3.7
	53 451	960.0	−0.2	3.4
1.055	59.013	815.0	4.3	3.6
	56.912	820.0	3.7	3.6
	57.093	825.0	−1.7	3.6
	57.851	819.0	2.7	3.6
	76.668	781.0	5.5	3.6
	76.825	782.0	4.3	3.6
0.840 8	80.407	653.0	6.1	3.2
	79.959	656.0	3.8	3.2
	59.413	697.0	0.2	3.2
	59.614	692.0	4.8	3.2
	59.506	696.0	1.1	3.2
0.662 6	35.402	681.0	5.3	2.1
	35.426	687.0	−0.8	2.1
	35.402	689.0	−2.7	2.1
	61.450	618.0	5.3	2.1
	61.450	620.0	3.3	2.1
0.512 9	32.879	651.0	2.2	1.6
	32.696	656.0	−2.2	1.6
	32.684	655.0	−1.2	1.6
	32.971	656.0	−3.1	1.6
0.360 3	40.145	603.0	−4.6	1.7
	40.094	599.0	−0.4	1.7
	39.980	599.0	−0.1	1.7
	39.930	600.0	−1.0	1.7
	33.143	622.0	−3.1	1.7
	33.109	620.0	−1.0	1.7
0.230 7	6.4567	712.7	−0.9	2.7
	12.496*	666.9	0.7	3.3
	6.2500	717.1	−3.4	2.7
	12.510*	665.4	2.1	3.3
	22.753	615.0	2.5	3.1
	25.020	609.0	−0.4	3.1
0.202 9	27.019	588.0	0.7	1.6
	19.598	621.0	−2.6	1.6
	28.966	581.0	0.8	1.6
0.115 4	14.646	560.0	16.0	2.9
	15.801	552.0	17.9	2.9
0.001 716	8.335[b]	50.0	3.6	4.0
0.001 751	8.868	61.3	−10.1	4.0
0.002 310	10.883	67.4	−5.8	6.5
0.002 172	10.824	59.6	−3.3	6.5
0.003 227	15.817	72.6	−7.0	6.5
0.001 828	8.655	75.6	−19.1	3.5
0.001 821	8.697	69.0	−13.2	3.5
0.002 907	14.432	57.7	4.7	3.9
0.002 879	14.493	63.6	−2.5	3.9
0.001 927	9.193	65.6	−8.6	3.9
0.002 046	9.309	82.5	−21.0	3.9
0.003 328	16.557	65.7	−0.7	4.2
0.003 340	16.540	69.9	−4.4	4.2
0.006 810	36.724	77.8	−6.0	6.6
0.006 815	36.518	75.6	−3.1	6.6
0.007 900	40.196	84.2	−3.2	6.0
0.007 893	39.930	82.5	−0.9	6.0
0.006 727	32.753	89.6	−7.3	3.9
0.006 719	32.501	82.4	0.5	3.9
0.009 197	44.316	95.3	−5.0	4.3
0.009 264	44.409	94.0	−3.0	4.3
0.011 41	53.978	101.0	−3.9	4.0
0.011 54	53.802	102.3	−3.1	4.0
0.001 251	6.250	51.7	−5.5	3.6
0.001 250	6.457	45.8	−1.6	3.6
		Lutetium Perchlorate		
4.634	11.096	7233.1	−4.4	4.7
	21.874*	7175.9	−2.6	5.8
	11.062	7229.0	−0.1	4.7
	22.212*	7166.4	5.5	5.8
4.039	14.319	5851.2	−6.7	5.1
	29.225*	5772.3	8.5	6.3
	14.992	5828.6	12.3	5.1
	30.714*	5759.0	16.8	6.3
3.567	12.076	4829.5	−12.3	3.7
	26.657*	4753.1	−3.7	4.5
	12.795	4815.9	−3.1	3.7
	24.621*	4760.6	−3.5	4.5
3.196	12.681	4045.3	−11.0	3.1
	24.493*	3985.1	−6.7	3.8
	14.799	4013.5	8.8	3.1
	27.479*	3963.4	3.9	3.8
2.870	11.202	3392.0	4.7	2.8
	12.027	3386.9	4.5	2.4
	24.671*	3327.3	3.5	3.0
2.529	20.867	2713.7	4.3	3.0
	38.390*	2653.9	3.8	3.2
	18.250	—	—	—
	36.132*	2663.0	1.2	3.9
2.232	16.941	2236.3	2.0	2.5
	31.764*	2178.9	1.0	3.0
1.980	17.181	1863.7	−6.1	1.6
	35.713*	1791.3	−3.1	1.9
	17.741	—	—	—
	35.617*	1790.7	−2.3	1.7

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}
1.676	23.561	1431.6	0.7	2.0
	47.458*	1358.3	1.2	2.4
	22.307	1436.3	1.1	2.0
	46.690*	1359.0	2.4	2.4
1.432	27.741	1152.8	−1.0	1.9
	55.249*	1074.4	2.4	2.3
	26.988	1153.7	0.8	1.9
	56.355*	1069.9	4.6	2.3
1.174	35.653	902.6	1.0	1.7
	64.609*	831.6	3.5	2.1
	32.024	914.3	0.5	2.0
1.006	36.216	792.5	−2.1	1.6
	69.789*	713.1	0.8	1.9
	36.192	792.4	−2.0	1.6
	71.944*	709.1	1.0	1.9
0.806 8	54.716	645.0	0.9	2.5
	53.832	648.0	−0.2	2.5
0.640 9	51.251	595.0	3.9	2.2
	50.623	599.0	1.3	2.2
0.494 4	36.084	609.0	−2.8	1.6
	37.259	607.0	−4.2	1.6
0.358 6	26.615	614.0	0.5	1.3
	27.783	610.0	0.3	1.3
0.249 6	11.683	656.0	4.9	2.9
	13.690	650.0	−1.1	2.9

m_i	$10^4\ m_f$	$-\Delta H_{i,f}$, cal mol^{-1}	Exptl − calcd cal mol^{-1}	σ, cal mol^{-1}
0.154 6	9.3269	635.0	−0.6	3.5
	8.8209	633.0	5.1	3.5
0.098 80	5.7696	603.0	8.0	3.9
	6.3706	601.0	4.2	3.9
0.067 17	5.7360	560.0	−2.5	10.0
	4.9640	570.0	−4.6	10.0
0.009 869	0.9187	363.0	−20.4	10.0
0.002 221	11.062	62.6	−5.6	6.4
0.002 187	11.096[b]	57.2	−1.9	6.4
0.003 071	14.992	69.6	−4.6	7.0
0.002 922	14.319	78.9	−15.2	7.0
0.002 462	12.795	55.3	0.5	5.0
0.002 666	12.076	76.4	−8.7	5.0
0.002 748	14.799	50.1	4.9	4.2
0.002 449	12.681	60.2	−4.2	4.2
0.002 467	12.027	59.6	1.0	3.3
0.003 839	20.867	59.8	0.5	3.6
0.003 176	16.941	57.4	1.0	3.3
0.003 571	17.181	72.4	−2.9	2.1
0.004 669	22.307	77.3	−1.3	2.7
0.004 746	23.561	73.3	−0.5	2.7
0.005 636	26.988	83.8	−3.7	2.5
0.005 525	27.741	78.4	−3.4	2.5
0.006 461	35.653	71.0	−2.6	2.3
0.007 194	36.192	83.3	−2.9	2.1
0.006 979	36.216	79.4	−3.0	2.1

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

Table II. Heats of Solution of Some Rare Earth Perchlorate 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
$La(ClO_4)_3 \cdot 8H_2O$	5.693	9 305.4	145.2	9450.6
	12.454*[a]	9 239.3	203.0	9442.3
	5.741	9 258.5	145.7	9404.2
	11.861*	9 207.9	198.9	9406.8
			Average	9426 ± 21
$Nd(ClO_4)_3 \cdot 8H_2O$	6.061	9 304.7	134.7	9439.4
	15.155*	9 232.5	198.3	9430.8
	8.952	9 239.6	159.2	9398.8
	14.123*	9 201.1	192.6	9393.7
			Average	9416 ± 20
$Gd(ClO_4)_3 \cdot 8H_2O$	8.439	10 068.4	157.0	10225.4
	11.951*	10 054.8	182.0	10236.8
	6.381	10 135.9	139.2	10275.1
	13.727*	10 067.2	192.9	10260.1
			Average	10249 ± 19
$Er(ClO_4)_3 \cdot 8H_2O$	3.667	13 333.3	107.4	13440.7
	2.088	13 306.8	83.6	13390.4
			Average	13416 ± 26

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

limiting law power in molality. Third, approximately equally good fits were obtained whether A_1 was fixed at the limiting slope, 6990 (3), or allowed to vary. Therefore A_1 was fixed at the limiting law value. Fourth, all the possible fits with combinations of six multiples of $m^{1/4}$ between $m^{3/4}$ and $m^{16/4}$ were performed. The final powers were chosen from those fits with low reduced χ^2 values, subject to the constraint that adjacent rare earth perchlorates should have similar sets of powers as far as possible.

It should be pointed out that the coefficients in eq 13 cannot be determined using standard least-squares programs, since there are two independent variables, m_i and m_f; specifically, the independent variable terms are not $(\Delta m)^{p_i}$. However, linear least-squares regression analysis can still be used if the two independent variables are incorporated into the matrix building steps.

The advantages of the present method of data treatment are twofold. First, the two-step $\bar{P}_i$ analysis is reduced to a simple and direct one-step fit of the measured ΔH values. Second, the whole data set is fitted to one least-squares equation, avoiding discontinuities in ϕ_L and derived quantities which occur when the data set is fitted in segments. These advantages depend on the existence of empirical equations that are capable of fitting the data within the statistical errors in the data, in addition to extrapolating to zero concentration correctly. Even if such equations cannot be found, the $\bar{P}_i$ fit, eq 10, can still be replaced

Table III. Parameters for Equations 11 and 13

Salt[a]	p_2 A_2	p_3 A_3	p_4 A_4	p_5 A_5	p_6 A_6	p_7 A_7
	1.00	1.25	1.50	1.75	2.75	4.00
$La(ClO_4)_3$	−53 930.420	119 602.8009	−110 785.3187	39 847.259 9	−849.299 91	17.608 558
	0.75	1.25	2.00	3.25	3.75	4.00
$Pr(ClO_4)_3$	−9 866.816	4 762.0196	−1 736.5413	1 487.968 31	−1 465.468 192	587.561 198
	0.75	1.25	2.00	3.25	3.75	4.00
$Nd(ClO_4)_3$	−9 789.311	4 543.8264	−1 569.9242	1 354.352 59	−1 330.857 723	532.680 189
	0.75	1.25	2.00	3.25	3.75	4.00
$Sm(ClO_4)_3$	−9 804.321	4 781.3713	−1 733.9837	1 417.622 61	−1 387.953 071	555.814 673
	0.75	1.25	2.00	3.25	3.75	4.00
$Gd(ClO_4)_3$	−9 422.495	4 341.3987	−1 245.6835	1 005.995 37	−985.614 470	394.371 910
	0.75	1.25	2.00	2.25	2.50	2.75
$Dy(ClO_4)_3$	−9 989.583	7 097.0994	−20 609.1495	32 196.835 6	−18 034.138 58	3504.302 75
	0.75	1.25	2.00	2.25	2.50	2.75
$Er(ClO_4)_3$	−10 126.464	7 609.3830	−23 931.1872	37 654.248 2	−21 236.443 33	4157.844 04
	0.75	1.25	2.00	2.25	2.50	2.75
$Lu(ClO_4)_3$	−10 064.327	7 102.3011	−20 755.8581	32 350.593 8	−18 042.102 01	3484.477 10

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

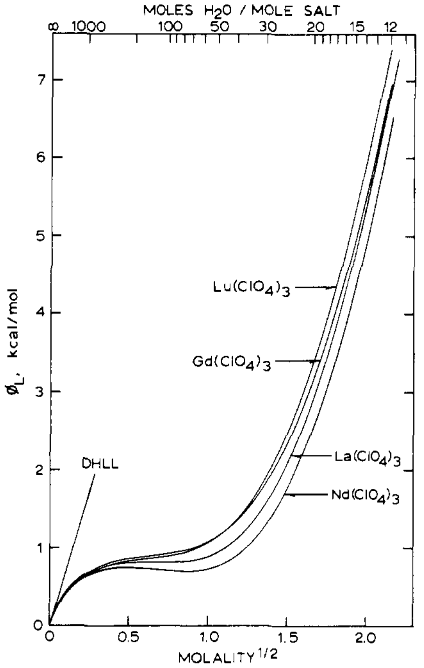

Figure 3. Relative apparent molal heat content of some aqueous rare earth perchlorates: from eq 11; DHLL, Debye–Hückel limiting law.

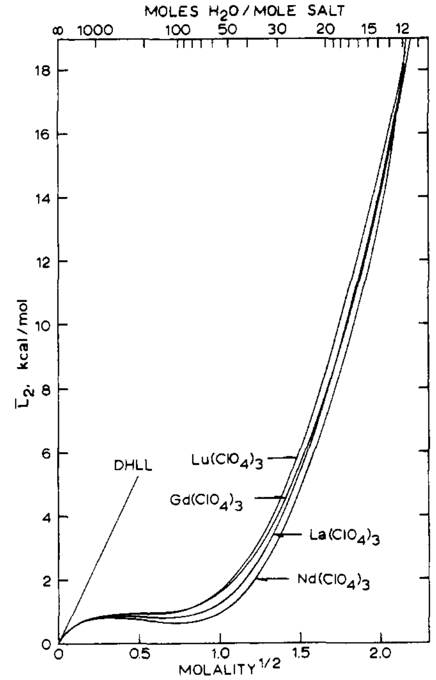

Figure 4. Relative partial molal heat content of some aqueous rare earth perchlorates: from eq 11; DHLL, Debye–Hückel limiting law.

by the ΔH fit, eq 13, where the $\Delta H_{i,f}$ values are restricted to the "short chords", $\Delta H_{3,2}$. This avoids the error introduced by the approximation to the derivative, indicated in eq 10.

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

$$\bar{L}_2 = \phi_L + m \left(\frac{\partial \phi_L}{\partial m}\right)_{T,P,n_1} \tag{14}$$

$$\bar{L}_1 = \frac{-M_1 m^2}{1000} \left(\frac{\partial \phi_L}{\partial m}\right)_{T,P,n_1} \tag{15}$$

where M_1 is the molecular weight of water, 18.0154 g mol^{-1}. Graphs of ϕ_L, $\bar{L}_2$, and $\bar{L}_1$ for representative rare earths are shown in Figures 3, 4, and 5.

The heats of solution to infinite dilution fo the rare earth perchlorate octahydrates, $-\bar{L}^*$, were calculated from eq 7 and 8, using $\Delta H_{x,f}$ from Table II and with $\phi_L(m_2)$ and $\phi_L(m_3)$ calculated from eq 11. The $\bar{L}^*$ are listed in Table II.

Errors. Random errors in the heat measurements were found to be correlated with the actual heat evolved during a run, q. The standard deviation expected for each ΔH measurement, σ, based on the heat evolved, q, is listed in the fifth column in Table I. These standard deviations in ΔH ranged from σ = 10 cal mol^{-1} for the very few runs where q was less than 0.3 cal, to an optimum of about σ = 1 cal mol^{-1} at q = 1.5 cal, and rising to σ = 4.5 cal mol^{-1} at q = 6 cal. These standard deviations were used to obtain weighting factors, $1/\sigma^2$, for the ΔH fits. The standard deviation of the least-squares fits of ΔH ranged from 4 to 6 cal mol^{-1}. These standard deviations of the fits compare favorably with the standard deviations of the experimental ΔH values, and indicate that the systematic deviations of the experimental ΔH values from the equations were very small.

In order to determine the propagation of the random errors, σ, in ΔH, to the derived quantities ϕ_L, $\bar{L}_1$, and $\bar{L}_2$, a random variable technique was used (*3*). In Table IV we list ϕ_L, $(d\phi_L/$

Table IV. Thermodynamic Properties and Errors for $La(ClO_4)_3$ Solutions at 25 °C

Molality	ϕ_L, cal mol^{-1}	$d\phi_L/dm^{1/2}$	$-\bar{L}_1$, cal mol^{-1}	$\bar{L}_2$, cal mol^{-1}
0.001 794	235.7 ± 5.1	4 483.2 ± 39.9	0.003 07 ± 0.000 03	330.6 ± 5.2
0.002 625	273.9 ± 5.4	4 141.8 ± 33.4	0.005 02 ± 0.000 04	380.0 ± 5.5
0.003 678	311.4 ± 3.5	3 818.2 ± 27.5	0.007 67 ± 0.000 06	427.2 ± 3.6
0.005 011	348.5 ± 8.2	3 506.7 ± 22.3	0.011 20 ± 0.000 07	472.6 ± 8.2
0.006 410	379.8 ± 2.4	3 250.6 ± 18.2	0.015 03 ± 0.000 08	509.9 ± 2.5
0.009 061	426.1 ± 2.8	2 882.5 ± 13.1	0.022 39 ± 0.000 10	563.3 ± 2.9
0.010 27	443.4 ± 10.0	2 748.0 ± 11.5	0.025 76 ± 0.000 11	582.7 ± 10.0
0.039 91	636.2 ± 10.0	1 361.1 ± 9.0	0.097 75 ± 0.000 64	772.1 ± 10.0
0.089 12	735.0 ± 3.7	712.7 ± 7.6	0.170 8 ± 0.001 8	841.4 ± 3.9
0.161 1	787.7 ± 3.2	345.9 ± 4.9	0.201 5 ± 0.002 8	857.1 ± 3.4
0.250 0	810.6 ± 2.7	134.4 ± 4.6	0.151 4 ± 0.005 2	844.2 ± 2.9
0.350 4	817.2 ± 1.8	22.8 ± 4.9	0.042 6 ± 0.009 2	823.9 ± 2.3
0.493 9	817.2 ± 1.6	0.1 ± 4.5	0.000 ± 0.014	817.3 ± 2.2
0.644 8	821.3 ± 1.3	103.4 ± 3.7	0.482 ± 0.017	862.9 ± 2.0
0.816 7	842.7 ± 1.3	344.9 ± 3.1	2.293 ± 0.020	998.5 ± 1.9
1.005	894.4 ± 1.7	726.8 ± 2.8	6.596 ± 0.025	1 258.7 ± 2.2
1.176	970.8 ± 1.7	1 153.3 ± 2.6	13.248 ± 0.029	1 596.1 ± 2.2
1.465	1166.5 ± 2.3	1 988.2 ± 2.4	31.756 ± 0.039	2 369.7 ± 2.8
1.733	1421.1 ± 2.3	2 831.3 ± 2.8	58.184 ± 0.057	3 284.7 ± 2.9
1.982	1716.0 ± 2.4	3 630.5 ± 3.2	91.252 ± 0.081	4 251.6 ± 3.3
2.238	2071.5 ± 3.0	4 437.6 ± 3.4	133.83 ± 0.10	5 390.8 ± 4.0
2.565	2591.6 ± 2.9	5 415 ± 3.3	200.39 ± 0.12	6 928.1 ± 3.9
2.902	3191.1 ± 3.2	6 338.7 ± 3.8	282.27 ± 0.17	8 590.2 ± 4.6
3.255	3873.3 ± 3.0	7 210.6 ± 5.4	381.43 ± 0.29	10 377.8 ± 5.7
3.581	4541.7 ± 6.7	7 944.0 ± 6.4	484.91 ± 0.39	12 058.1 ± 9.1
4.093	5651.0 ± 4.4	9 032.3 ± 6.2	673.72 ± 0.46	14 787.8 ± 7.7
4.465	6499.8 ± 3.1	9 861.9 ± 15.6	838.1 ± 1.3	16 919.1 ± 16.8
4.791	7277.6 ± 4.2	10 693.6 ± 35.8	1010.1 ± 3.4	18 980.9 ± 39.4

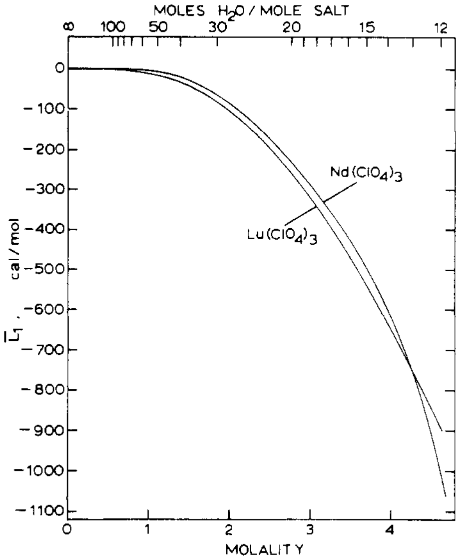

Figure 5. Relative partial molal heat content of water in some aqueous rare earth perchlorates, from eq 11.

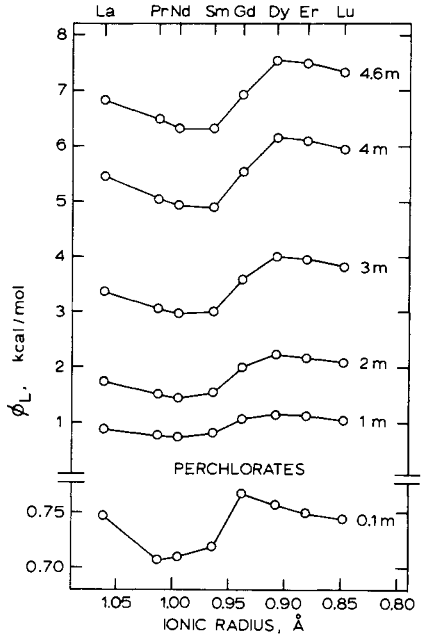

Figure 6. Relative apparent molal heat content of some aqueous rare earth perchlorates, from eq 11.

$dm^{1/2}$), $\bar{L}_1$, and $\bar{L}_2$ for $La(ClO_4)_3$ as calculated fom eq 11, 14, and 15, together with the standard deviations expected in these quantities. The random errors in ϕ_L are equal to the random errors in ΔH for the same concentration. Even though the errors in ϕ_L are rather uniform over the whole concentration range, the errors for the derivative of ϕ_L increase at both ends of the data set. This reflects the fact that the equation is not constrained as well at the endpoints as in the center of the data set.

In addition to the above random errors, the following systematic errors should be noted. The possible error in the calorimeter calibration is about 0.2% in ΔH (and ϕ_L), which amounts to at most 20 cal. The error due to 0.1% error in the concentration of the solutions ranges from being negligible at low concentrations, to 10 cal at the highest concentrations. From a comparison of the results from the $\bar{P}_i$ analysis and the results of various ΔH fits tried, we feel the extrapolation to infinite dilution results in a possible error of at most 10 cal in ϕ_L. In summary, the errors in ϕ_L, $\bar{L}_2$, and $\bar{L}_1$ should be as indicated in Table IV for $La(ClO_4)_3$ with the addition of the above possible systematic errors.

The ϕ_L values for $La(ClO_4)_3$ reported by Vanderzee and Nutter (*19*) are systematically larger than those reported here, the difference increasing to approximately 18 cal. This difference is well within the estimated errors of either data set.

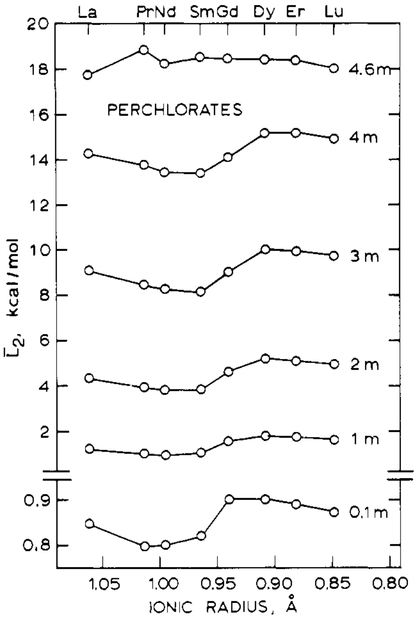

Figure 7. Relative partial molal heat content of some aqueous rare earth perchlorates, from eq 11.

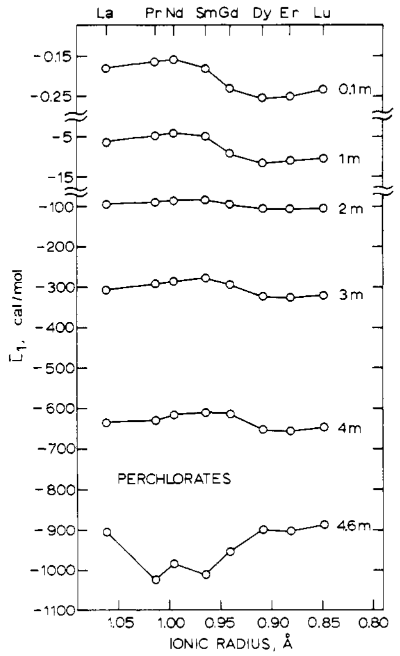

Figure 8. Relative partial molal heat content of water in some aqueous rare earth perchlorates, from eq 11.

Discussion

The general shape of the ϕ_L and $\bar{L}_2$ curves is typical of ϕ_L and $\bar{L}_2$ curves for "normal salts" such as the alkali, alkaline earth, and transition element perchlorates (*20*). As was the case for the dilute solution studies of the rare earth chloride and nitrate solutions (*11, 13*), the rare earth perchlorates approach the Debye-Hückel theoretical behavior in dilute solutions. This was also found by Vanderzee and Nutter for $La(ClO_4)_3$ (*19*). Between approximately 0.1 and 1 *m* the ϕ_L curves go through a pronounced inflection point which is also evident for other perchlorate solutions, although the inflection points occur at higher concentrations for the monovalent and divalent perchlorates. Above 1 *m* the ϕ_L curves rise rapidly to very high values, typical of strongly hydrated ions. When the rare earth perchlorates, $Ca(ClO_4)_2$ (*20*) and $NaClO_4$ (*20*), are plotted on the same graph, the rare earth salts fall about where one would expect them with respect to charge and size of the rare earth ions as a group.

ϕ_L, $\bar{L}_2$, and $\bar{L}_1$ are plotted at even molalities across the rare earth series in Figures 6, 7, and 8, respectively. ϕ_L and $\bar{L}_2$ decrease from La to about Nd, then increase to around Gd-Dy and then decrease again for the rest of the series. This behavior has also been observed in the heat properties of the rare earth chlorides in dilute solutions (*11, 13*), the partial molal volume properties of the rare earth chlorides (*15*), perchlorates (*17*), and nitrates (*16*), and the expansibilities of the rare earth chlorides (*4*). The displacement of these properties in the middle of the rare earth series has been attributed to changes in the inner and outer hydration spheres, caused by a decrease in the number of waters in the inner hydration sphere of the rare earth cations (*14*). Owing to the decreasing size of the rare earth ion, the inner sphere water coordination of Tb to Lu is thought to be lower than the inner sphere water coordination of La to Nd by one water molecule. The ions between Nd and Tb have mixtures of the higher and lower water coordination. The position of the hydration change in the rare earth series at infinite dilution or in very dilute solutions has invariably been between Nd and Tb. At the lowest concentration shown for ϕ_L, $\bar{L}_2$, and $\bar{L}_1$ the position of the break is near these two ions for the rare earth perchlorates.

The fact that the break in the series remains evident over most of the concentration range indicates that the rare earth ions do not form inner sphere rare earth perchlorate complexes, in agreement with commonly held views. However, it does not of course rule out outer sphere ion pairing. The leveling out of $\bar{L}_2$ at 4.6 *m* across the series does appear to be real, since this behavior also occurs in the partial molal volumes of the rare earth perchlorates (*17*). This leveling out at 4.6 *m* in $\bar{L}_2$ does not appear in ϕ_L and points out that the partial molal property often gives information not present in the apparent molal property, particularly at high concentrations.

From graphs of ϕ_L for the alkali and alkaline earth halides and perchlorates (*20*) it becomes immediately evident that ϕ_L decreases quite regularly with increasing ion size for a common cation or anion series. ϕ_L also increases with cation charge for a given cation size. This relationship holds over the whole concentration range for all the salts, and has been quantified for dilute solutions in the case of monovalent and divalent halides by Leung and Millero (*6*). The rare earth perchlorate values fall above the divalent and monovalent perchlorates of similar cation size (i.e., $Ca(ClO_4)_2$ and $NaClO_4$), as expected. However, from Figure 6 it is clear that the ϕ_L-cation size relationship within the rare earth series does not hold for the rare earth perchlorates, since, for a given inner sphere hydration series, ϕ_L decreases with decreasing cation size. Whether this anomaly holds for all trivalent salt solutions will have to await ϕ_L measurements for smaller and larger trivalent cations than the rare earths.

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Vapor–Liquid Equilibrium Constants of Alkylbenzenes in *n*-Alkane Solvents at Infinite Dilution by Gas–Liquid Chromatography

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Vapor–liquid equilibrium constants at infinite dilution of benzene and alkylbenzenes in *n*-octacosane, *n*-dotriacontane, and *n*-hexatriacontane solvents were measured by gas–liquid chromatography at five temperatures, 78.0, 84.0, 90.0, 96.0, and 102.0 °C. The thermodynamic properties of solution of alkylbenzenes from the gas phase to *n*-alkane solvent were also determined from the data of vapor–liquid equilibrium constants. The partial molar enthalpy of solution is related with the structure of alkylbenzenes through an equation by a set of values of structural parameters.

The properties of molecules in liquid phases have been greatly studied by experimental methods of static and dynamic techniques. Theoretical approaches of the behavior of molecules in pure liquids and liquid mixtures are mainly limited to ideal or simple liquid systems. Study for theoretical research demands therefore determining the thermodynamic properties of liquid in simple systems. In liquids consisting of pure substance, molecules frequently have association by hydrogen bonding or other strong intermolecular interaction. The molecular association distorts the liquid phase from the ideal to nonideal liquid system, e.g., polyassociation of alcohols. In solutions at infinite dilution, solute molecules no longer associate with each other, but associate with surrounding solvent molecules since the solute molecule is enveloped by solvent molecules only. Thermodynamic properties of solute molecules are highly dependent on the nature of solvent molecules. The variation of the thermodynamic properties with solvents will give us the characteristics of many interacting abilities of solute molecules, such as dispersion, induced dipole, dipole–dipole interaction, Coulomb force, charge transfer interaction, coordinate bond, and hydrogen bonding energies. Solution at infinite dilution is an ideal state for solute molecules. The properties of the solution are easily combined with current theories of solutions of molecules. Gas–liquid chromatography (GLC) provides the properties at infinite dilution on the basis of GLC conditions. Recently, GLC is a rapid and reliable method for determinination of accurate thermodynamic properties (*1, 2, 4–12, 15–21*).

In this paper, GLC was used here to study alkylbenzenes in three high-molecular-weight normal alkane solvents. Vapor–liquid equilibrium constants at infinite dilution are obtained at five temperatures. Heat of solution from the gas phase to *n*-alkane solvent is also determined and can be given by a relation with structure of the solute molecule by a consistent set of parameters.

Experimental Section

The gas chromatograph used was an Hitachi K53 equipped with a thermal conductivity detector. Column temperatures for measurement of retention volumes are 78.0, 84.0, 90.0, 96.0, and 102.0 °C. The column temperatures were maintained constant within 0.1 °C. Hydrogen was used as a carrier gas. The carrier gas flow rate was measured at room temperature with a soap-film flowmeter placed at the detector outlet. Inlet and outlet pressure of carrier gas was determined to 0.1 mmHg by mercury manometers.

Three stationary liquid phases were used: *n*-octacosane (n-$C_{28}H_{58}$), *n*-dotriacontane (n-$C_{32}H_{66}$), and *n*-hexatriacontane (n-$C_{36}H_{74}$). These phases were obtained from the Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. n-$C_{32}H_{66}$ was purified three times by recrystallization from ethanol, while n-$C_{28}H_{58}$ and n-$C_{36}H_{74}$ were purified once similarly.

Benzene, toluene, ethylbenzene, *p*-, *m*-, and *o*-xylenes, cumene, and 1,3,5-, 1,2,4-, and 1,2,3-trimethylbenzenes were chosen for this study of alkylbenzenes and used without further purification.

The liquid for stationary phase was coated on to solid support material in the usual manner. The solid support used was Celite 545, 80–100 mesh, hexamethyldisilazane (HMDS) treated. The amount of each liquid phase on the support material was changed from 10 to 15 wt %. The coated support material was packed into 1 m × 3 mm i.d. stainless steel tubing. For reference, stationary-liquid-uncoated support material was also packed into different tubing. Each column was conditioned at 110 °C for about 24 h with a gentle flow of a carrier gas. The smallest detectable sample sizes were used at all times so as to ensure operation in the Henry's law region of solute con-

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