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## Hydration Thermodynamics of the Lanthanide Ions

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The solubilities and the heats of solution of the lanthanide iodates have been measured at 25°. From these data the thermodynamic parameters of hydration were calculated. It is proposed that the variations of the entropies of hydration across the lanthanide series support the suggestion of a change in the hydration number of the lanthanide ions somewhere in the middle of the series. The magnitude and trends of these parameters suggest that the variations in thermodynamic properties observed in complexation reactions are often the consequence of the dehydration of the ions rather than of the ligation.

### Introduction

A variety of thermodynamic data on the lanthanide ions in aqueous solution (*e.g.*, stability constants, heats of complexation, equivalent conductances, relative viscosities) show no simple correlation with cationic radii. A plot of the thermodynamic data as a function of radius most often exhibits a break somewhere in the middle of the series. Although there has been frequent reference to a "gadolinium break," the discontinuity usually occurs over several lanthanides and the elements involved vary slightly. A feature common to all of these data is an aqueous system and it has been suggested that this break may reflect a discontinuous variation in the thermodynamic hydration parameters of the lanthanide ions.<sup>1-4</sup> With a few exceptions, the values in the literature for the free energies, enthalpies, and entropies of hydration of the lanthanide ions were calculated from theoretical or semiempirical equations. Since these equations include an inverse relation to the ionic radii, a smooth trend in the  $\Delta G$ , etc., values is obtained.

The lanthanide iodates were chosen for this study for several reasons. They are neither hydrated nor deliquescent; their relative insolubility allowed easy determination of the  $K_{sp}$  values. They exhibited desirable precipitation characteristics with no evidence of colloidal suspensions, a factor important in both the solubility and calorimetric experiments. Owing to their small stability constants, no excessive correction was required on the measured solubilities in calculating the free energy of solution of the cations. The contribution of the heats of complexation to the heats of solution was small enough to be omitted as a correction.

### Experimental Section

**Reagents.  $\text{LiIO}_3$ ,  $\text{NaIO}_3$ , and  $\text{Ln}(\text{ClO}_4)_3$  Solutions.**—The lithium iodate solutions were prepared with reagent grade chemical (K & K Laboratories, Inc.). The pH was adjusted to 3.25 with  $\text{HIO}_3$  and its concentration was determined by iodimetry. The sodium iodate solutions were prepared by neutralizing a

solution of  $\text{HIO}_3$  with sodium hydroxide until a pH of 3.25 was obtained.

The rare earth perchlorate solutions were prepared by dissolving the oxides (Lindsay Chemical Division, 99.9%) in a slight excess of 2 *M*  $\text{HClO}_4$ . These solutions were evaporated under a heat lamp to remove excess acid so their pH values could be adjusted between 3.0 and 3.3. The solutions were then filtered, the filtrates were diluted to 100 ml, and their concentrations were determined by passing an aliquot (usually 1 ml) through a cation-exchange column (Dowex 50  $\text{H}^+$  form) and titrating the eluent with standard sodium hydroxide.

**Solid Rare Earth Iodates.**— $\text{Ln}(\text{IO}_3)_3$  was precipitated from a vigorously stirred dilute solution of lanthanide perchlorate by addition of an equivalent amount of  $\text{NaIO}_3$  solution. The solid precipitate was washed several times with slightly acidified distilled water ( $\text{HClO}_4$ , pH 3.25). Thermal balance curves for several lanthanide iodates indicated that there were no waters of crystallization. The purity, better than 99% in all cases, was determined by conversion of the iodate to the oxide and comparing weights. In this analysis it was necessary to decompose the  $\text{Ln}(\text{IO}_3)_3$  with hydrochloric acid and then dry and ignite the residue since direct thermal decomposition of the  $\text{Ln}(\text{IO}_3)_3$  resulted in sufficiently vigorous evolution of  $\text{I}_2$  to cause spattering.

**Procedures.**—To determine the solubilities, samples of the lanthanide iodates were heated in water of pH 3.25 at 80° for 4 days with magnetic stirring and refluxing. After cooling at room temperature, the solutions were kept in a water bath at 25° for several days before analysis for iodate ion concentrations by iodimetry. Three or four measurements were made of each lanthanide iodate.

The solvent extraction technique for determining stability constants was a standard one.<sup>5</sup> The values of the stability constants,  $k_1$ , for formation of  $\text{LnIO}_3^{2+}$  were determined at 0.1 *M* ionic strength with  $\text{NaClO}_4$  as the inert electrolyte with the  $\text{NaIO}_3$  concentration varying from 0.0 to 0.1 *M*. The values for Ce, Pm, Eu, Tb, Er, and Tm were obtained using radioactive tracers of these ions. The organic phase was a solution (5 × 10<sup>-5</sup> *M*) of dinonylnaphthalenesulfonic acid in hexene.

The calorimeter used was similar to one described previously.<sup>6</sup> The accuracy of the calorimeter technique was checked by running an acid-base reaction of known heat evolution. For the measurement of the heat of precipitation of the lanthanide iodates, an ampoule of about 3-ml capacity containing a known amount of  $\text{LiIO}_3$  solution was broken in 50.0 ml of an equivalent amount of lanthanide perchlorate solution. The heat released upon precipitation was measured and recorded. Both prior to and after precipitation several scale calibrations were made by supplying from the heater known quantities of heat; thus, the heat of precipitation could be obtained by direct comparison of

(1) F. H. Spedding and G. Atkinson, "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley & Sons, Inc., New York, N. Y., 1959, Chapter 22.

(2) I. Grenthe, *Acta Chem. Scand.*, **18**, 293 (1964).

(3) P. L. E. de la Praudiere and L. A. K. Staveley, *J. Inorg. Nucl. Chem.*, **26**, 1713 (1964).

(4) G. R. Choppin and A. J. Graffeo, *Inorg. Chem.*, **4**, 1254 (1965).

(5) G. R. Choppin and W. F. Strazik, *ibid.*, **4**, 1250 (1965).

(6) G. R. Choppin and H. G. Friedman, Jr., *ibid.*, **8**, 1599 (1966).

the recorder displacements of the calibrations and the precipitation. In separate experiments it was shown that the heats of dilution of  $\text{Ln}(\text{ClO}_4)_3$  solutions were negligible in our experiments. The heats of dilution of  $\text{LiIO}_3$  were measured and subtracted from the over-all heat changes. The heat of precipitation was determined in three or four separate experiments for each lanthanide. In separate experiments, the fraction precipitated in each experiment was determined by iodimetry using the supernatant solution.

### Data and Results

**Free Energies of Solution.**—The solubilities of the lanthanide iodates agreed well with the data of Firsching and Paul.<sup>7</sup> It was necessary to correct the measured solubilities of the lanthanide iodates for the presence of ion pairs since the free energies for formation of the hydrated ions was desired. The values<sup>8</sup> of the stability constants,  $k_1$ , for formation of  $\text{LnIO}_3^{2+}$  were determined for Ce, Pm, Eu, Tb, Er, and Tm and values for the other lanthanide ions were interpolated from these. The extent of complexation was sufficiently small that it was possible to neglect corrections for higher order complexes. The stability constants at infinite dilution ( $\mu = 0.0 M$ ) were calculated using the equation

$$\log {}^T K_1 = \log k_1 - \frac{\Delta Z^2 A \sqrt{\Gamma}}{1 + B a \sqrt{\Gamma}} - C\Gamma \quad (1)$$

where  $\Gamma$ ,  ${}^T K_1$ , and  $k_1$  are the ionic concentration (twice the ionic strength), the thermodynamic stability constant, and the stability constant at  $0.1 M$  ionic strength, respectively.  $\Delta Z^2$  is the difference in the square of the ionic charge of  $\text{LnIO}_3^{2+}$  and the sum of the squares of the charges of  $\text{Ln}^{3+}$  and  $\text{IO}_3^-$  (here  $\Delta Z^2 = -6$ ). The values of  $A$ ,  $B$ , and  $C$  used in ref 5 were also employed in our calculations. The parameter  $\hat{a}$  (the mean of distance of closest approach) was estimated by setting it equal to the sum of the iodate and the cation radii. This was based on the correlation of  $\hat{a}$  with such estimates for other lanthanide ion pairs.<sup>5,9</sup>

To obtain the correlation for ion pairing, it was necessary to use the  ${}^T K_1$  values to calculate stability constants at the correct ionic strength of the saturated solutions. Since the exact value of the ionic strength was not known owing to lack of exact knowledge on the extent of ion pairing, it was necessary to employ successive approximations. A  $k_1$  was first calculated using an ionic strength based on no ion pairing (*i.e.*,  $\mu = 6[\text{Ln}^{3+}]$ ). As a second approximation a better  $\mu$  was obtained using this  $k_1$  to estimate the concentrations of the various ionic species. Generally only two or three such iterations were necessary until a consistent ionic strength was obtained. The final  $k_1$  was used to determine the concentration of free ions in solution which

gave the solubility product constant at that ionic strength. The  $K_{sp}$  for a standard state of infinite dilution was then calculated by employing mean activity coefficients from the Debye-Hückel equation. Values of the solubilities,  $k_1$  ( $\mu = 0.10 M$ ),  ${}^T K_1$ ,  $\mu$ ,  $k_1$  ( $\mu$ ),  $K_{sp}$ , and  $\Delta G^\circ(\text{aq})$  are listed in Table I. The standard deviation is approximately 12% for the stability constants; the estimated error in the solubilities is 2% or less.

**Heats of Solution.**—Heat of precipitation experiments have often been criticized for providing less accurate results. In the precipitation there is an initial precipitation and then a period of crystal stabilization. The error involved in ignoring this second stage can be serious if it is a slow process involving significant change. In this work precautions were taken to minimize this type of error. When we added an equivalent amount of  $\text{Ln}(\text{ClO}_4)_3$  solution to the  $\text{LiIO}_3$  solution and measured the heat evolved, we also measured the moment of precipitation (bulb breaking). A standard of 30 sec was used for the heat measurement. In separate experiments the fraction precipitated in 30 sec was determined (precipitation was 98% complete after this time and further precipitation was quite slow).

The enthalpy values obtained calorimetrically had to be converted to the standard state of infinite dilution. An attempt was made using the Debye-Hückel equations,<sup>10</sup> but the calculated corrections were unreasonable, presumably because the Debye-Hückel equation fails for 1:3 salts at these ionic strengths. Enthalpies of solution were obtained at several ionic strengths, including the lowest ionic strength at which a heat of precipitation could be reliably measured. Measurements made at  $\mu = 0.05 M$  gave smaller values by about 10%, but these were considered unreliable since only a very small fraction precipitated as a much finer precipitate which showed evidence of colloidal suspension. Since it was found that the values were almost constant (Figure 1), the enthalpy data were used without correction as the standard-state values. The values of  $\Delta H(\text{aq})$  are listed in Table II.

**Entropies of Hydration.**—The entropy of hydration is the difference between the absolute entropy of the ion in solution,  $\tilde{S}^\circ(\text{aq})$ , and the absolute entropy of the gaseous ion,  $\tilde{S}^\circ(\text{g})$ . The standard state for the entropy of ions in solution was chosen to be  $\tilde{S}^\circ(\text{H}^+) = 0.0$ .  $\tilde{S}^\circ(\text{g})$  was calculated with the Sackur-Tetrode equation for monatomic ions using values of  $J$  and  $E_J$  from Carnall<sup>11</sup> to evaluate the electronic contribution to the total entropy for gaseous lanthanide ions.

$\tilde{S}^\circ(\text{Ln}(\text{aq})^{3+})$  was obtained indirectly from eq

$$\tilde{S}^\circ(\text{Ln}(\text{aq})^{3+}) = \Delta S^\circ(\text{aq}) + \tilde{S}^\circ(\text{Ln}(\text{IO}_3)_3(\text{c})) - 3\tilde{S}^\circ(\text{IO}_3(\text{aq})^-) \quad (2)$$

2 where  $\Delta S^\circ(\text{aq})$  is the entropy of solution of  $\text{Ln}(\text{IO}_3)_3$  calculated from the  $\Delta G^\circ(\text{aq})$  and  $\Delta H^\circ(\text{aq})$  values,

(7) F. H. Firsching and T. R. Paul, *J. Inorg. Nucl. Chem.*, **28**, 2414 (1966).

(8) Material supplementary to this article has been deposited as Document No. NAPS-00205 with the ASIS National Auxiliary Publications Service, % CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and remitting \$3.00 for photocopies or \$1.00 for microfiche. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

(9) F. H. Spedding and S. Jaffe, *J. Am. Chem. Soc.*, **76**, 884 (1954).

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., p 77.

(11) W. T. Carnall, D. M. Gruen, and R. L. Beth, *J. Phys. Chem.*, **66**, 2159 (1962); **67**, 1206 (1963).

TABLE I  
 DATA USED TO CALCULATE FREE ENERGIES OF SOLUTION

	$10^3 \times$ solubility of $\text{Ln}(\text{IO}_3)_3$ , mol l. <sup>-1</sup>	$k_1$ ( $\mu = 0.10 M$ ) (interpolated)	$10^3\mu$	$k_1$ ( $\mu$ )	$10^{12}K_{sp}$	$+\Delta G^\circ(\text{aq})$ , kcal mol <sup>-1</sup>
La	1.07	17	5.71	49	10.2	14.99 $\pm$ 0.23
Ce	1.15	16	6.20	45	13.7	14.53 $\pm$ 0.22
Pr	1.13	15	6.12	42	12.8	14.86 $\pm$ 0.22
Nd	1.03	14	5.65	40	9.56	15.04 $\pm$ 0.23
Sm	0.86	13	4.80	41	5.07	15.41 $\pm$ 0.23
Eu	0.80	14	4.44	43	3.89	15.57 $\pm$ 0.23
Gd	0.83	15	4.92	46	4.29	15.51 $\pm$ 0.23
Tb	0.93	16	5.06	50	6.44	15.27 $\pm$ 0.23
Dy	1.03	17	5.51	52	9.03	15.07 $\pm$ 0.23
Ho	1.17	18	6.12	54	13.4	14.83 $\pm$ 0.22
Er	1.31	19	6.72	55	19.3	14.62 $\pm$ 0.22
Tm	1.47	19	7.46	54	28.3	14.39 $\pm$ 0.22
Yb	1.63	19	8.20	53	40.1	14.18 $\pm$ 0.21
Lu	1.78	19	8.96	51	55.9	13.99 $\pm$ 0.21
Y	1.93	18	9.59	49	71.0	13.85 $\pm$ 0.21

 TABLE II  
 HEATS OF SOLUTION OF  $\text{Ln}(\text{IO}_3)_3$ 

Ion	$\Delta H^\circ(\text{aq})$ , kcal/mol	Ion	$\Delta H^\circ(\text{aq})$ , kcal/mol
La	6.9	Dy	3.6
Ce	6.8	Ho	3.2
Pr	6.7	Er	3.1
Nd	6.4	Tm	2.6
Sm	5.8	Yb	2.3
Eu	5.1	Lu	2.0
Gd	4.2	Y	2.2
Tb	4.1		

and  $S^\circ(\text{Ln}(\text{IO}_3)_3(\text{c}))$  and  $S^\circ(\text{IO}_3(\text{aq}))$  are the absolute entropies of crystalline  $\text{Ln}(\text{IO}_3)_3$  and aqueous  $\text{IO}_3^-$ .  $S^\circ(\text{IO}_3(\text{aq})^-)$  is known.<sup>12</sup>

The absolute entropies of the crystalline iodates were calculated by using Latimer's method<sup>13</sup> which simply adds the individual contributions of the cation and the anion. For the set of values for the lanthanide metal ion contribution we have used those of Gronvold and Westrum<sup>14</sup> which successfully predicted the entropies of the lanthanide sesquioxides. Since no experimental values are reported for a salt of the form  $\text{M}(\text{IO}_3)_3$ , it was not possible to obtain directly a value for the iodate contribution. However, the absolute entropies of aqueous  $\text{Gd}(\text{III})$ <sup>15</sup> and aqueous  $\text{IO}_3^-$  are reported allowing the calculation of the absolute entropy of  $\text{Gd}(\text{IO}_3)_3(\text{c})$ . In turn, using the value for  $\text{Gd}(\text{III})$  of Gronvold and Westrum with the electronic entropy added (*i.e.*,  $14.0 + 4.1 = 18.1$ ), the entropy contribution of iodate in  $\text{Ln}(\text{IO}_3)_3$  crystals could be evaluated (20.1 cal/deg). The entropies of the aqueous lanthanide ions as well as their entropies of hydration were

(12) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952.

(13) W. M. Latimer, *J. Am. Chem. Soc.*, **43**, 818 (1921).

(14) F. Gronvold and E. F. Westrum, *Inorg. Chem.*, **1**, 40 (1962).

(15) (a) J. W. Cobble, *Ann. Rev. Phys. Chem.*, **17**, 15 (1966). (b) In a private communication J. W. Cobble reported a value of  $-53.4$  eu for  $\text{Gd}(\text{III})$ . However, in the absence of experimental details, we did not feel justified in using this value. A change in the  $\text{Gd}(\text{III})$  value would change the  $S^\circ(\text{aq})$  and  $\Delta S_h^\circ$  values by the same amount.

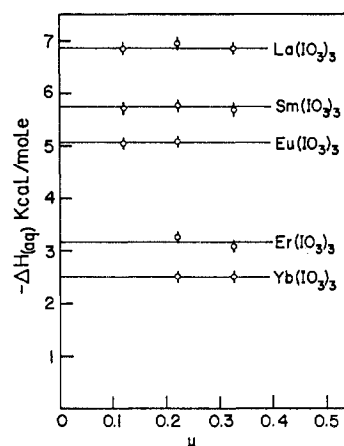


Figure 1.—Values of  $\Delta H(\text{aq})$  of several lanthanide iodates as a function of ionic strength.

based on this value. The values for  $\Delta S^\circ(\text{aq})$ ,  $S^\circ(\text{Ln}(\text{IO}_3)_3(\text{c}))$ ,  $S^\circ(\text{Ln}(\text{aq})^{3+})$ ,  $S^\circ(\text{Ln}(\text{g})^{3+})$ , and  $\Delta S_h^\circ$  are given in Table III.

It should be noted that the absolute values of  $\Delta S_h^\circ$  depend on the values of  $S^\circ(\text{Ln}(\text{IO}_3)_3(\text{c}))$ ,  $S^\circ(\text{IO}_3^-)$ , and  $S^\circ(\text{Gd}(\text{aq})^{3+})$ . However, the trend in  $\Delta S_h^\circ$  with atomic number is affected only by the first of these three. The variation in  $S^\circ(\text{Ln}(\text{IO}_3)_3(\text{c}))$  is, with the exception of La, Lu, and Y, only about 3 cal mol<sup>-1</sup> deg<sup>-1</sup> and erratic. Consequently, the variation in  $\Delta S_h^\circ$  with atomic number reflects primarily the experimental values of  $\Delta S(\text{aq})$ .

**Enthalpies of Hydration.**—The enthalpies of hydration were calculated from a Born-Haber cycle with the expression

$$\Delta H_h(\text{Ln}^{3+}) = \Delta H(\text{aq}) + \Delta H_1 - 3\Delta H_h(\text{IO}_3^-) \quad (3)$$

$\Delta H(\text{aq})$  is the experimentally determined quantity and  $\Delta H_h(\text{IO}_3^-)$  has been reported as  $-113$  kcal mol<sup>-1</sup>.<sup>16</sup> Unfortunately, it was necessary to estimate values of  $\Delta H_1$ , the lattice enthalpy of  $\text{Ln}(\text{IO}_3)_3$ , indirectly.

The enthalpies of formation of  $\text{La}(\text{aq})^{3+}$  and  $\text{La}(\text{g})^{3+}$

(16) A. Finch and P. J. Gardner, *J. Phys. Chem.*, **69**, 384 (1965).

TABLE III  
 ENTROPY VALUES FOR  $\text{Ln}^{3+}$  IONS AND  $\text{Ln}(\text{IO}_3)_3$  (CAL MOL<sup>-1</sup> DEG<sup>-1</sup>)

	$\Delta S(\text{aq})$	$\bar{S}^\circ(\text{c})$	$\bar{S}^\circ(\text{aq})$	$\bar{S}^\circ(\text{g})$	$\Delta S_h^\circ$
La	-27.3 ± 0.8	70.4	-40.9	40.7	-81.6 ± 0.8
Ce	-26.0 ± 0.8	73.5	-36.5	44.3	-80.8 ± 0.8
Pr	-27.0 ± 0.8	74.2	-36.8	45.1	-81.9 ± 0.8
Nd	-29.0 ± 0.8	74.3	-39.4	45.4	-84.8 ± 0.8
Sm	-32.5 ± 0.8	73.0	-43.5	44.6	-88.1 ± 0.8
Eu	-35.2 ± 0.8	71.0	-48.2	42.7	-90.0 ± 0.8
Gd	-37.3 ± 0.8	73.3	-48.0	45.2	-93.3 ± 0.8
Tb	-37.6 ± 0.8	74.1	-47.5	46.2	-93.7 ± 0.8
Dy	-38.6 ± 0.8	74.3	-48.3	46.7	-95.0 ± 0.8
Ho	-38.9 ± 0.7	74.3	-48.6	46.9	-95.5 ± 0.8
Er	-38.6 ± 0.7	74.0	-48.6	46.8	-95.4 ± 0.7
Tm	-39.5 ± 0.7	73.3	-50.0	46.4	-96.4 ± 0.7
Yb	-40.0 ± 0.7	72.4	-51.6	45.5	-97.1 ± 0.7
Lu	-40.2 ± 0.7	68.2	-56.0	41.4	-97.4 ± 0.7
Y	-39.2 ± 0.7	67.2	-56.0	39.4	-95.4 ± 0.7

are known<sup>17</sup> so the enthalpy of hydration of  $\text{La}^{3+}$  could be calculated from

$$\Delta H_h(\text{La}^{3+}) = \Delta H_f(\text{La}(\text{aq})^{3+}) - \Delta H_f(\text{La}(\text{g})^{3+}) + 3\Delta H_H \quad (4)$$

where  $\Delta H_H$  is the correction suggested by Noyes.<sup>18</sup> This value of  $\Delta H_h(\text{La}^{3+})$  was used in turn in eq 2 to calculate a value of  $\Delta H_1$  for  $\text{La}(\text{IO}_3)_3$ . The value of  $\Delta H_1$  was used with the Born-Meyer equation to determine the Madelung constant.

Assuming  $n = 12$  and  $R_0$  is the sum of the crystal radii, 15.08 was calculated for the Madelung constant. The values of  $\Delta H_1$  were calculated to vary from -1150 (La) to 1220 (Lu) kcal mol<sup>-1</sup>. In turn, the enthalpies of hydration were found to vary smoothly from -806 (La) to -878 (Lu) kcal mol<sup>-1</sup>. Unfortunately, the small value of  $\Delta H(\text{aq})$  and the larger uncertainties in  $\Delta H_1$  are such that we can only say that  $\Delta H_h(\text{Ln}^{3+})$  is about 850 kcal mol<sup>-1</sup>.

**X-Ray Powder Studies.**—Many lanthanide compounds have been shown to undergo a structural change around the middle of the series. The X-ray powder diffraction patterns were taken of the  $\text{Ln}(\text{IO}_3)_3$  crystals to see if this effect was present. Two different crystal groups were found: one from La to Dy and the other from Ho to Lu. The patterns of these crystals were extremely complex and an exact correlation with cubic, tetragonal, hexagonal, or orthorhombic symmetries could not be obtained. However, both groups seemed to fit hexagonal symmetry best. Many lines in the patterns appeared as doublets suggesting that the crystal structure had less than its ideal symmetry owing to a slight distortion. The conclusion reached was that both groups are probably hexagonal in symmetry but belong to different space groups and are distorted toward orthorhombic, monoclinic, or triclinic forms.

### Discussion

Since the entropy of hydration represents the difference between the entropies of the gaseous and of the hy-

drated ion, the variation of  $\Delta S_h^\circ$  with the atomic number would be expected to reflect any change in hydration other than the regular trend to be associated with the lanthanide contraction. The data in Table III show values of  $\Delta S_h^\circ$  of  $81 \pm 1$  eu for La-Pr and  $96 \pm 1$  eu for Dy-Lu. This would be consistent with a model of two differently sized hydration spheres,<sup>1-4</sup> one associated with the La-Pr ions and a larger one with the Dy-Lu ions. The ions from Nd through Gd form a transition group.

Considering the general problem of defining a hydration number experimentally, we do not wish to imply any belief in definite values in the preceding discussion. Nevertheless, several estimates of lanthanide hydration numbers,  $h$ , have been reported and their correlation with our values of  $\Delta S_h^\circ$  are of interest. Glueckauf has calculated values of 7.5 for La and 8.7 for Lu.<sup>19</sup> The ratio of these values is 1.2, which is also the ratio of  $\Delta S_h^\circ(\text{Lu})$  to  $\Delta S_h^\circ(\text{La})$ . This might imply that the hydration sphere is approximately 20% larger in the heavier lanthanides.

Conductance data were used by Choppin and Graffeo to calculate hydration numbers.<sup>4</sup> Values of  $h$  of  $12.8 \pm 0.1$  (La-Nd) and  $13.9 \pm 0.1$  (Dy-Yb) kcal mol<sup>-1</sup> were obtained (a ratio of 1.1). In Figure 2 the values of  $\Delta S_h^\circ$  are plotted as a function of these hydration numbers. The slope of the line is approximately 13 eu per hydrated water which may be compared to the value of 16.7 eu reported for the release of 1 mol of hydrated water from a hydrated cation in solution.<sup>20</sup> Padova<sup>21</sup> has used molar volumes to obtain hydration numbers for a number of the lanthanide ions. These vary from  $9.0 \pm 0.5$  (La-Nd) to 11.0 (Dy-Er). The ratio  $h(\text{Er}):h(\text{La})$  is again 1.2. Again, as with the values of  $h$  calculated from conductance data, correlation is found between the trends in  $h$  and in  $\Delta S_h^\circ$  as a function of lanthanide atomic number.

Previous estimates of the hydration entropy, in gen-

(17) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular No. 500, U. S. Government Printing Office, Washington, D. C., 1952.

(18) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962).

(19) E. Glueckauf, *Trans. Faraday Soc.*, **51**, 1235 (1955).

(20) F. J. C. Rossotti, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

(21) J. Padova, *J. Phys. Chem.*, **71**, 2347 (1967).

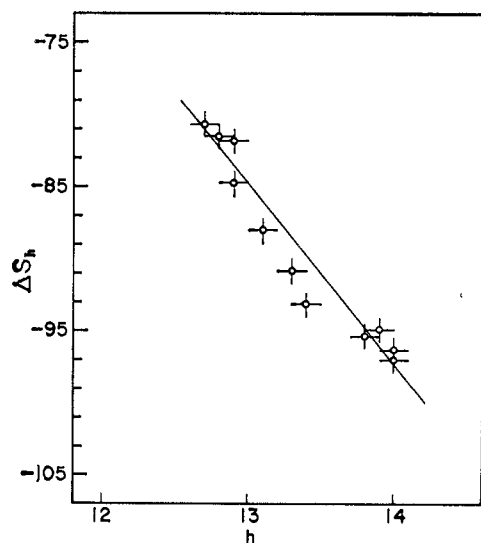


Figure 2.—Relation between the entropy of hydration and estimated hydration numbers for the lanthanide ions.

eral, used the Latimer–Powell equation.<sup>10</sup> Our experimental data have been compared with values calculated by the Latimer–Powell equation as well as by equations suggested by others.<sup>22–25</sup> The values calculated (using the Powell–Latimer equation and normalizing to  $S^\circ(\text{aq})(\text{Gd}) = -48$  eu) were in closest agreement although even these failed to show a very analogous trend with atomic number.

The  $\Delta S_h^\circ$  data can be used in a rough test of the idea that the thermodynamics of lanthanide complexing in aqueous solution can be attributed primarily to cation dehydration. EDTA is a ligand for which reliable values of the entropy of complexing exist; furthermore, the 1:1 complex (MY) should release most if not all of the waters of hydration of the cation (in the crystal three molecules of  $\text{H}_2\text{O}$  remain). Defining  $\Delta S_g$  as the entropy of complexation in the gas phase and  $\Delta S_s$  as that in aqueous solution, we can write

$$\Delta S_g = \Delta S_s - \Delta S_h(\text{LnY}) + \Delta S_h(\text{Ln}) + \Delta S_h(\text{Y})$$

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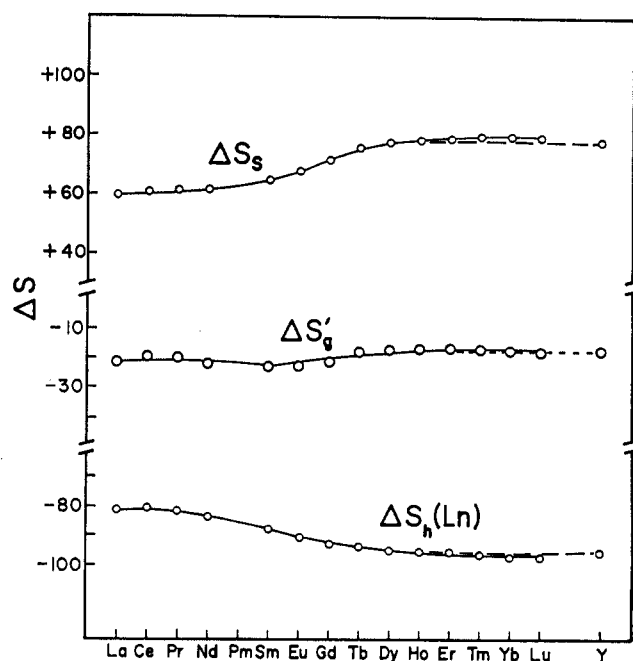


Figure 3.—Plot of the variation of  $\Delta S_s$ ,  $\Delta S_g'$ , and  $\Delta S_h$  as a function of lanthanide ion for EDTA complexing.

$\Delta S_h(\text{Y})$  is constant and we assume  $\Delta S_h(\text{MY})$  to be small and relatively constant, so that

$$\Delta S_g' = \Delta S_g - \Delta S_h(\text{Y}) + \Delta S_h(\text{LnY}) = \Delta S_s + \Delta S_h(\text{Ln})$$

The data for  $\Delta S_s$  were measured in an ionic medium of  $0.10 M$ <sup>26</sup> but this should not materially affect these approximations. In Figure 3,  $\Delta S_g'$ ,  $\Delta S_s$ , and  $\Delta S_h(\text{Ln})$  are plotted for the lanthanides and it is readily apparent that addition of  $\Delta S_h(\text{Ln})$  has corrected most of the variation in  $\Delta S_s$ . Recently, Staveley and coworkers used enthalpy measurements to reach similar conclusions.<sup>27</sup>

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