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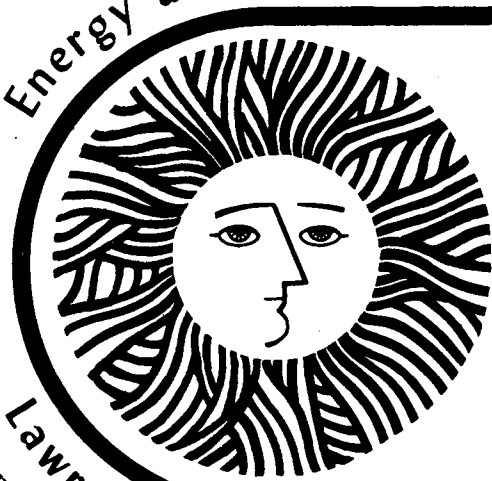
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Thermodynamics Of Electrolytes. IX.  
Rare Earth Chlorides, Nitrates, And  
Perchlorates

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and Leonard F. Silvester*

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THERMODYNAMICS OF ELECTROLYTES. IX. RARE  
EARTH CHLORIDES, NITRATES, AND PERCHLORATES

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## ABSTRACT

The extensive data for the osmotic coefficients, heats of dilution, and densities of aqueous solutions of rare earth chlorides, nitrates, and perchlorates are fitted to a single type of equation found satisfactory for many other solutes. Good agreement is obtained. The various parameters do not show simple trends with cation radius. While there are some plausible explanations of these complexities, the total picture is far from clear.

## Key words

Rare earth salts, lanthanides, osmotic coefficient, activity coefficient, heat of dilution, apparent molal volume, density.

## 1. INTRODUCTION

In a very extensive series of papers<sup>1-11</sup> Spedding and associates have presented various thermodynamic data for the nitrates, chlorides, and perchlorates of most of the rare earths. While excellent comparative treatments of the results for any one series are given in these papers, it seemed to us to be of some interest to fit a general array of these data to a single type of equation. We have considered the osmotic coefficient, the heat of dilution, and the volumetric data for all of the chlorides, perchlorates, and nitrates. Thus, in effect, we consider the Gibbs energy and its temperature and pressure derivatives. Activity coefficients may be calculated from these results.

The equation selected is that used extensively in this series of papers.<sup>12-15</sup> It was hoped that the trends of the parameters along the rare earth series would yield more reliable and interesting structural information than were obtained by Spedding and his associates in their direct examination of the original data. Our results in this respect are discussed below. The parameters obtained are also useful for various thermodynamic calculations and will be especially valuable for mixtures where the other components have been treated in the same system. The Equations for mixtures are given in papers IV<sup>14</sup> and V<sup>15</sup> of this series.

## 2. EQUATIONS

The theoretical background for these equations was given in paper I<sup>12</sup> and in a recent review.<sup>16</sup> In addition to a term for the long-range electrostatic effects treated by Debye and Hückel, the equation contains second and third virial coefficients representing the effects of short-range forces (hydration effects, etc.) between ion pairs and triplets. As indicated in the theory presented elsewhere, an ionic strength dependence is expected for the second virial coefficient. For the osmotic and activity coefficients of pure electrolytes, one obtains

$$\begin{aligned} \phi-1 = & |z_M z_X| f^\phi + m(2\nu_M \nu_X / \nu) B_{MX}^\phi \\ & + m^2 [2(\nu_M \nu_X)^{3/2} / \nu] C_{MX}^\phi \end{aligned} \quad (1)$$

$$\begin{aligned} \ln \gamma_{\pm} = & |z_M z_X| f^\gamma + m(2\nu_M \nu_X / \nu) B_{MX}^\gamma \\ & + m^2 [2(\nu_M \nu_X)^{3/2} / \nu] C_{MX}^\gamma \end{aligned} \quad (2)$$

where  $\nu_M$  and  $\nu_X$  are the numbers of M and X ions in the formula and  $z_M$  and  $z_X$  give their respective charges in electric units; also  $\nu = \nu_M + \nu_X$  and  $m$  is the molality. The other quantities are further defined

$$f^\phi = -A_\phi I^{1/2} / (1 + bI^{1/2}) \quad (3)$$

$$f^\gamma = -A_\phi \left[ \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{5} \ln(1 + bI^{1/2}) \right] \quad (4)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2}) \quad (5)$$

$$B_{MX}^Y = 2\beta_{MX}^{(0)} + (2\beta_{MX}^{(1)}/\alpha^2 I) \times [1 - (1 + I^{1/2} - 1/2\alpha^2 I) \exp(-\alpha I^{1/2})] \quad (6)$$

$$C_{MX}^Y = (3/2) C_{MX}^\phi \quad (7)$$

where  $I$  is the ionic strength,  $1/2 \sum m_i z_i^2$ , and  $A_\phi$  is the Debye-Hückel coefficient for the osmotic function  $[1/3 (2\pi N_o d_w/1000)^{1/2} (e^2/DkT)^{3/2}]$  which has the value 0.391 for water at 25°C. The general parameters are given the values  $b = 1.2$  and  $\alpha = 2.0$  throughout this and most other work with these equations. The specific parameters for each solute are  $\beta_{MX}^{(0)}$ ,  $\beta_{MX}^{(1)}$ , and  $C_{MX}^\phi$  and it is convenient to report them as multiplied by the preceding coefficients in equations (1) and (2); thus for 3-1 electrolytes we report  $3/2 \beta^{(0)}$ ,  $3/2 \beta^{(1)}$ , and  $(3^{3/2}/2) C^\phi$ .

The appropriate equations for the enthalpy and the volume are obtained from temperature and pressure derivatives of the excess Gibbs energy per mole of solute

$$G^{ex}/n_2 = \nu RT(1 - \phi + \ln \gamma_\pm). \quad (8)$$

This derivation has been given in some detail<sup>17</sup> for the enthalpy and yields for the apparent relative molal enthalpy

$$\begin{aligned} \phi_L = \nu |z_M z_X| (A_H/3b) \ln(1 + bI^{1/2}) \\ - 2\nu_M \nu_X RT^2 (m B_{MX}^L + m^2 C_{MX}^L) \end{aligned} \quad (9)$$

where

$$B_{MX}^L = (\partial\beta_{MX}^{(0)}/\partial T)_{I,P} + (\partial\beta_{MX}^{(1)}/\partial T)_{I,P} \\ \times (2/\alpha^2 I) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (10)$$

$$C_{MX}^L = 1/2(\nu_M \nu_X)^{1/2} (\partial C_{MX}^\phi/\partial T)_{I,P} \quad (11)$$

and  $A_H$  is the Debye-Hückel coefficient for enthalpy

$$A_H/RT = -9A_\phi [1 + T(\partial \ln D/\partial T)_P] + T\alpha_w/3 \quad (12)$$

with  $\alpha_w = (\partial \ln V/\partial T)_P$  the coefficient of thermal expansion of the solvent. In this derivation the general parameters  $b$  and  $\alpha$  are held constant with respect to temperature; the same assumption will be made with respect to pressure. The value<sup>17</sup> of  $A_H/RT$  is 1.177 for water at 25°C.

For the volumetric properties the derivation is similar and will not be given in detail. The measured property, however, is the density rather than the heat of dilution and this yields the absolute rather than the relative apparent molal volume. The additional term, the partial molal volume of the solute at infinite dilution  $\bar{V}^\circ$ , must be evaluated. One has, then,

$$\phi_V = \bar{V}^\circ + \nu |z_M z_X| (A_V/3b) \ln (1 + bI^{1/2}) \\ - 2\nu_M \nu_X RT (mB_{MX}^V + m^2 C_{MX}^V) \quad (13)$$

where

$$B_{MX}^V = (\partial\beta_{MX}^{(0)}/\partial P)_{I,T} + (\partial\beta_{MX}^{(1)}/\partial P)_{I,T} \\ \times (2/\alpha^2 I) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (14)$$



$$C_{MX}^V = 1/2(v_M v_X)^{1/2} (\partial C_{MX}^\phi / \partial P)_{I,T} \quad (15)$$

The density is related to the apparent molal volume by the expression

$$d = \frac{1000 + M_2 m}{(1000/d_0) + \phi V_m} \quad (16)$$

where  $d_0$  is the density of the pure solvent and  $M_2$  the molecular weight of the solute. The Debye-Hückel parameter for volume is

$$A_V = -3A_\phi RT [3(\partial \ln D / \partial P)_T + (\partial \ln V_w / \partial P)_T] \quad (17)$$

where the last term is the negative of the compressibility of the solvent. This definition differs from that of Redlich and Meyer<sup>18</sup> and others by the factor 3/2 (and the square root of the density of water). The equations for the volume and the dielectric constant for water which were adopted in paper VIII<sup>17</sup> were used to calculate  $A_V$ . The value of  $A_V$  is 2.626 cc kg<sup>1/2</sup> mole<sup>-1/2</sup> for water at 25°C.

### 3. EVALUATION OF PARAMETERS

The specific parameters for each rare earth salt were evaluated by least squares from the original data of Spedding, et al.,<sup>1-11</sup> together with any other published data<sup>11,19</sup> which was judged to be of comparable accuracy. For the chlorides good fits were obtained up to the highest concentrations, frequently saturation. For the perchlorates and especially for the nitrates, it was possible to get good fits only up

to about 2M and the final calculations were based only on data up to this maximum molality for these salts. For each function the square of the deviation in the measured quantity was minimized, i.e., the osmotic coefficient, the heat of dilution, or the density. These data were given unit weight up to  $I = 4$  and then weights  $(4/I)^2$ .

Since the parameter  $\beta^{(1)}$  and its derivatives have an important effect only for very dilute solutions, we explored the significance of differences in this parameter for various salts. For  $\beta^{(1)}$  itself, which is obtained from osmotic data, it appeared that the variation among salts of the same anion was random and not significant. Hence averaged values of 8.4, 7.7, and 9.8 were used for  $\beta^{(1)}$  for the chlorides, nitrates, and perchlorates, respectively. Somewhat to our surprise, the corresponding differences in  $\partial\beta^{(1)}/\partial T$  appeared to be significant, and the results based on individual values of  $\partial\beta^{(1)}/\partial T$  for each salt are reported. Apparently in dilute solutions the heat of dilution experiment is enough more precise than that for the osmotic coefficient to yield this difference. Since the enthalpy equation involves only  $\partial\beta^{(1)}/\partial T$  and not  $\beta^{(1)}$ , the apparent inconsistency in this procedure is not serious, and it yields the most reliable values for other parameters.

The parameters for the osmotic or activity coefficients and for the apparent molal enthalpies are given in Tables I, II, and III, respectively, for the chlorides, nitrates, and perchlorates.

For the volumetric data the  $\bar{V}^\circ$  values obtained by Spedding and his associates<sup>7-9</sup> were first considered. These molal volumes at zero concentration must be additive for the ions present. Thus the difference in  $\bar{V}^\circ$  for a pair of anions must be the same regardless of the cation. For most perchlorate and chloride pairs the difference in volume ( $\bar{V}^\circ$ ) was very nearly the same, and the average 78.7<sub>7</sub> cc was adopted. The small differences were allocated equally to the individual chlorides and perchlorates to yield the results shown in Table IV. The data for the nitrates were somewhat less concordant; the average difference, nitrate less chloride, was 34.3<sub>7</sub> cc, and this was added to the adjusted chloride values to obtain individual  $\bar{V}^\circ$  values for the nitrates. The volumes for the chlorides are given in Table IV; those for the nitrates and perchlorates can be obtained from the differences given above.

The least squares regression with  $\bar{V}^\circ$  fixed at these adjusted values yielded the results for the pressure derivatives of  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^\phi$  given in Tables IV and V. The significance of differences in  $(\partial\beta^{(1)}/\partial P)$  for the different salts of a given anion is doubtful.

The accuracy of fit is good throughout with standard deviations usually less than 0.0001 for densities, 0.006 for osmotic coefficients, and 10 cal for heats of dilution. Maximum deviations are roughly three times these values except for a few heats of dilution of concentrated chlorides where deviations rise to 100 cal.

Spedding and associates report no data for cerium salts. The values in Table I are based on the earlier data reported by Robinson and Stokes.<sup>19</sup> Similar data for other chlorides are included in our calculations along with the more recent measurements and the agreement is quite good. The small differences between the parameters for  $\text{CeCl}_3$  from those for  $\text{LaCl}_3$  and  $\text{PrCl}_3$  are probably not significant, however.

#### 4. DISCUSSION

It is interesting to note the magnitude of the temperature and pressure derivatives in relation to the parent functions. For the important parameters  $\frac{3}{2} \beta^{(0)}$ , which is of the order unity, the temperature derivative is less than  $0.0004 \text{ K}^{-1}$ . Consequently, a  $25^\circ$  change in temperature causes less than 1% change in  $\beta^{(0)}$  or 2% change in  $\gamma$  at 1 M. The pressure derivative is less than  $0.00006 \text{ atm}^{-1}$ ; hence a 160 atm change causes less than 1% change in  $\beta^{(0)}$ . The Debye-Hückel coefficient is somewhat more sensitive to temperature, with  $25^\circ$  causing a 4% change, but is even less sensitive to pressure. Thus the properties of these solutions do not change rapidly with temperature or pressure, and the dominant effect is the change of Debye-Hückel parameter with temperature.

The more significant parameters are shown as a function of the ionic radius of the positive ion in figures 1-5. The radii of Templeton and Dauben<sup>20</sup> are used for the rare earths. For yttrium the radius is derived from the structure of  $\text{Y}_2\text{O}_3$  determined by Paton and Maslen.<sup>21</sup> For other ions in figure 3 the radii of Zachariasen<sup>22</sup> were used. Many of these figures

show the s-shaped curves noted before by Spedding and others and often attributed to a change in the inner-sphere hydration number of the cation. It is assumed that the inner sphere contains nine water molecules from La to Nd and eight water molecules from Tb to Lu with a transition between Nd and Tb. It is not entirely clear to us why a reduction in hydration number should lead to an actual increase in volume from Nd to Tb (see figure 1), but we have no better explanation. The trend with radius of the primary parameter for short-range pairwise interaction  $\beta^{(0)}$  is shown in figures 2 and 3. The larger absolute value for perchlorates than chlorides indicates a more repulsive interaction for the perchlorate anion. The trend over a wider range of radii in figure 3 indicates that  $\beta^{(0)}$  decreases with increase in radius. Thus the trend from Tb to Nd appears to be normal and the regions Lu and Dy and Pr to La anomalous. This is in contrast to the explanation for  $\bar{V}^\circ$  values where the middle group of rare earths Tb to Nd was said to be the anomalous region.

The rare earth nitrates show more tendency toward inner-shell complex formation at high concentration than the chlorides (or perchlorates) and this would be expected to yield lower values of the interaction parameters. This is most apparent in the relatively large negative values of the triple interaction parameter  $C^\phi$  (see Table II). The pairwise interaction parameter  $\beta^{(0)}$  also shows somewhat lower values for the nitrates of the larger cations but not for the smaller cations (as compared to the chlorides). Presumably this indicates that a nitrate ion can compete with water for a place in the inner

shell of a large cation such as  $\text{La}^{+3}$  but not for a smaller +3 ion.

The interpretation of the temperature and pressure derivatives of  $\beta^{(0)}$ , shown in figures 4 and 5, is even more uncertain. Figure 4 shows the familiar s-shaped curves. The trends in figure 5, while not closely linear, are better described as showing a dip in the middle region near Gd for the chlorides and perchlorates at least.

Our primary conclusion is just that these parameters do not show smooth trends with ionic radius. When one recalls the considerable success of simple models based on radius in explaining ionic properties for other sets of ions, this behavior for the rare earth series is indeed anomalous and deserves further study by a wider variety of techniques.

#### ACKNOWLEDGEMENT

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Table I. Rare Earth Chlorides; Osmotic  
and Activity Coefficients and Enthalpies

	$\frac{3}{2} \beta^{(0)}$	$\frac{3}{2} \beta^{(1)}$	$\frac{3^{3/2}}{2} C^\phi$	$\frac{3}{2} \frac{\partial \beta^{(0)}}{\partial T}$	$\frac{3}{2} \frac{\partial \beta^{(1)}}{\partial T}$	$\frac{3^{3/2}}{2} \frac{\partial C^\phi}{\partial T}$
				$\times 10^4$	$\times 10^2$	$\times 10^4$
La	0.883 <sub>4</sub>	8.40	-0.061 <sub>9</sub>	3.79 <sub>0</sub>	1.19 <sub>7</sub>	-9.65
Ce	.907 <sub>2</sub>	8.40	-0.074 <sub>6</sub>	-	-	-
Pr	.883 <sub>8</sub>	8.40	-0.054 <sub>9</sub>	3.62 <sub>2</sub>	1.32 <sub>7</sub>	-9.10
Nd	.878 <sub>4</sub>	8.40	-0.049 <sub>3</sub>	3.71 <sub>5</sub>	1.33 <sub>5</sub>	-8.93
Sm	.900 <sub>0</sub>	8.40	-0.053 <sub>5</sub>	2.27 <sub>9</sub>	1.27 <sub>1</sub>	-8.79
Eu	.911 <sub>5</sub>	8.40	-0.054 <sub>7</sub>	0.23 <sub>7</sub>	1.27 <sub>8</sub>	-8.34 <sub>5</sub>
Gd	.913 <sub>9</sub>	8.40	-0.049 <sub>4</sub>	-0.89 <sub>7</sub>	1.25 <sub>0</sub>	-8.29
Tb	.922 <sub>9</sub>	8.40	-0.046 <sub>8</sub>	-1.87 <sub>2</sub>	1.28 <sub>5</sub>	-8.54
Dy	.929 <sub>0</sub>	8.40	-0.045 <sub>6</sub>	-1.76 <sub>6</sub>	1.22 <sub>9</sub>	-8.51
Ho	.937 <sub>6</sub>	8.40	-0.045 <sub>0</sub>	-1.63 <sub>3</sub>	1.28 <sub>9</sub>	-8.46
Er	.928 <sub>5</sub>	8.40	-0.038 <sub>9</sub>	-1.73 <sub>1</sub>	1.30 <sub>4</sub>	-8.16
Tm	.926 <sub>2</sub>	8.40	-0.036 <sub>2</sub>	-1.43 <sub>8</sub>	1.31 <sub>4</sub>	-7.98
Yb	.923 <sub>5</sub>	8.40	-0.033 <sub>5</sub>	-0.87 <sub>8</sub>	1.30 <sub>9</sub>	-8.14
Lu	.922 <sub>8</sub>	8.40	-0.033 <sub>2</sub>	-1.96 <sub>5</sub>	1.28 <sub>0</sub>	-7.19 <sub>5</sub>
Y	.936 <sub>7</sub>	8.40	-0.040 <sub>7</sub>	-	-	-

Table II. Rare Earth Nitrates; Osmotic and Activity Coefficients and Enthalpies

	$\frac{3}{2} \beta^{(0)}$	$\frac{3}{2} \beta^{(1)}$	$\frac{3^{3/2}}{2} C^\phi$	$\frac{3}{2} \frac{\partial \beta^{(0)}}{\partial T}$	$\frac{3}{2} \frac{\partial \beta^{(1)}}{\partial T}$	$\frac{3^{3/2}}{2} \frac{\partial C^\phi}{\partial T}$
				$\times 10^3$	$\times 10^2$	$\times 10^3$
La	0.740	7.70	-0.199	2.59 <sub>2</sub>	1.64 <sub>3</sub>	-1.17 <sub>2</sub>
Pr	.737	7.70	-0.188	2.43 <sub>9</sub>	1.85 <sub>4</sub>	-1.12 <sub>1</sub>
Nd	-	-	-	2.36 <sub>4</sub>	2.06 <sub>8</sub>	-1.11 <sub>4</sub>
Sm	.701	7.70	-0.131	2.15 <sub>2</sub>	2.53 <sub>3</sub>	-1.00 <sub>3</sub>
Gd	.776	7.70	-0.170	2.18 <sub>1</sub>	2.00 <sub>2</sub>	-1.05 <sub>3</sub>
Tb	.838	7.70	-0.202	1.80 <sub>7</sub>	1.58 <sub>5</sub>	-1.01 <sub>2</sub>
Dy	-	-	-	1.98 <sub>8</sub>	1.63 <sub>9</sub>	-1.04 <sub>9</sub>
Ho	-	-	-	1.68 <sub>1</sub>	1.63 <sub>1</sub>	-1.01 <sub>0</sub>
Er	.938	7.70	-0.226	1.72 <sub>4</sub>	1.65 <sub>0</sub>	-1.10 <sub>5</sub>
Tm	.952	7.70	-0.222	1.83 <sub>6</sub>	1.66 <sub>9</sub>	-1.20 <sub>8</sub>
Yb	.948	7.70	-0.208	1.89 <sub>8</sub>	1.68 <sub>5</sub>	-1.23 <sub>3</sub>
Lu	-	-	-	1.92 <sub>7</sub>	1.70 <sub>9</sub>	-1.20 <sub>9</sub>

Table III. Rare Earth Perchlorates; Osmotic and Activity Coefficients and Enthalpies

	$\frac{3}{2} \beta^{(0)}$	$\frac{3}{2} \beta^{(1)}$	$\frac{3^{3/2}}{2^2} C^\phi$	$\frac{3}{2} \frac{\partial \beta^{(0)}}{\partial T}$	$\frac{3}{2} \frac{\partial \beta^{(1)}}{\partial T}$	$\frac{3^{3/2}}{2} \frac{\partial C^\phi}{\partial T}$
				$\times 10^3$	$\times 10^2$	$\times 10^3$
La	1.15 <sub>8</sub>	9.80	0.001 <sub>6</sub>	2.27 <sub>9</sub>	2.25 <sub>4</sub>	-1.74 <sub>5</sub>
Pr	1.13 <sub>2</sub>	9.80	.016 <sub>3</sub>	2.40 <sub>8</sub>	2.27 <sub>0</sub>	-1.74 <sub>2</sub>
Nd	1.13 <sub>1</sub>	9.80	.019 <sub>4</sub>	2.39 <sub>4</sub>	2.31 <sub>1</sub>	-1.70 <sub>1</sub>
Sm	1.14 <sub>6</sub>	9.80	.014 <sub>0</sub>	2.26 <sub>9</sub>	2.25 <sub>0</sub>	-1.61 <sub>1</sub>
Gd	1.17 <sub>3</sub>	9.80	.014 <sub>0</sub>	2.01 <sub>1</sub>	2.17 <sub>5</sub>	-1.65 <sub>7</sub>
Tb	1.19 <sub>3</sub>	9.80	.012 <sub>3</sub>	-	-	-
Dy	1.20 <sub>1</sub>	9.80	.014 <sub>2</sub>	1.89 <sub>2</sub>	2.20 <sub>6</sub>	-1.71 <sub>9</sub>
Ho	1.19 <sub>8</sub>	9.80	.013 <sub>2</sub>	-	-	-
Er	1.20 <sub>2</sub>	9.80	.014 <sub>4</sub>	1.99 <sub>9</sub>	2.17 <sub>5</sub>	-1.79 <sub>4</sub>
Tm	1.19 <sub>3</sub>	9.80	.024 <sub>5</sub>	-	-	-
Yb	1.20 <sub>6</sub>	9.80	.013 <sub>7</sub>	-	-	-
Lu	1.18 <sub>6</sub>	9.80	.029 <sub>0</sub>	1.90 <sub>2</sub>	2.30 <sub>4</sub>	-1.65 <sub>7</sub>

Table IV. Rare Earth Chlorides; Volumetric Data<sup>a</sup>

	$\bar{V}^\circ$	$\frac{3}{2} \frac{\partial \beta^{(0)}}{\partial P}$ x 10 <sup>5</sup>	$\frac{3}{2} \frac{\partial \beta^{(1)}}{\partial P}$ x 10 <sup>4</sup>	$\frac{3^{3/2}}{2} \frac{\partial C^\phi}{\partial P}$ x 10 <sup>6</sup>
La	14.7 <sub>3</sub>	3.46 <sub>6</sub>	-2.4 <sub>9</sub>	-5.3 <sub>0</sub>
Pr	11.2 <sub>5</sub>	3.45 <sub>1</sub>	-2.8 <sub>2</sub>	-3.9 <sub>4</sub>
Nd	10.2 <sub>3</sub>	3.29 <sub>2</sub>	-2.7 <sub>3</sub>	-2.9 <sub>5</sub>
Sm	11.5 <sub>0</sub>	2.50 <sub>2</sub>	-2.8 <sub>9</sub>	-3.3 <sub>0</sub>
Eu	12.4 <sub>3</sub>	2.19 <sub>6</sub>	-2.3 <sub>9</sub>	0.0 <sub>4</sub>
Gd	13.3 <sub>5</sub>	2.40 <sub>7</sub>	-2.7 <sub>4</sub>	-1.3 <sub>6</sub>
Tb	13.4 <sub>1</sub>	2.84 <sub>1</sub>	-2.8 <sub>7</sub>	-3.0 <sub>7</sub>
Dy	12.8 <sub>6</sub>	3.02 <sub>3</sub>	-2.9 <sub>5</sub>	-3.4 <sub>9</sub>
Ho	11.8 <sub>9</sub>	3.07 <sub>6</sub>	-2.8 <sub>9</sub>	-3.2 <sub>3</sub>
Er	10.9 <sub>4</sub>	3.14 <sub>0</sub>	-2.6 <sub>7</sub>	-3.4 <sub>5</sub>
Tm	9.6 <sub>3</sub>	3.07 <sub>7</sub>	-2.5 <sub>8</sub>	-2.8 <sub>8</sub>
Yb	9.4 <sub>9</sub>	3.20 <sub>6</sub>	-3.3 <sub>9</sub>	-3.2 <sub>2</sub>
Lu	7.8 <sub>5</sub>	2.99 <sub>1</sub>	-2.2 <sub>5</sub>	-2.1 <sub>7</sub>
Y	13.3 <sub>5</sub>	2.99 <sub>8</sub>	-3.4 <sub>3</sub>	-3.0 <sub>9</sub>

<sup>a</sup> Units are cc for  $\bar{V}^\circ$  and atm<sup>-1</sup> for other quantities.

Table V. Rare Earth Nitrates and Perchlorates;  
Volumetric Data<sup>a</sup>

	Nitrates			Perchlorates		
	$\frac{3}{2} \frac{\partial \beta^{(0)}}{\partial P}$	$\frac{3}{2} \frac{\partial \beta^{(1)}}{\partial P}$	$\frac{3^{3/2}}{2} \frac{\partial C^{\phi}}{\partial P}$	$\frac{3}{2} \frac{\partial \beta^{(0)}}{\partial P}$	$\frac{3}{2} \frac{\partial \beta^{(1)}}{\partial P}$	$\frac{3^{3/2}}{2} \frac{\partial C^{\phi}}{\partial P}$
	$\times 10^5$	$\times 10^4$	$\times 10^6$	$\times 10^5$	$\times 10^4$	$\times 10^6$
La	5.54 <sub>4</sub>	-0.7 <sub>2</sub>	-10.1 <sub>2</sub>	4.13 <sub>8</sub>	-4.9 <sub>1</sub>	-6.2 <sub>5</sub>
Pr	4.46 <sub>1</sub>	2.6 <sub>3</sub>	- 3.6 <sub>6</sub>	3.98 <sub>9</sub>	-5.6 <sub>1</sub>	-4.9 <sub>9</sub>
Nd	1.87 <sub>0</sub>	5.2 <sub>4</sub>	14.7 <sub>6</sub>	3.79 <sub>5</sub>	-4.7 <sub>3</sub>	-4.4 <sub>0</sub>
Sm	2.43 <sub>7</sub>	2.4 <sub>2</sub>	6.4 <sub>9</sub>	2.83 <sub>5</sub>	-5.7 <sub>6</sub>	-2.5 <sub>8</sub>
Eu	-	-	-	2.32 <sub>0</sub>	-5.0 <sub>5</sub>	-1.8 <sub>2</sub>
Gd	2.65 <sub>8</sub>	-1.6 <sub>5</sub>	3.9 <sub>8</sub>	2.00 <sub>9</sub>	-5.2 <sub>7</sub>	-1.4 <sub>0</sub>
Tb	2.50 <sub>3</sub>	-2.6 <sub>5</sub>	7.2 <sub>7</sub>	2.18 <sub>0</sub>	-4.4 <sub>2</sub>	-2.6 <sub>2</sub>
Dy	2.39 <sub>7</sub>	-2.6 <sub>9</sub>	8.7 <sub>6</sub>	2.48 <sub>2</sub>	-4.0 <sub>4</sub>	-4.1 <sub>4</sub>
Ho	3.11 <sub>3</sub>	-3.2 <sub>3</sub>	4.7 <sub>9</sub>	2.57 <sub>7</sub>	-4.5 <sub>8</sub>	-3.4 <sub>4</sub>
Er	2.44 <sub>2</sub>	-3.0 <sub>0</sub>	12.2 <sub>2</sub>	2.72 <sub>5</sub>	-4.8 <sub>4</sub>	-3.6 <sub>9</sub>
Tm	-	-	-	2.90 <sub>9</sub>	-4.8 <sub>4</sub>	-4.2 <sub>4</sub>
Yb	2.99 <sub>3</sub>	-4.3 <sub>4</sub>	8.2 <sub>5</sub>	3.10 <sub>0</sub>	-5.9 <sub>2</sub>	-4.7 <sub>2</sub>
Lu	2.54 <sub>8</sub>	-2.2 <sub>6</sub>	9.7 <sub>6</sub>	3.13 <sub>3</sub>	-4.9 <sub>6</sub>	-4.9 <sub>5</sub>

<sup>a</sup> Units are atm<sup>-1</sup>.

## Figure Captions

- Fig. 1. The partial molal volume at zero molality for rare earth salts as a function of cation radius.
- Fig. 2. The pairwise short-range interaction parameter  $\beta^{(0)}$  as a function of cation radius for rare earth salts. Chlorides are shown as circles, nitrates as triangles, and perchlorates as squares.
- Fig. 3. The pairwise short-range interaction parameter  $\beta^{(0)}$  for a series of +3 ion chlorides as a function of cation radius. The current results are shown as triangles; previous results (ref. 13) as triangles.
- Fig. 4. The enthalpy-of-dilution parameter  $(\partial\beta^{(0)}/\partial T)$  as a function of cation radius.
- Fig. 5. The volumetric parameter  $(\partial\beta^{(0)}/\partial P)$  as a function of cation radius. Chlorides are shown as squares except a solid triangle for yttrium, perchlorates as circles, and nitrates as open triangles.

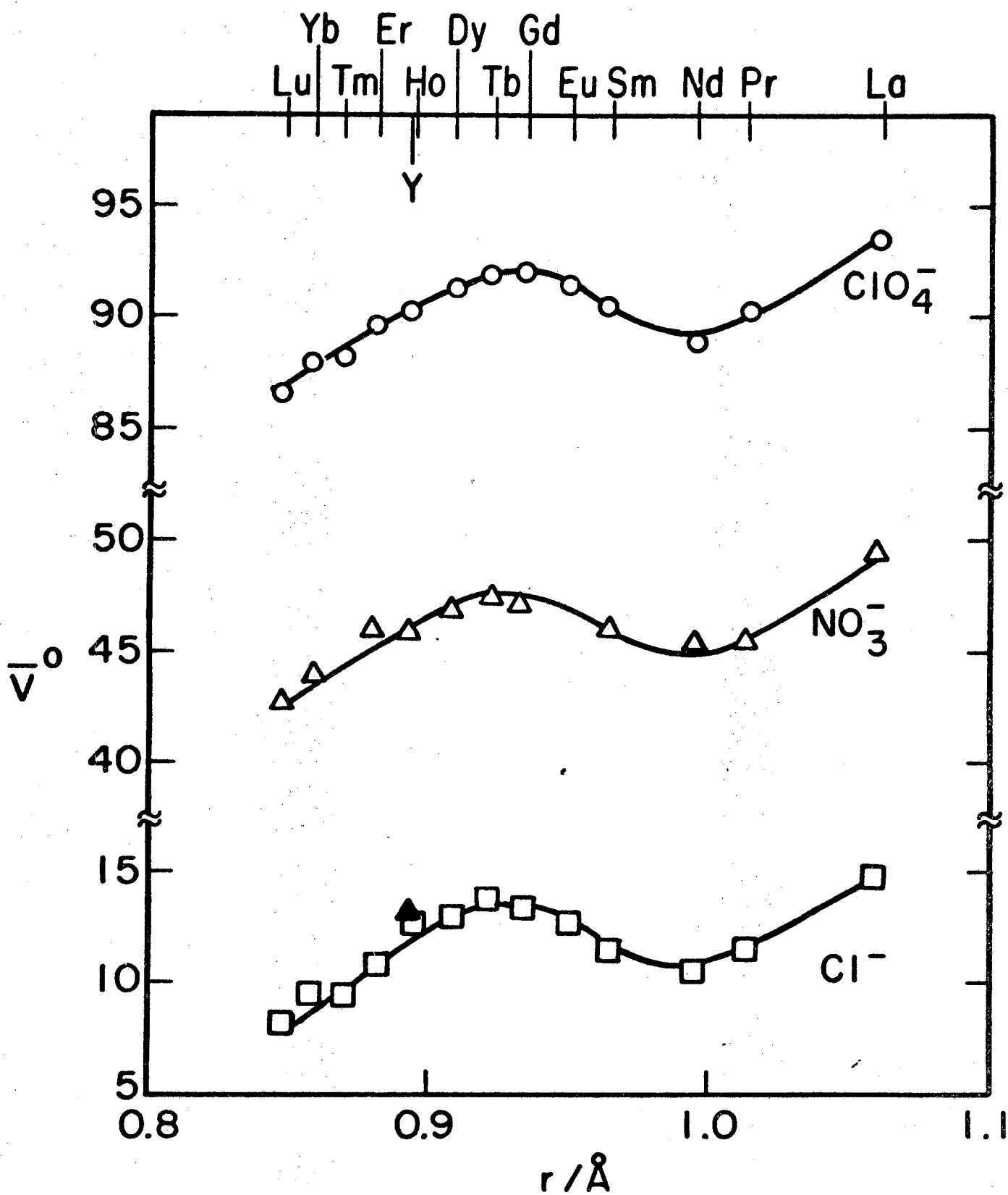


Fig. 1. The partial molal volume at zero molality for rare earth salts as a function of cation radius.

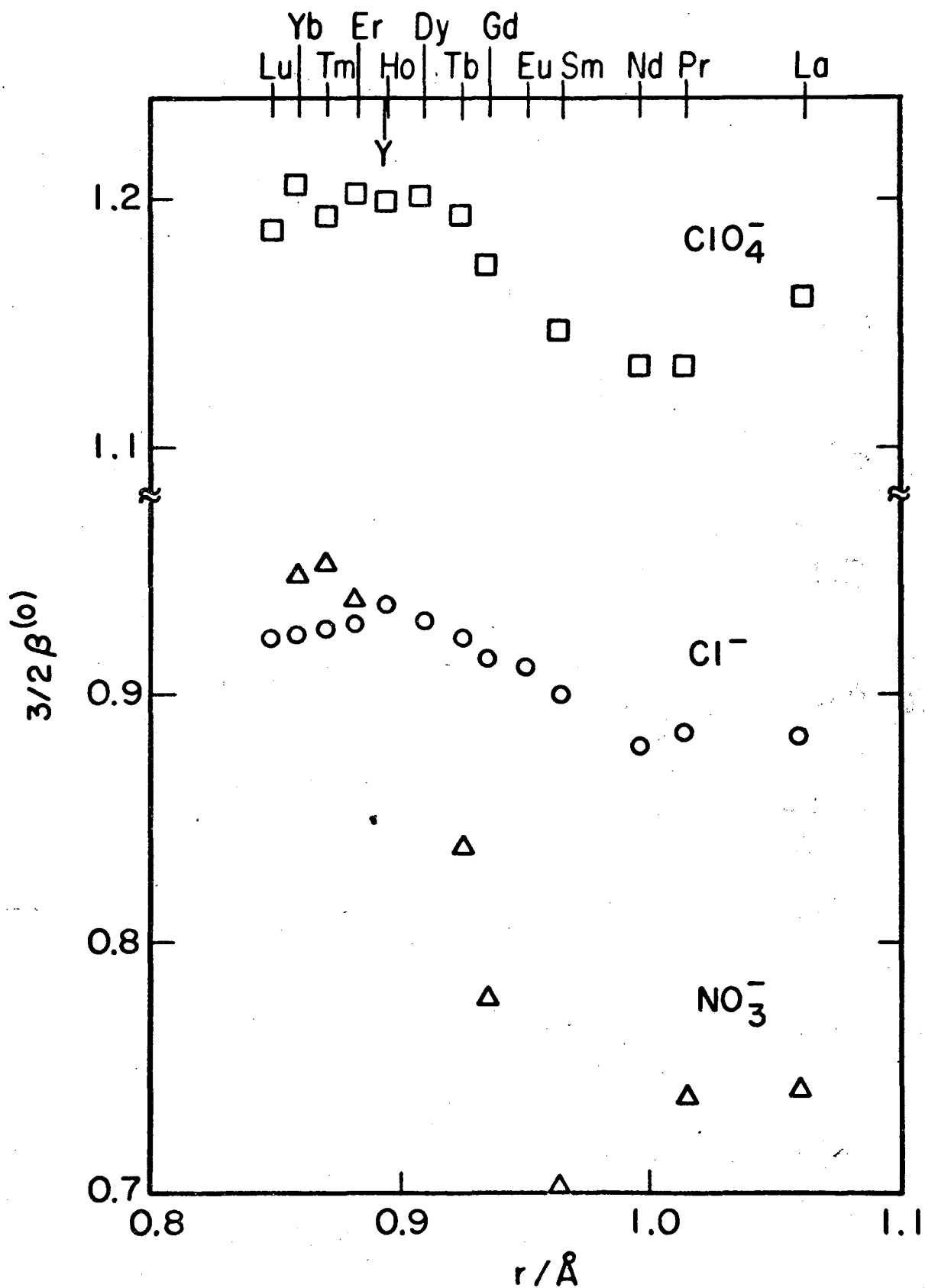


Fig. 2. The pairwise short-range interaction parameter  $\beta^{(0)}$  as a function of cation radius for rare earth salts. Chlorides are shown as circles, nitrates as triangles, and perchlorates as squares.



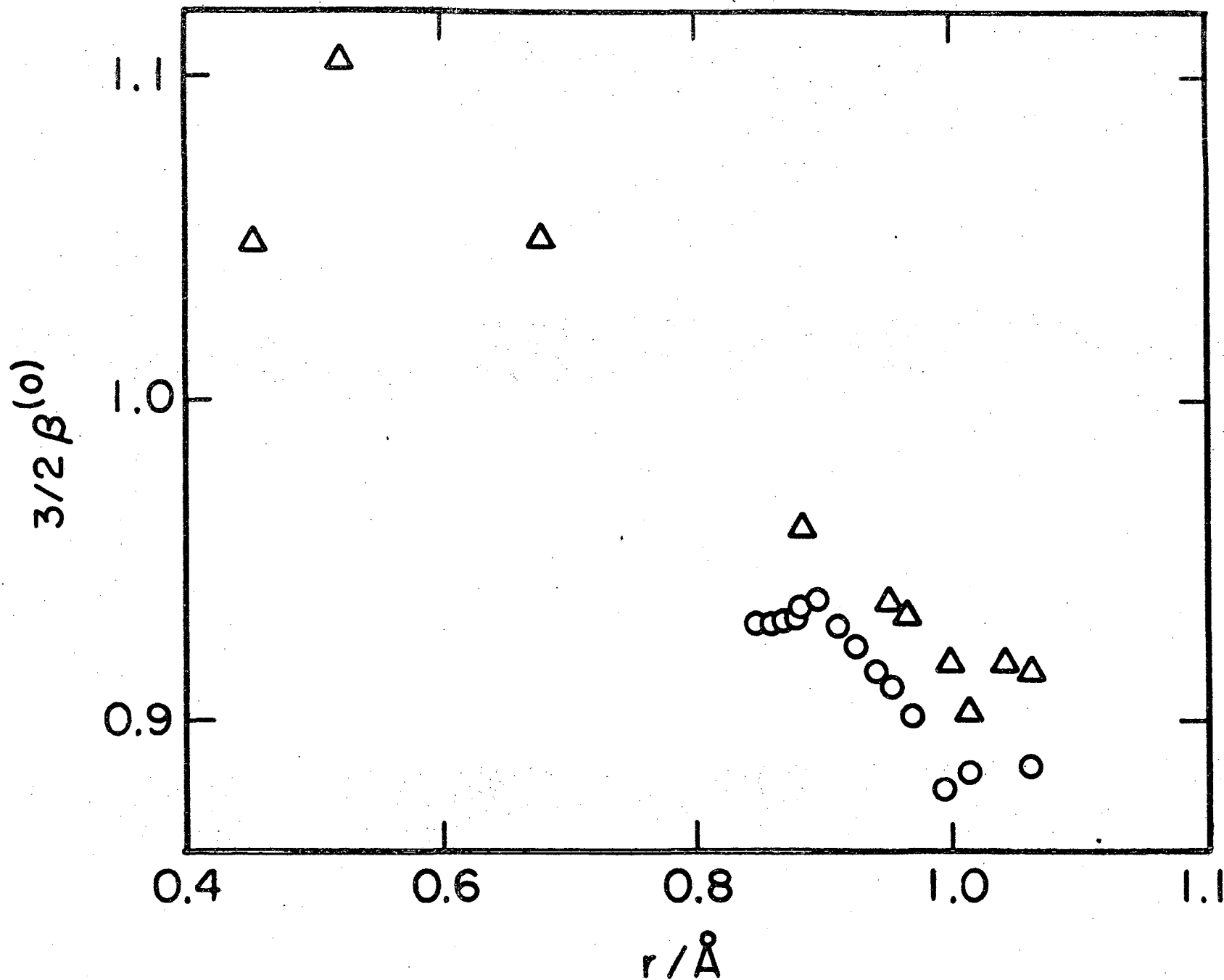


Fig. 3. The pairwise short-range interaction parameter  $\beta^{(0)}$  for a series of +3 ion chlorides as function of cation radius. The current results are shown as triangles; previous results (ref. 13) as triangles.

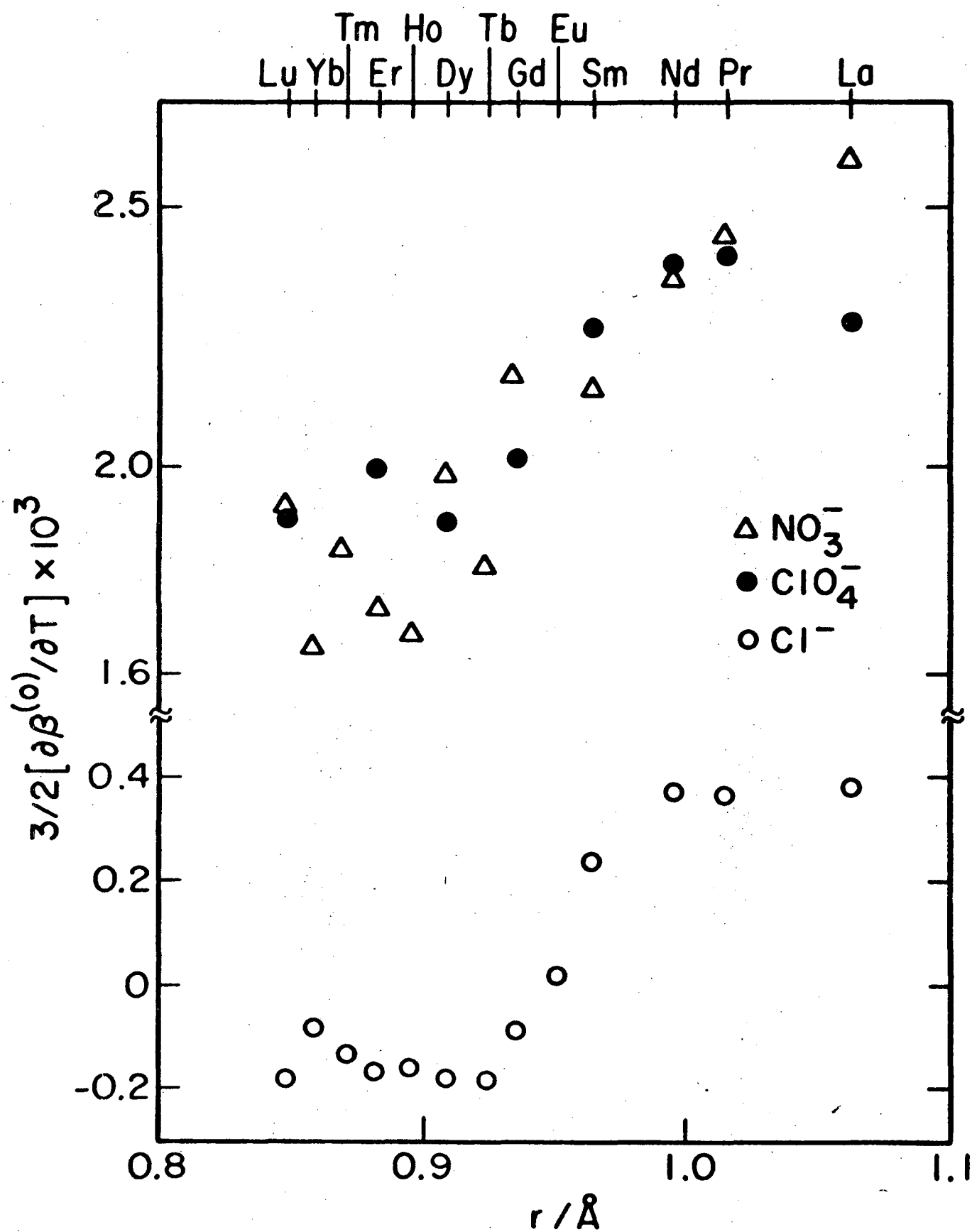


Fig. 4. The enthalpy-of-dilution parameter  $(\partial\beta^{(0)}/\partial T)$  as a function of cation radius.

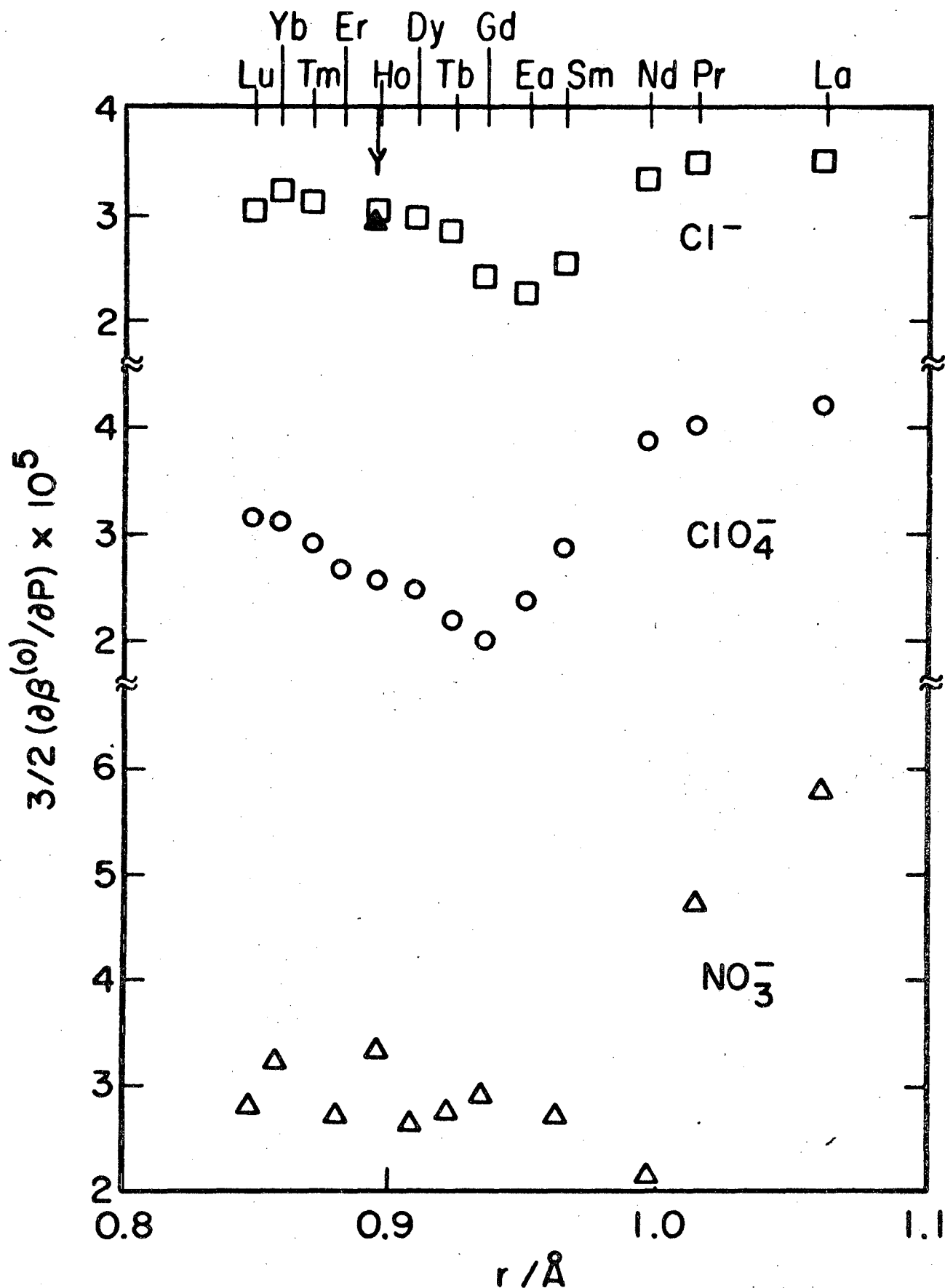


Fig. 5. The volumetric parameter  $(\partial\beta^{(0)}/\partial P)$  as a function of cation radius. Chlorides are shown as squares except a solid triangle for yttrium, perchlorates as circles, and nitrates as open triangles.

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