

The results of Clusius and Goldmann agree well with those of Keesom and Clark, and join well with the results of the present research. The results of Keesom and Clark made extrapolation necessary only below 1°K. in obtaining the entropy.

The thermodynamic properties of nickel calculated from the present results are given in Table II.

Calculations were extended to 800°K. on the basis of available data; however, the increments above 298.16°K. were in substantial agreement with calculations of Kelley,<sup>10</sup> who has summarized all available results as increments above 298.16°. To combine the results

$$S = 7.14 + (S - S_{298.16})_{\text{Kelley}}$$

$$\frac{H^\circ - H_0^\circ}{T} = \frac{3.837 \times 298.16 + (H_T - H_{298.16})_{\text{Kelley}}}{T}$$

and

$$\frac{F^\circ = H_0^\circ}{T} = \frac{H^\circ - H_0^\circ}{T} - S$$

TABLE II  
THERMODYNAMIC PROPERTIES OF NICKEL

$T, ^\circ\text{K.}$	$C_p$	$S$	$\frac{H^\circ - H_0^\circ}{T}$	$-\frac{(F^\circ - H_0^\circ)}{T}$
15	0.043	0.033	0.018	0.015
20	.081	.050	.029	.021
25	.142	.074	.045	.029
30	.234	.107	.068	.039
35	.367	.153	.101	.052
40	.534	.213	.145	.068
45	.732	.287	.199	.088
50	.956	.375	.263	.112

(10) K. K. Kelley, *U. S. Bureau of Mines Bulletin*, No. 476, 121 (1949).

60	1.448	.592	.418	.174
70	1.953	.853	.601	.252
80	2.433	1.145	.800	.345
90	2.868	1.456	1.005	.451
100	3.258	1.778	1.211	.568
110	3.605	2.105	1.413	.692
120	3.903	2.432	1.608	.824
130	4.164	2.755	1.795	.960
140	4.401	3.073	1.974	1.099
150	4.614	3.384	2.143	1.241
160	4.802	3.688	2.304	1.384
170	4.969	3.984	2.455	1.529
180	5.118	4.272	2.599	1.673
190	5.250	4.552	2.735	1.817
200	5.370	4.824	2.863	1.961
210	5.477	5.089	2.986	2.103
220	5.573	5.346	3.101	2.245
230	5.662	5.596	3.211	2.385
240	5.747	5.839	3.315	2.524
250	5.831	6.075	3.413	2.662
260	5.914	6.305	3.508	2.797
270	5.996	6.530	3.599	2.931
280	6.078	6.750	3.686	3.064
290	6.160	6.965	3.770	3.195
298.16	6.227	7.137	3.837	3.300
300	6.242	7.175	3.851	3.324

We thank Professor Leo Brewer and Dr. R. K. Edwards for treating the nickel sample *in vacuo* at high temperatures with subsequent careful annealing, Dr. T. H. Geballe for assistance with the heat capacity measurements and Drs. Paul D. Merica, E. M. Wise and G. L. Lee of the International Nickel Company for the specially prepared nickel sample used in this work.

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## The Heat Capacities and Heat Contents of Solutions of Cerium and Neodymium Chlorides at 25°

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The change in heat capacities of solution and dilution and the change in heat content of solution and dilution of the chlorides of cerium and neodymium have been measured for concentrations up to 0.35 and 0.40 molal, respectively. Both properties of these two electrolytes show agreement with the limiting Debye-Hückel equations within limits of experimental error.

### Introduction

Previous studies on the solutions of rare earth compounds<sup>2</sup> have illustrated the need for further data on the physical properties of the rare earth elements and their compounds in regard to the role that they can play in checking physical chemistry theories.

The partial molal heat contents and partial molal heat capacities of higher charged electrolytes in solution should be sensitive to deviations from the ideal ionic solution and to deviations from the

theoretical equations which describe these two properties due to such phenomena as association, changes in hydration of the ions, and compound formation. Since the charge on the ion is a constant factor for all the rare earth elements and the ionic radius of these elements is known to decrease with atomic number<sup>3</sup> the heat of solution of a given type of compound of these elements should increase with atomic number. Smaller ions of the same charge would, by presenting a relatively larger surface charge density to the surrounding water molecules, orient these water dipoles more strongly and to a greater degree than larger ions of like charge.

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) F. H. Spedding, P. E. Porter and J. M. Wright, *THIS JOURNAL*, **74**, 2778 (1952).

(3) W. H. Zachariassen, *Phys. Rev.*, **73**, 1104 (1948).

The present paper describes results of experiments on the change in heat capacities and the change in heat contents on solution and dilution of the chlorides of cerium and neodymium. The heats of solution of these chlorides have previously been reported.<sup>4</sup> However, there is only one report in the literature on the heat of dilution of a 3-1 electrolyte.<sup>5</sup> There are no reported data on the heat capacities of solutions of 3-1 electrolytes. With a view toward countering this void in the literature, a large number of heat of solution measurements have been very carefully performed and the results have been used to describe the change in these two properties with concentration and to test the conformance of these electrolytes to the limiting slopes as given by the Debye-Hückel theory.

### Experimental

**Preparation of Materials.**—The source materials and the methods of preparation of the chlorides of cerium and neodymium were the same as those given by Spedding, Wright and Porter.<sup>3</sup> The source materials were found, by spectrographic analysis, to be free from other rare earths and all common elements. The above authors kindly furnished a supply of freshly fused potassium chloride which they had previously purified. The anhydrous rare earth chlorides were analyzed for composition by precipitation of the rare earth as the oxalate and firing it to the oxide for weighing; the chloride was precipitated as silver chloride for weighing. Two out of every three final solutions were analyzed to check the initial weighings of the salt samples. Samples for the heat of solution were prepared by loading various sizes of thin-walled Pyrex bulbs with the salt; this was done in a dry-box in a dry nitrogen atmosphere. Conductance water was weighed, prior to loading in the calorimeter, in a 1300-ml. buret. All weights were corrected to vacuum at standard conditions.

**Apparatus and Procedure.**—The isothermal calorimeter and its accessories were constructed to follow somewhat the calorimeter described by Southard.<sup>6</sup> The calorimeter vessel was an open-top two-quart dewar flask sealed with Apiezon wax onto a brass cylindrical flange by means of which the flask was bolted to the calorimeter frame. The thermometer was a Maier transposed bridge<sup>7</sup> with 370 ohms of No. 42 AWG enameled copper and No. 38 AWG enameled manganin wire in alternate arms. With a set current of five milliamps the bridge had a sensitivity of  $3 \times 10^{-4}$  degree per microvolt. The e.m.f. was read to 0.1 microvolt on a White Double Potentiometer. The thermometer and a manganin heater coil of about 120 ohms were wound on a thin-walled copper cylinder three inches long and three inches in diameter. During calibrations, the current through the heater was determined by measuring the e.m.f. drop across a 0.1-ohm Reichsanstalt type standard resistor, calibrated by the National Bureau of Standards, which was kept in an oil-bath at 25°. The thermometer was calibrated in an absolute sense by comparing the e.m.f. generated by the thermometer with the resistance of a calibrated platinum resistance thermometer as read on a Mueller G-2 type temperature bridge. During operation, the calorimeter was immersed in a water-bath thermostatically controlled at  $25.00 \pm 0.01^\circ$ . A six-pronged, stainless steel spider, onto which six sample bulbs could be waxed, was held in place by a  $3/16$ -inch stainless steel rod which passed through a hollow monel stirring rod to the outside where it was clamped to the frame. A  $1/8$ -inch stainless steel rod, bent at the bottom end, was used as a sample breaker. A notched knob at the top of the sample-holder indicated which sample was over the breaker. Oil seals over the stirrer-bearings and rubber stoppers with Vaseline holes for passing the sample breaker restricted evaporation to the outside. This manner of load-

ing the calorimeter permitted the measurement of six values of the heat of solution over a concentration range and seven calibrations without having to dismantle the calorimeter. Maier<sup>8</sup> discusses the merits of such a procedure in the localization of systematic errors of the calorimetric method. The thermal leakage corrections were calculated by the methods outlined by King and Grover,<sup>9</sup> Jessup,<sup>10</sup> Coops, Van Nes, Kentie and Dienske<sup>11</sup> and Dickinson.<sup>12</sup> The heater resistance was frequently compared to a National Bureau of Standards calibrated resistor. Time was measured on two calibrated stopwatches with an additional electric timer to aid in determining the heat input. The factor, 1 calorie = 4.1840 absolute joules, was used.

### Results

The calorimetric apparatus, the procedure of operation, and the analytical treatment of the observations were tested by measuring the heat of solution of potassium chloride, which is known. To further test the procedure, three separate sets of experiments were performed. In the first set three samples were consecutively dissolved, in the second set only one sample, and in the third set, two samples were dissolved. The results are given in Table I. The values of the relative apparent molal heat content,  $\phi_L$ , were taken from a plot of the smoothed values as compiled by Harned and Owen<sup>13</sup> from various experimental data reported in the literature. Since our value for the heat of solution at infinite dilution,  $-L_2(s)$ , appeared to be somewhat higher than the accepted value, a check was made of the literature from which the accepted value was taken. These and other data were corrected to 25° by the equation

$$\Delta C_{pM} = -41.2 + 11.2m^{1/2} \quad (1)$$

which was also derived from data given by Harned and Owen, and to infinite dilution. The results are given in Table II. The average value, 4134 cal./mole, for the heat of solution at infinite dilution obtained by the use of both isothermal and adiabatic calorimeters furnishes a very favorable comparison.

TABLE I

HEATS OF SOLUTION OF POTASSIUM CHLORIDE AT 25°						
No.	<i>m</i>	<i>m</i> <sup>1/2</sup>	$-\Delta C_p^a$	$\Delta H$	$\phi_L^a$	$-L_2(s)$
1	0.02641	0.1625	39.3	4202	57	4145
2	.08931	.2988	37.8	4208	77	4131
3	.1676	.4092	36.6	4217	81	4136
4	.1547	.3933	36.8	4205	81	4124
5	.04087	.2022	38.9	4198	65	4133
6	.1882	.4338	36.3	4216	81	4135
Average						4134 ± 5

<sup>a</sup>  $-\Delta C_p$  and  $\phi_L$  are smoothed values.

The data for the change in heat capacity for the reaction of dissolving *m* moles of salt in 1000 g. of water are plotted in Fig. 1. The limiting slope in each case is 244.9 calories mole<sup>-1</sup> degree<sup>-1</sup>. The radius of the circles indicates the probable deviation as calculated by least squares methods.

(8) C. G. Maier, *THIS JOURNAL*, **52**, 2160 (1930).

(9) A. King and H. Grover, *J. Applied Phys.*, **12**, 557 (1941).

(10) R. S. Jessup, *ibid.*, **13**, 128 (1942).

(11) J. Coops, K. Van Nes, A. Kentie and J. W. Dienske, *Rec. trav. chim.*, **66**, 113 (1947).

(12) H. C. Dickinson, *Bull. Natl. Bur. Stds.*, **11**, 189 (1941).

(13) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950.

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

(5) C. C. Nathan, W. E. Wallace and A. L. Robinson, *THIS JOURNAL*, **65**, 790 (1943).

(6) J. C. Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

(7) C. G. Maier, *J. Phys. Chem.*, **34**, 2860 (1930).

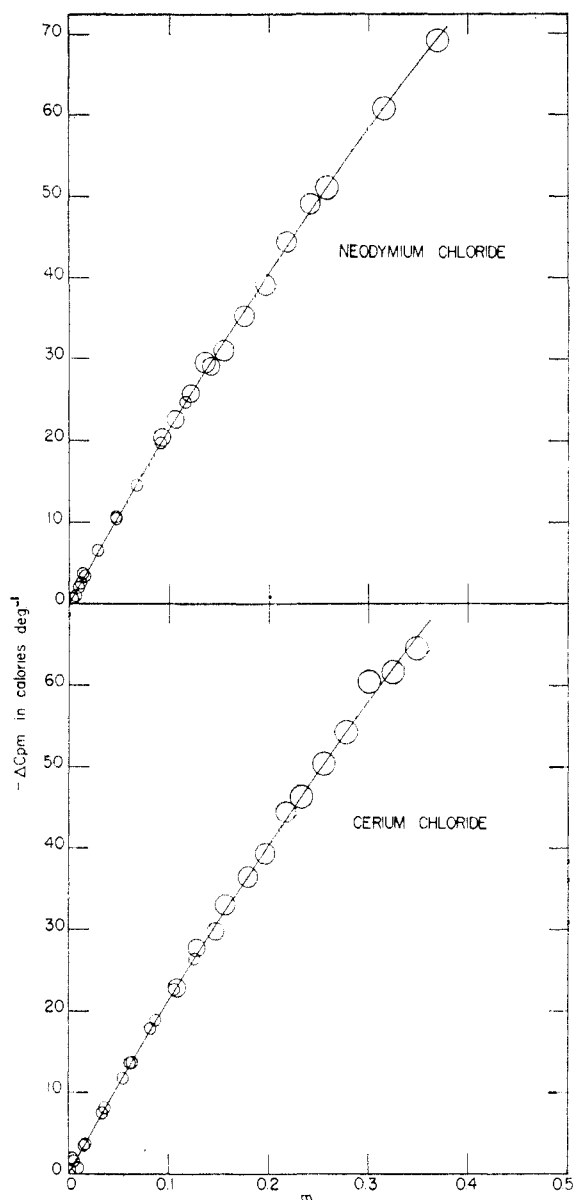


Fig. 1.—The change in the molal heat capacity,  $\Delta C_{pM}$ , for the dissolution of the chlorides of cerium and neodymium at 25°.

The change in heat capacity for the dissolution reaction is given by

$$\Delta C_{pM} = \phi_{cp} - C_p(s) \quad (2)$$

and at infinite dilution

$$\Delta C_{pM}^0 = \phi_{cp}^0 - C_p(s) \quad (3)$$

Therefore, the relative apparent molal heat capacity  $\phi_J$ , is given by

$$\phi_J = \phi_{cp} - \phi_{cp}^0 \quad (4)$$

$$= \Delta C_{pM} - \Delta C_{pM}^0 \quad (5)$$

in which  $\Delta C_{pM}^0$  is the value of the limiting slope of the curves in Fig. 1 or the value of  $\Delta C_{pM}$  at  $m^{1/2} = 0$  in a plot of  $\Delta C_{pM}$  vs.  $m^{1/2}$ . The experimental values of  $\phi_J$  are plotted in Fig. 2 and smoothed values are given in Tables III and IV. The lengths of the vertical lines indicate the probable deviations. The average slopes are 92.1 for cerium chloride and

TABLE II  
HEAT OF SOLUTION AT INFINITE DILUTION OF POTASSIUM CHLORIDE CORRECTED TO 25°

Authors	$t$ , °C.	$-L_2$ (s)
Cohen, Heldermaun and Moesveld <sup>14</sup>	18	4072
Wust and Lange <sup>15</sup>	25	4175 ± 10
Cohen and Kooy <sup>16</sup>	18	4122 ± 5
	20	4119 ± 5
	20	4162
	25	4113 ± 5
Roth and Eymann <sup>17</sup>	12.5	4150
	18	4124
	20	4118
	21	4112
Large and Monheim <sup>18</sup>	12.5	4148 ± 7
Miscenko <sup>19</sup>	25	4134 ± 8
Spedding and Miller	25	4134 ± 5

92.6 for neodymium chloride; the limiting Debye-Hückel slope for a 3-1 electrolyte should be 90 according to the revised values from Harned and Owen. The fact that values of the relative apparent heat capacities are obtained from the difference of two large numbers is a disadvantage since a precision of only 1% in the relative apparent heat capacity would require a precision of approximately 0.005 to 0.01% in the determination of the heat capacity of the calorimetric system. However, such accuracy is difficult to obtain by any method especially in the dilute solution range. Use was

TABLE III  
SMOOTHED VALUES OF THE APPARENT AND PARTIAL MOLAL HEAT CAPACITIES AND HEAT CONTENTS OF CERIUM CHLORIDE SOLUTIONS AT 25°

$m^{1/2}$	$\phi_J$	$\bar{J}_2$	$\bar{J}_1$	$\phi_L$	$\bar{L}_2$	$-\bar{L}_1$
0.01	0.9	1.4	0.0682	68	102	0.0461
.02	1.8	2.4	.0566	135	200	.0347
.05	4.6	6.9	.0310	324	475	.0268
.1	9.2	13.8	.03823	606	868	.0474
.2	18.4	27.6	.02658	1062	1457	.2843
.3	27.6	41.5	.0222	1407	1858	.7315
.4	36.9	55.3	.0527	1676	2164	1.407
.5	46.1	69.1	.103	1907	2468	2.523
.6	55.3	82.9	.178	2137	2860	4.690

TABLE IV  
SMOOTHED VALUES OF THE APPARENT AND PARTIAL MOLAL HEAT CAPACITIES AND HEAT CONTENTS OF NEODYMIUM CHLORIDE SOLUTIONS AT 25°

$m^{1/2}$	$\phi_J$	$\bar{J}_2$	$\bar{J}_1$	$\phi_L$	$\bar{L}_2$	$-\bar{L}_1$
0.01	0.9	1.4	0.0683	68	102	0.0461
.02	1.9	2.8	.0567	134	200	.0347
.05	4.6	6.9	.0310	321	470	.0267
.1	9.3	13.9	.03834	596	848	.0456
.2	18.5	27.8	.02667	1026	1387	.2606
.3	27.8	41.7	.0225	1333	1722	.6233
.4	37.0	55.5	.0534	1560	1959	1.159
.5	46.3	69.4	.104	1749	2206	2.078
.6	55.5	83.3	.180	1943	2567	4.099

(14) E. Cohen, W. D. Heldermaun and H. I. Th. Moesveld, *Z. physik. Chem.*, **96**, 259 (1920).

(15) J. Wust and E. Lange, *ibid.*, **116**, 161 (1925).

(16) E. Cohen and J. Kooy, *ibid.*, **139**, 273 (1928).

(17) W. A. Roth and C. Eymann, *ibid.*, **143A**, 321 (1929).

(18) E. Lange and J. Monheim, *ibid.*, **150A**, 349 (1930).

(19) K. P. Miscenko, *Z. Elektrochem.*, **36**, 777 (1930).

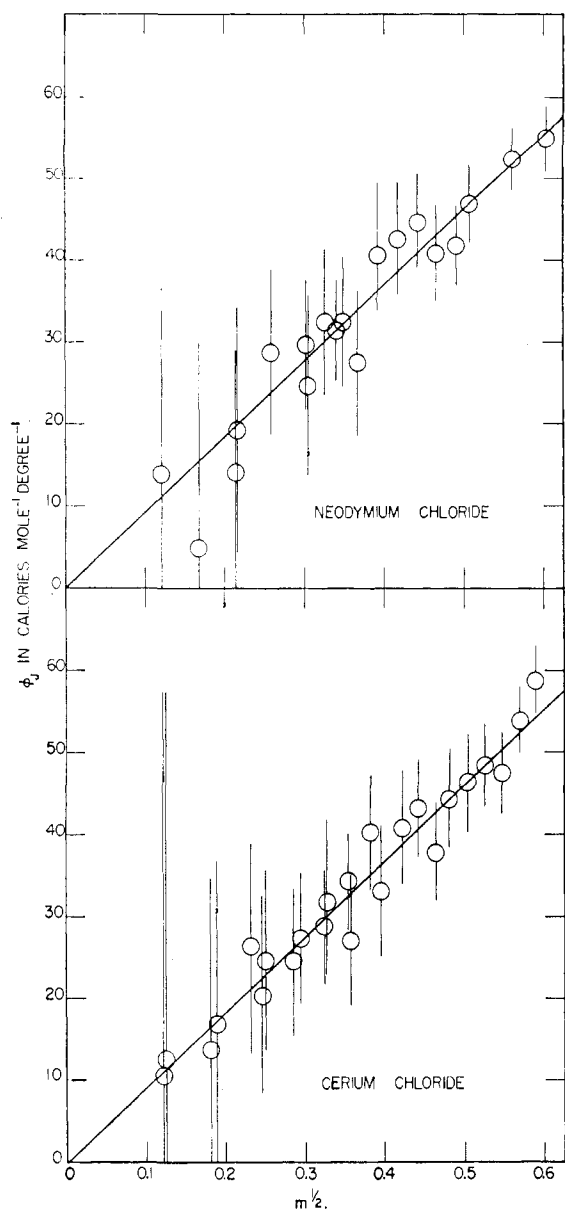


Fig. 2.—The relative apparent molal heat capacities of solutions of the chlorides of cerium and neodymium at 25°.

made of the values of  $\Delta C_{pM}$  to make the small corrections to 25° for the heat of solution values.

The data for the heats of solution of the chlorides of cerium and of neodymium are plotted in Fig. 3. The data were analyzed by the chord method; the results therefrom are plotted in Fig. 4 and show that, with the limits of experimental error, the limiting slope of 6925 as given by the Debye-Hückel equation is approached. The heat of solution at infinite dilution,  $-L_2(s)$ , was determined by fitting a cubic equation in  $m^{1/2}$  to the data in which the coefficient of  $m^{1/2}$  was taken to be 6925. The method of successive approximations was used. The equation which represents the data for the heat of solution of cerium chloride at 25° was found to be

$$\Delta H = -34,423 + 6,925m^{1/2} - 9,294m + 6,147m^{3/2} \quad (6)$$

and for neodymium chloride

$$\Delta H = -37,489 + 6,925m^{1/2} - 10,402m + 7,096m^{3/2} \quad (7)$$

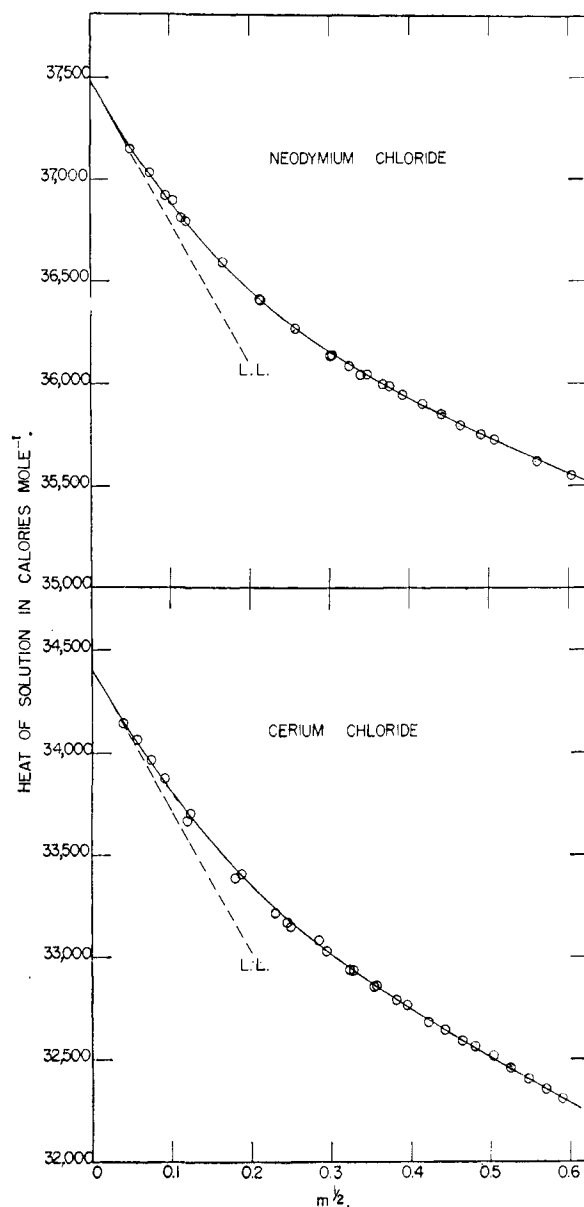


Fig. 3.—The heats of solution and dilution of the chlorides of cerium and neodymium at 25°.

The average difference between the observed values and those calculated by Equations (6) and (7) was 12 cal./mole for cerium chloride and 14 cal./mole for neodymium chloride. The average of the probable deviations was calculated to be approximately 20 cal./mole.

The heats of solution of the chlorides of many of the rare earth elements were reported by Bommer and Hohmann<sup>4</sup>; they gave an average value of  $32.7 \pm 0.1$  kcal./mole at 20° for the heat of solution of cerium chloride in which the concentrations of the final solutions varied from about 0.05 to 0.12 molal. For the heat of solution of neodymium chloride they reported a single value of 35.9 kcal./mole at 20°; Matignon<sup>20</sup> gave it as 35.4 kcal./mole at 17°.

The heats of solution of a series of ionic crystals like the anhydrous chlorides of the rare earth compounds at infinite dilution are a measure of the

(20) C. A. Matignon, *Compt. rend.*, **141**, 53 (1905).

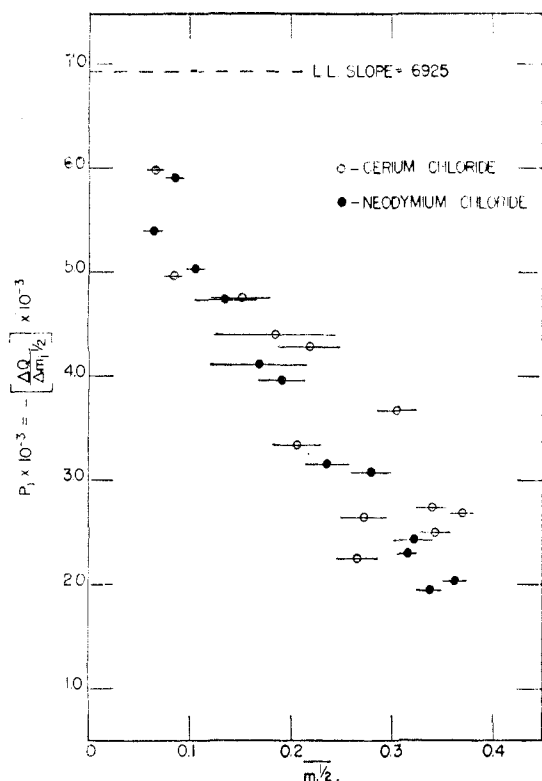


Fig. 4.—Plot of the short chords,  $P_1$ , against  $M_1^{1/2}$  for the heats of solution of the chlorides of cerium and neodymium.

differences between the lattice energies of the crystals and the energies of hydration of the ions in an ideal solution. The lattice energies, for a series of similar crystals of the rare earths and in which the ionic radius of the rare earth ion decreases with increasing atomic number, should increase with the atomic number of the rare earth. The heats of hydration of the rare earth ions should also increase with atomic number due to a progressively higher degree of polarization of the water molecules. Hence the difference in the heats of solution at infinite dilution between two rare earth chlorides includes the differences in the lattice energies of the two salts and the difference in the hydration energies of the two rare earth ions. The correlation of these hydration energies with the effective ions radius in solution and with the coordination numbers of these ions when more data are available will be of considerable aid in furthering the understanding of the behavior of ions in solution.

The relative apparent and relative partial molal heat contents of the two electrolytes are plotted in Fig. 5. Their smoothed values are given in Tables III and IV. The derived equations which represent the data for  $L_2$  up to concentrations of about 0.35 molal are

$$\bar{L}_2 = 1.0387 \times 10^4 m^{1/2} - 1.859 \times 10^4 m + 1.537 \times 10^4 m^{3/2} \quad (8)$$

for cerium chloride solutions, and

$$\bar{L}_2 = 1.0387 \times 10^4 m^{1/2} - 2.080 \times 10^4 m + 1.770 \times 10^4 m^{3/2} \quad (9)$$

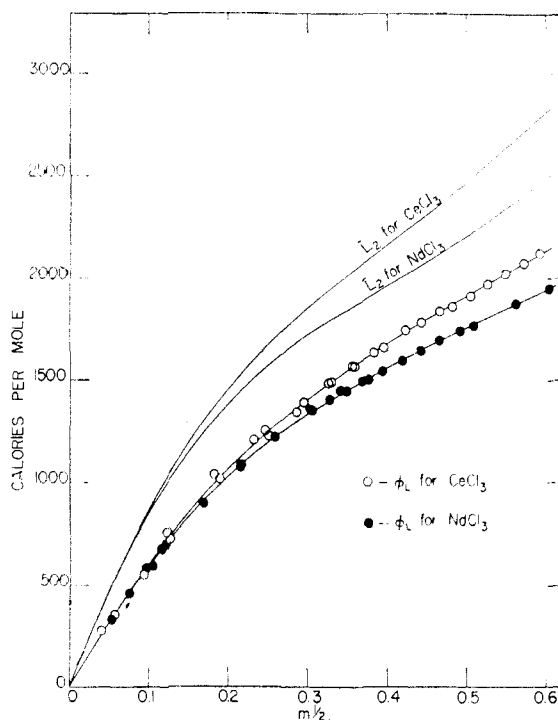


Fig. 5.—The relative apparent and partial molal heat contents for solutions of the chlorides of cerium and neodymium at 25°.

for neodymium chloride solutions. Some of the factors which could cause differences in the partial molal heat contents of the two electrolytes are: (1) the apparent diameters of the hydrated rare earth ions; (2) differences in the dielectric constant of the water due to a different degree of distortion of the water molecules near the highly charged positive ion; (3) differences in the coordination number between the positive ions; (4) a change in the relative population of ions of a given coordination number with concentration where ion-size permits more than one coordination; and (5) differences in tendency of the two cations to form ion pairs. Although there is evidence that cerium due to its larger ion size,<sup>21</sup> can have more water coordinated with it in the first layer surrounding the ion than neodymium, it would be difficult to ascribe just what portion of the differences in the relative partial molal heat contents would be due to this factor from the available information. We are reserving detailed discussion on these points for later when information on more of the rare-earths will be made available.

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AMES, IOWA

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