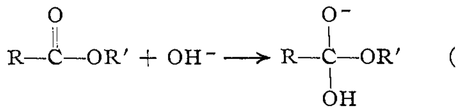
forming the transition state of the hydrolytic reaction.

Since the rate-determining step of this reaction is



$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OR' + OH^- \longrightarrow R{-}\overset{\displaystyle O^-}{\overset{|}{\underset{\underset{\displaystyle OH}{|}}{C}}}{-}OR' \qquad (5)$$

and the transition state carries a negative charge in the same position as the ionized carboxyl groups, the identity of ΔF_{el}^{ion} and $\Delta F_{el}^{\ddagger}$ is not unexpected *in this case.*

In the case of the quaternization of PVPy by bromoacetate, a comparison of the last two columns of Table I shows that the dissociation constant of the pyridinium residues K_a is considerably more sensitive than the quaternization rate constant k_2 to the charge density of the polymer and the counterion atmosphere. This means that the anionic charge of the bromoacetate is, in the transition state of the quaternization reaction, in a region of lower electrostatic potential than the charge of a pyridinium residue. Only if the transition state involved an attack of an un-ionized pyridine residue on the C–Br bond with simultaneous ion-pair formation of the carboxylate with a second ionized pyridine group, would variations in k_2 be expected to be proportional to variations in K_a. Such a simultaneous attack of two polymer groups on two distinct sites of the low molecular weight reagent, analogous to the postulated action of enzymes, may not be realizable with polymers consisting of fairly flexible chains. It seems much more probable with polymers which maintain in solution a tightly coiled helical configuration,[16] so that the spacing between their functional groups is closely defined.

(16) P. Doty and J. T. Yang, THIS JOURNAL, **78**, 498 (1956).

BROOKLYN, N. Y.

[CONTRIBUTION NO. 591 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Heats of Dilution and Related Thermodynamic Properties of Aqueous Rare Earth Salt Solutions at 25°; Integral Heats of Solution of $NdCl_3{\cdot}6H_2O$[1]

BY F. H. SPEDDING, A. W. NAUMANN AND R. E. EBERTS

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The heats of dilution at 25° of $LaCl_3$, $NdCl_3$, $ErCl_3$, $YbCl_3$, $La(NO_3)_3$ and $Yb(NO_3)_3$ solutions have been measured for concentrations up to about 0.2 molal. Relative apparent molal heat contents of the solute, ϕ_L, have been calculated for the solutions used and empirical expressions have been derived for the concentration dependence of ϕ_L. The integral heats of solution of $NdCl_3{\cdot}6H_2O$ have been measured and the relative apparent molal heat content of $NdCl_3$ derived from these quantities. The results are compared to theoretical predictions and to previous measurements. A tentative explanation has been given for the anomalous behavior of the erbium and ytterbium salts at very low concentrations.

Introduction

Ion-exchange separation techniques have made kilogram quantities of all the rare earth elements available in high purity.[2] This has made possible, and created a need for, the measurement of the properties of aqueous solutions of soluble rare earth salts.

The chemical similarity of the rare earth elements, their ability to form what may be considered strong electrolytes and the regular decrease in ionic radius through the rare earth series make the lanthanide elements attractive for theoretical studies of solution phenomena. A program was undertaken in this Laboratory to determine the properties of aqueous rare earth solutions, with the general aim of obtaining a consistent set of precise data with which to check and develop theories of aqueous solutions.[3] The determination of the heats of dilution of solutions of rare earth salts of the 3–1 type was an extension of this program.

Measurements of heats of dilution of 3–1 salts have been published by Nathan, Wallace and Robinson[4] on lanthanum chloride and by Lange and Miederer[5] on lanthanum nitrate. Both of these salts have been measured here, as a check on the data obtained in this Laboratory and to extend the data to higher concentrations. Spedding and Miller[6a] have reported ϕ_L's for neodymium and cerium chlorides from measurements of the heats of solution of the anhydrous salts. The measurements on the heat of solution of hydrated neodymium chloride were made in an attempt to explain the discrepancy in the neodymium chloride data of Spedding and Miller and those reported here from heats of dilution.

Experimental. Heats of Dilution

Apparatus.—The apparatus was patterned after one developed by Gucker, Pickard and Planck.[7] Aside from several minor changes, the apparatus differed from the one

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. This paper is based on theses by A. W. Naumann and R. E. Eberts, which were submitted to Iowa State College in partial fulfillment for degrees of Doctor of Philosophy.

(2) (a) F. H. Spedding, A. F. Voigt, E. M. Gladrow and N. R. Sleight, THIS JOURNAL, **69**, 2777 (1947); (b) F. H. Spedding, J. E. Powell and E. J. Wheelwright, *ibid.*, **76**, 612, 2557 (1954).

(3) (a) F. H. Spedding, P. E. Porter and J. M. Wright, *ibid.*, **74**, 2055, 2778, 2781 (1952); (b) F. H. Spedding and I. S. Yaffe, *ibid.*, **74**, 4751 (1952); (c) F. H. Spedding and J. L. Dye, *ibid.*, **76**, 879 (1954); (d) F. H. Spedding and S. Jaffe, *ibid.*, **76**, 882, 884 (1954).

(4) C. C. Nathan, W. E. Wallace and A. L. Robinson, *ibid.*, **65**, 790 (1943).

(5) E. Lange and W. Miederer, *Z. Elektrochem.*, **60**, 362 (1956).

(6) (a) F. H. Spedding and C. F. Miller, THIS JOURNAL, **74**, 3158 (1952); (b) **74**, 4195 (1952).

(7) F. T. Gucker, Jr., H. B. Pickard and R. W. Planck, *ibid.*, **61**, 459 (1939).

described by Gucker, *et al.*, only in the manner in which the temperature difference between the calorimeter containers was measured, and in the type of sample holders employed. The details of construction have been described elsewhere.[8]

The temperature difference between the calorimeter containers was measured with a 60 junction copper–constantan thermel. The output of the thermel was amplified by a model 14 Liston–Becker breaker type d.c. amplifier and was recorded on a recording potentiometer. With this arrangement a sensitivity of 4.9×10^{-4} cal. per mm. of chart displacement was realized.

Each sample holder consisted of two threaded cylinders held together by a cross piece. The cylindrical tubes of the sample holders had inside diameters of two cm. and were four cm. long. The sample holders were mounted in the calorimeter by attaching the cross pieces to supporting stems extending through the lids of the calorimeter containers. Screw-on caps held platinum disks 0.0005 inch thick firmly against the ends of the tubes. The sample holders were opened by punching holes in the platinum foils. With a two chambered sample holder in each container, it was possible to obtain two "short chord" heats of dilution without dismantling the apparatus.

Ten-ml. samples were measured into the sample holders with a pipet, and the samples were weighed. The tantalum containers were filled with water to give a total liquid content, water plus samples, of 900 g. for each container; the weighings were made to the nearest drop with a 2 kg. capacity analytical balance.

Materials.—The rare earths employed in this research were obtained as the oxides from the rare earth separation group of the Ames Laboratory of the U. S. Atomic Energy Commission. The methods of rare earth separation and purification have been described elsewhere.[2] The results of spectrographic analyses of the oxides showed the rare earths to contain less than 0.15% total impurities. The impurities consisted of traces of calcium and adjacent rare earths.

The experimental measurements were carried out on solutions that were prepared by diluting stock solutions. One stock solution of each salt was prepared by adding a slight excess of the oxides to C.P. Baker and Adamson hydrochloric or nitric acid. The resulting solutions were held near boiling for several hours and the excess oxides removed by filtration. The filtrates were diluted to approximately 0.25 molal, and aliquots were titrated with the appropriate acid. Typical strong acid–weak base titration curves resulted. The bulk solutions were brought to the *p*H of the inflection points of the titration curves, held near boiling for several hours and aliquots again taken for titration. This procedure was repeated until reproducible equivalence *p*H's were obtained and the bulk solutions showed no Tyndall cones.

A second neodymium chloride stock solution was prepared by treating neodymium oxide with a slight excess of redistilled hydrochloric acid. Conductivity water was added, and the solution was evaporated until crystals had formed three times. After the third heating, the solution was diluted to about one molal and titrated as described above.

A second erbium chloride stock solution was prepared from hydrated erbium chloride crystals. The crystals were grown by dissolving erbium oxide in a slight excess of acid, heating the resulting solution until viscous and drying over calcium chloride in an evacuated desiccator.

In the case of the chlorides, the stock solutions were analyzed for both rare earth content and chloride ion content; for the nitrates, only a rare earth analysis was made. The rare earth and chloride analyses agreed to better than one or two parts per thousand.

Dilutions of the stock solutions were made by weight. The density data of B. O. Ayers[9] were used to calculate vacuum corrections. Conductivity water with a specific conductivity of 1.5×10^{-6} mho or less was used for all dilutions.

Results. Heats of Dilution

The experimental determinations were of two types. In the first type, samples containing n_2' moles of salt in n_1' moles of water were diluted with X grams of water. In determinations of the second type, samples containing n_2'' moles of salt in n_1'' moles of water were diluted by solutions resulting from determinations of the first type.

The heat, q, evolved by these determinations was given by

$$q_1 = -n_2'[\phi_{L(m_2)} - \phi_{L(m_1)}] + q_B \qquad (1)$$

and

$$q_2 = -(n_2' + n_2'')\phi_{L(m_3)} + n_2''\phi_{L(m_1)} + n_2'\phi_{L(m_2)} + q_B \qquad (2)$$

In the expressions above, m_1 is the molality of the samples; m_2, the molality following a dilution of the first type; m_3, the molality following a dilution of the second type; ϕ_L, the relative apparent molal heat content of the solute; and q_B, the heat of opening of the same holders.

The experimentally determined quantities were converted to intermediate integral heats of dilution by means of the relationships

$$\Delta H_{1,2} = \phi_{L(m_2)} - \phi_{L(m_1)} = -\frac{q_1 - q_B}{n_2'} \qquad (3)$$

$$\Delta H_{1,3} = \phi_{L(m_3)} - \phi_{L(m_1)} = -\frac{q_1 + q_2 - 2q_B}{n_2' + n_2''} \qquad (4)$$

and when $n_2' \approx n_2''$, as was the case for these experiments

$$\Delta H_{3,2} = \phi_{L(m_2)} - \phi_{L(m_3)} = -\frac{q_1 - q_2}{n_2' + n_2''} \qquad (5)$$

The "short chord" method of Young and coworkers[10] as extended by Wallace and Robinson[11] was used to analyze the intermediate heats of dilution. In this treatment, $\bar{P}_i$, the average slope of ϕ_L *versus* $m^{1/2}$ for the very dilute concentration range, is calculated by

$$\bar{P}_i = \frac{-\Delta H_{3,2}}{\Delta m^{1/2}} \qquad (6)$$

An equation of the form

$$\bar{P}_i = S^0 + BX_i + C\left(X_i^2 + \frac{\delta^2}{12}\right) \qquad (7)$$

is derived for the concentration dependence of $\bar{P}_i$ for this concentration range. Equation 7 is then integrated to give $\phi_{L(m_k)}$, the relative apparent molal heat content for the extremely dilute solutions of molality m_k. The values of ϕ_L for the solutions used are obtained from the expression

$$\phi_{L(m_i)} = \phi_{L(m_k)} - \Delta H_{1,k} \qquad (8)$$

where $\Delta H_{1,k}$ = an intermediate heat of dilution corresponding to some $\Delta H_{1,2}$ or $\Delta H_{1,3}$.

Blank Experiments

Forty-two measurements were made with water samples to determine the "heat of opening" of the sample holders. The results of these measurements were as

Average heat of opening, cal.	12.3×10^{-3}
Standard deviation, cal.	2.5×10^{-3}

Results of Dilution Experiments

The experimentally determined heats of dilution of the rare earth salt solutions at 25° are summarized in Table I and shown in Figs. 1 through 4.

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[8] (a) A. W. Naumann, Ph.D. Dissertation, Iowa State College Library, Ames, Iowa, 1956; (b) R. E. Eberts, Ph.D. Dissertation, Iowa State College Library, Ames, Iowa, 1957.

[9] B. O. Ayers, Ph.D. Dissertation, Iowa State College Library, Ames, Iowa, 1954.

[10] (a) T. F. Young and O. G. Vogel, This Journal, **54**, 3030 (1932); (b) T. F. Young and W. L. Groenier, *ibid.*, **58**, 187 (1936).

[11] W. E. Wallace and A. L. Robinson, *ibid.*, **63**, 958 (1941).

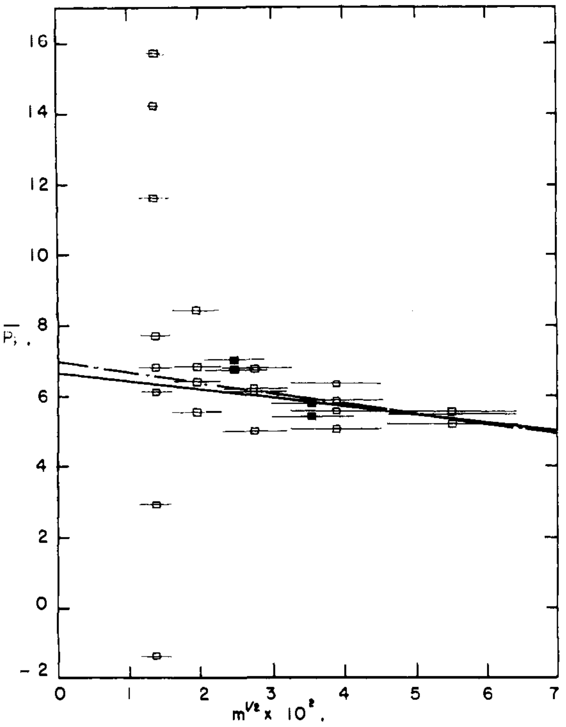

Fig. 1.—Short chord data for neodymium chloride solutions: ——, $\bar{P}_i = a + bX_i$; — · —, $\bar{P}_i + 6925 + bX_i$.

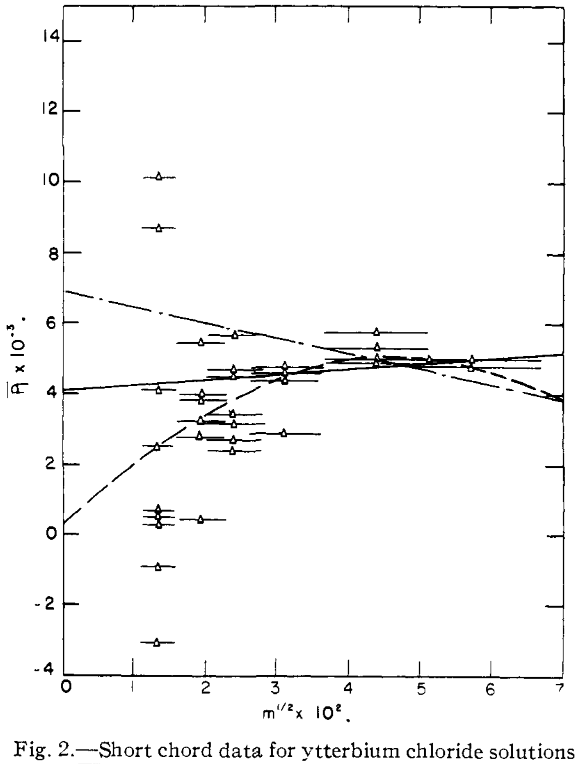

Fig. 2.—Short chord data for ytterbium chloride solutions: ——, $\bar{P}_i = a + bX_i$; — · —, $\bar{P}_i = 6925 + bX_i$; - - - -, $\bar{P}_i = a + bX_i = + c(X_i^2 + \delta^2/12)$.

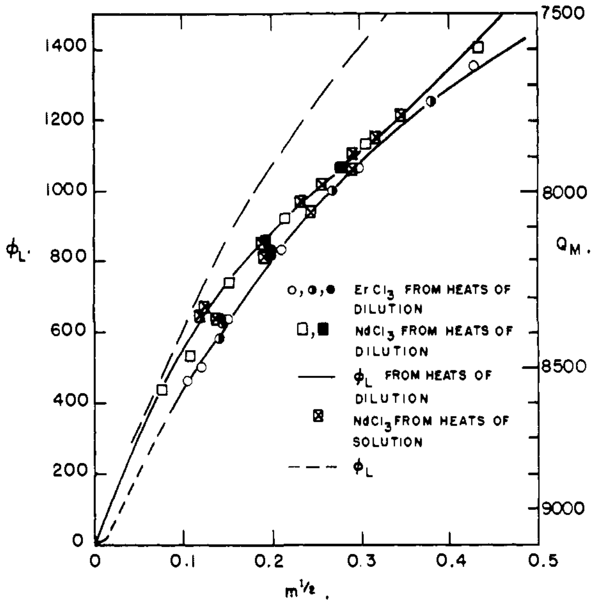

Fig. 3.—Relative apparent molal heat contents of $NdCl_3$ and $ErCl_3$ solutions at 25° and integral heats of solution of $NdCl_3{\cdot}6H_2O$; - - - ϕ_L for $NdCl_3$ by Spedding and Miller.

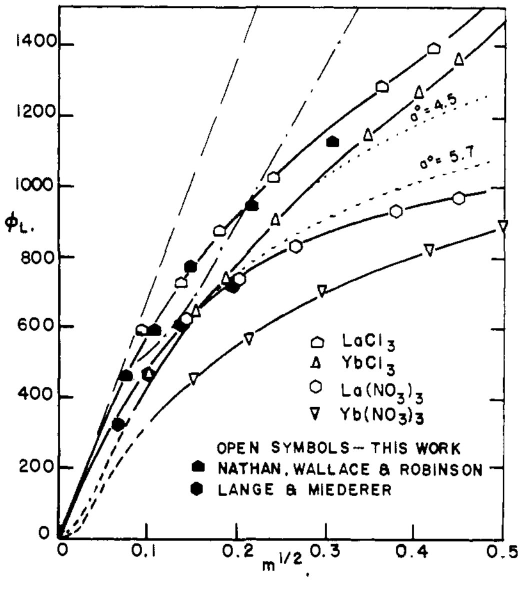

Fig. 4.—Relative apparent molal heat contents of $LaCl_3$, $YbCl_3$, $La(NO_3)_3$ and $Yb(NO_3)_3$ solutions at 25°; theoretical curves.

In Figs. 1 and 3, the neodymium chloride solutions prepared by the excess acid method are represented as filled squares; in Fig. 3 erbium chloride solutions prepared from hydrated crystals are represented as half-filled circles and the solutions prepared by acidifying these to *p*H 4 as filled circles. In all figures open points represent solutions prepared by the excess oxide method. As seen in Fig. 3, the results were not influenced by the method of preparation.

The short chord data from which the concentration dependence of ϕ_L at extreme dilution was obtained are listed in column 5 with the probable error in $\bar{P}_i$ listed below each value.

The short chord data for neodymium chloride and ytterbium chloride are plotted in Figs. 1 and 2. The plots for the lanthanum salts were quite similar to that of neodymium chloride; those of

TABLE I

EXPERIMENTAL HEATS OF DILUTION AND RELATIVE APPARENT MOLAL HEAT CONTENTS OF RARE EARTH SALT SOLUTIONS AT 25°

No. of detns.	$m_1^{1/2}$	$m_k^{1/2} \times 10^2$	$q_1{}^a \times 10^3$ $q_2 \times 10^3$	Mean P_j P_{Pi}	$-\Delta H_{1,k}$	$\phi_{L(m_k)}$	$\phi_{L(m_1)}$
			Lanthanum chloride				
10	0.09821	1.039	63.0	8531	528	70	594
9		1.461	56.3	1480	493	98	
8	.1406	1.487	135.7	5845	626	100	727
8		2.092	121.8	479	591	138	
8	.1847	1.953	265.3	6262	745	129	872
7		2.747	230.4	468	692	179	
4	.2452	2.593	519.5	5758	847	169	1017
4		3.647	446.8	115	786	232	
5	.3684	3.892	1419.2	5788	1043	246	1287
5		5.473	1172.3	120	952	333	
4	.4253	4.493	2020.7	5185	1118	280	1398
4		6.319	1680.6	86	1023	376	
			Neodymium chloride				
6	.07658	0.8097	33.7	..	366	55	439
6		1.139	35.4	..	380	77	
8	.1084	1.146	66.6	7988	464	77	538
8		1.611	57.9	1158	427	108	
4	.1533	1.620	160.4	6823	634	109	741
4		2.278	139.4	579	588	150	
2	.1944[b]	2.055	285.9	6878	727	136	861
2		2.890	242.7	401	670	188	
4	.2167	2.291	371.9	6010	769	151	921
4		3.222	319.6	204	713	208	
2	.2783[b]	2.940	686.2	5612	875	191	1068
2		4.135	583.0	137	808	262	
4	.3065	3.238	874.8	5700	924	209	1134
4		4.555	734.6	178	848	286	
3	.4335	4.577	2092.2	5420	1116	287	1403
4		6.436	1712.3	62	1015	387	
			Erbium chloride				
8	.1050	1.110	60.1	278	436	19	461
8		1.561	59.8	1222	434	33	
4	.1214	1.283	82.0	2828	475	24	501
4		1.804	77.7	1118	461	42	
2	.1389	1.468	117.0	939	546	30	585
2		2.064	114.8	1058	540	53	
2	.1432[d]	1.514	137.0	4556	611	31	641
2		2.129	125.6	964	583	56	
2	.1436[c]	1.518	135.2	4181	599	32	630
2		2.135	124.6	954	573	56	
4	.1489	1.574	144.6	3135	599	34	636
4		2.214	135.7	605	579	59	
2	.2005[d]	2.119	319.7	5372	769	55	821
2		2.980	282.7	352	722	96	
2	.2013[c]	2.127	326.9	6574	781	56	829
2		2.991	281.1	347	724	97	
4	.2134	2.255	362.3	4407	773	61	836
4		3.172	325.7	206	732	106	
2	.2726	2.880	688.2	5774	915	91	1004
2		4.050	588.5	140	848	154	
4	.3024	3.196	881.7	5168	956	107	1066
4		4.494	759.6	114	889	179	
2	.3818	4.034	1603.8	5382	1099	153	1252
2		5.673	1348.1	107	1010	242	
4	.4293	4.533	2153.3	5107	1171	181	1352
4		6.375	1809.4	102	1077	274	
			Ytterbium chloride				
9	0.1057	1.118	62.1	2573	448	15	463
9		1.572	59.5	933	436	27	
7	.1530	1.619	154.5	3391	609	28	638
7		2.276	144.0	393	587	51	
7	.1887	1.996	260.4	3820	699	41	740
7		2.807	238.4	308	668	73	
5	.2457	2.598	515.7	4598	838	64	903
5		3.653	461.5	47	793	112	
4	.3468	3.663	1249.8	5273	1034	113	1146
4		5.157	1061.7	128	955	189	
2	.4050	4.280	1848.8	4965	1126	144	1271
2		6.020	1567.1	75	1040	232	
2	.4505	4.759	2413.4	4910	1192	169	1360
2		6.693	2031.0	54	1097	263	
			Lanthanum nitrate				
8	0.1445	1.457	114.2	5367	539	88	627
8		2.049	102.2	518	507	122	
7	.2024	2.039	240.7	5644	617	122	738
7		2.868	206.3	335	570	168	
4	.2683	2.701	448.5	5400	672	159	831
4		3.798	371.5	114	612	218	
3	.3804	3.818	938.2	5083	714	219	933
3		5.369	733.6	61	635	298	
3	.4530	4.537	1315.4	4833	712	256	968
3		6.380	989.1	38	622	346	
			Ytterbium nitrate				
8	0.1558	1.502	103.7	2660	455	6	465
8		2.112	97.2	492	439	29	
7	.2163	2.083	226.0	3269	553	20	574
7		2.928	204.6	159	525	49	
5	.3023	2.903	500.8	4472	651	48	698
5		4.082	421.6	117	598	99	
3	.4199	4.014	1055.2	4527	727	96	823
3		5.646	843.4	53	653	170	
3	.5038	4.797	1558.7	4110	757	132	887
3		6.746	1230.9	39	676	212	

[a] All heat quantities given in defined calories. [b] Prepared by excess acid method. [c] Prepared from hydrated crystals. [d] Prepared by acidifying solutions[c] to pH 4.

erbium chloride and ytterbium nitrate were like that of ytterbium chloride. These figures illustrate how the uncertainties in $\bar{P}_i$ increase rapidly with decreasing concentration.

The concentration dependence of $\bar{P}_i$ was determined by the method of least squares using the inverse square of the probable error in $\bar{P}_i$ as a weighting factor. Least squares treatments were made with three types of expressions

$$\bar{P}_i = a + bX_i \tag{9}$$

$$\bar{P}_i = 6925 + bX_i \tag{10}$$

which contains the Debye–Hückel limiting law value, and

$$\bar{P}_i = a + bX_i + c\left(X_i^2 + \frac{\delta^2}{12}\right) \tag{11}$$

where a, b and c = constants

$$X_i = \frac{m_3^{1/2} + m_2^{1/2}}{2}$$

and

$$\delta = m_3^{1/2} - m_2^{1/2}$$

In the case of the lanthanum and neodymium salts the data were best represented by a linear equation; for the erbium and ytterbium salts a parabolic equation was needed. The least squares constants obtained are listed in Table II; it is obvious from the constants which equations were used. While the parabolic equations for the erbium and ytterbium salts gave an excellent representation of the short chord data in the concentration range studied, their pronounced curvatures make them unsuitable for extrapolation to higher, and probably to lower, concentrations. The expressions for ϕ_L for the short chord range were obtained by integrating the equation deemed most suitable for the given salt. These are

TABLE II

LEAST SQUARES CONSTANTS FOR THE CONCENTRATION DEPENDENCE OF $\bar{P}$

Salt	S^0	B	C
$LaCl_3$	6630	−24,650	....
	6925	−15,413	....
$La(NO_3)_3$	6230	−25,466	....
	6925	−38,990	....
$NdCl_3$	6627	−22,325	....
	6925	−28,496	....
$ErCl_3$	4933	6,965	....
	6925	−39,433	....
	465	242,114	-2.867×10^6
$YbCl_3$	4100	15,626	....
	6925	−44,530	....
	247	202,890	-2.214×10^6
$Yb(NO_3)_3$	4166	1,221	....
	6925	−50,460	....
	−1393	267,000	-2.948×10^6

$$LaCl_3\text{: } \phi_L = 6925m^{1/2} - 15413m \quad (12)$$

$$NdCl_3\text{: } \phi_L = 6925m^{1/2} - 14248m \quad (13)$$

$$ErCl_3\text{: } \phi_L = 465m^{1/2} + 1.211 \times 10^5\, m - 0.9557 \times 10^6\, m^{3/2} \quad (14)$$

$$YbCl_3\text{: } \phi_L = 247\, m^{1/2} + 1.045 \times 10^5\, m - 0.7381 \times 10^6\, m^{3/2} \quad (15)$$

$$La(NO_3)_3\text{: } \phi_L = 6230m^{1/2} - 12733m \quad (16)$$

$$Yb(NO_3)_3\text{: } \phi_L = -1393m^{1/2} + 1.335 \times 10^5\, m - 0.9828 \times 10^6\, m^{3/2} \quad (17)$$

The long chord dilution data and the relative apparent molal heat contents are given in Table I. An empirical representation of the concentration dependence of ϕ_L was obtained by the method of least squares using the values for the more concentrated solutions and the ϕ_L value predicted for 0.005 molal by the equations for the very dilute range. The data were fitted with an equation of the type

$$\phi_L = Am^{1/2} + Bm + Cm^{3/2} \quad (18)$$

For $LaCl_3$ and $NdCl_3$ the constant A was assigned the value 6925.

Expressions for the relative partial molal heat content of solvent and solute, $\bar{L}_1$ and $\bar{L}_2$, respectively, can be derived easily from equation 18 by the relations

$$\bar{L}_1 = \frac{mM_1}{1000}(\phi_L - \bar{L}_2)$$

and

$$\bar{L}_2 = \phi_L + \frac{m^{1/2}}{2}\frac{\partial \phi_L}{\partial m^{1/2}}$$

The equations for ϕ_L which were derived are

$$LaCl_3\ \phi_L = 6925m^{1/2} - 14575m + 14178\, m^{3/2} \quad (19)$$

$$NdCl_3\text{: } \phi_L = 6925m^{1/2} - 16056m + 17523m^{3/2} \quad (20)$$

$$ErCl_3\text{: } \phi_L = 4952m^{1/2} - 5077m + 1926m^{3/2} \quad (21)$$

$$YbCl_3\text{: } \phi_L = 4783m^{1/2} - 5122m + 2644m^{3/2} \quad (22)$$

$$La(NO_3)_3\text{: } \phi_L = 6206m^{1/2} - 15180m + 13735m^{3/2} \quad (23)$$

$$Yb(NO_3)_3\text{: } \phi_L = 3696m^{1/2} - 5591m + 3469m^{3/2} \quad (24)$$

The experimentally derived relative apparent molal heat contents are plotted in Figs. 3 and 4, with the curves defined by the empirical expressions drawn through the points. The curves for the erbium and ytterbium salts were constructed by using the ϕ_L values for the very dilute solutions up to $m^{1/2} = 0.05$; a curve then was smoothed in to join the curve for higher concentrations at $m^{1/2} = 0.1$. In Fig. 4 the data of Nathan, Wallace and Robinson[4] and of Lange and Miederer[5] are also plotted for comparison; the agreement is within 3%.

Error Analysis. Heats of Dilution

Estimates of the uncertainties in ϕ_L were obtained by the method of propagation of precision indexes as described by Worthing and Geffner.[12] The error analysis showed that the probable error in $\phi_{L(m_1)}$ rose from about 25 cal./mole at 0.01 molal to about 60 cal./mole at 0.25 molal. A probable error of about ±700 was estimated in the limiting slope of equations 12 through 17.

Experimental. Heats of Solution

Apparatus.—The apparatus was very similar to that described by Spedding and Miller,[6a] as revised by Spedding and Flynn.[13] The only difference between this apparatus and that of the latter authors was that the thermometer and heater were enclosed in gold-plated copper cases, which decreased the lag-time of the calorimeter. The thermometer had a sensitivity of about 3.5×10^{-4} degree per microvolt.

Materials.—The neodymium chloride hexahydrate was prepared from neodymium oxide, which was dissolved in a slight excess of hydrochloric acid and the resulting solution boiled down twice to the point where crystals just began to form. The crystals were grown in an evacuated desiccator over a period of 2 weeks, dissolved in water and then recrystallized in the same manner. The crystals were powdered and further dried over anhydrous $CaCl_2$ for another 4 weeks. Analysis of the salt gave an $H_2O/NdCl_3$ ratio of 6.05 ± 0.01.

Results. Heats of Solution

The results of the heats of solution measurements are grouped into runs in Table III. Runs 3 and 5 were made into solutions to attain higher final molalities. In the table, q_i is the experimental heat of solution (corrected to 25°); Q_M, the integral heat of solution; and, ϕ_L, the relative apparent molal heat content. The concentration dependence of Q_M

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(12) A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

(13) F. H. Spedding and J. P. Flynn, THIS JOURNAL, **74**, 1477 (1954).

TABLE III

INTEGRAL HEATS OF SOLUTION OF NEODYMIUM CHLORIDE HEXAHYDRATE AT 25°

Run	$m^{1/2}$	q_i[a]	Q_M	ϕ_L
1	0.1225	190.40	8456	644
2	.1284	207.22	8441	658
	.1885	229.17	8236	863
	.2327	221.40	8130	969
3	.2228	....	..	..
	.2593	208.09	8088	1011
	.2926	221.97	8034	1066
4	.1401	247.95	8465	635
	.1954	224.95	8285	815
	.2419	240.33	8139	961
5	.2628	....	..	..
	.2957	213.38	8005	1095
	.3207	176.72	7944	1156
	.3479	209.69	7897	1203

[a] All heat quantities given in defined calories.

could be represented by the empirical equation

$$Q_M = 9103 - 6925m^{1/2} + 17987m - 24509m^{3/2} = -\Delta H_{\text{soln}} \quad (26)$$

from which the heat of solution at infinite dilution was obtained. For convenience in plotting Fig. 3 a limiting value of 9100 cal./mole was used to calculate the ϕ_L's by the relation

$$\phi_L = Q_M(m = 0) - Q_M(m_f)$$

The values of ϕ_L are plotted in Fig. 3 along with the curves representing the ϕ_L's derived from the heats of dilution of this work and those derived by Spedding and Miller.

Error Analysis. Heats of Solution

Again the method of propagation of precision indexes was used to estimate uncertainties. This gave a probable error in Q_M of 15 cal./mole at $m^{1/2} = 0.1$ and 35 cal./mole at $m^{1/2} = 0.3$; the probable error in $Q_{M(m = 0)}$ was estimated as 50 cal./mole. Thus the ϕ_L's have an uncertainty of from 50 to 85 cal./mole depending on the concentration.

Discussion

In Fig. 4, several theoretical curves are included. The Debye–Hückel limiting law is represented as a dashed line, the Debye–Hückel law with $a^0 = 5.7$ and 4.5 Å. and $da^0/dT = 0$ appear as dotted lines and Mayer and Poirier's[14,15] treatment as alternate dots and dashes. The a^0 values of 5.7 and 4.5 Å. are the averages for the distance of closest approach for rare earh chlorides[3d] and nitrates,[3c] respectively. The experimentally determined ϕ_L's follow none of these curves.

The ϕ_L values for the chlorides fall in a regular order for the rare earths, although showing only a slight specificity between the members. The nitrate curves fall below those for the chlorides; this is the opposite of what is predicted from the a^0 values. For concentrations above 0.02 molal, the thermodynamic properties for the chlorides were quite similar, but below 4×10^{-4} molal they divide into two groups.

The anomalous behavior of the ϕ_L's for the erbium and ytterbium salts for concentrations below 4×10^{-4} molal is unique. There is evidence[16] that the bivalent sulfates also have a maxima in $\bar{P}_i$ in the range 10^{-3} to 10^{-4} molal, but in these cases the $\bar{P}_i$ for the most dilute concentrations approach, rather than depart from, the theoretical values. Nathan, Wallace and Robinson[4] have reported a negative slope for $\bar{P}_i$ *versus* $m^{1/2}$ for lanthanum chloride; this, however, was deduced from fewer data than are reported here.

The behavior of heavier rare earth salts can be explained by assuming the formation of a polymeric aggregate when the solution is diluted. This possibility is confirmed by pH measurements made on the solutions. While the initial solutions had pH's in the range 5.0–5.2, the final pH's approached that of the water used, *i.e.*, 5.7. At these higher pH's, hydrolysis can occur. The reason for the normal behavior of the lighter rare earths can be attributed to the fact that they have less tendency to hydrolyze and to the slightly greater solubility of their hydroxides. Since carbon dioxide was present in the water used, the possibility of a carbonate or bicarbonate complex cannot be neglected. It is also known that insoluble oxychlorides can be formed, especially by the heavier rare earths.

The ϕ_L's derived from the integral heats of solution of $NdCl_3 \cdot 6H_2O$ definitely agree with those derived from the heats of dilution of $NdCl_3$ solutions, and not with those obtained from the heats of solution of anhydrous $NdCl_3$. The discrepancy in the ϕ_L values of Spedding and Miller may be due to the presence of a slow type reaction which accompanies the dissolution of the anhydrous salt. If the last chloride were held very energetically by the rare earth, the dissociation of this ion might take the form of a slow type reaction and the heat evolved would not have been detected. Since the final pH of their solutions ranged from 6.3 to 6.6,[6b] the possibility of hydrolysis accompanying the dissolution cannot be neglected.

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