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Transference Numbers of Rare Earth Chlorides in Aqueous Solution at 25°

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The cation transference numbers of the chlorides of lanthanum, cerium, praseodymium, neodymium, samarium, europium, erbium and ytterbium in aqueous solutions have been determined in the concentration range from 0.007 to 0.1 *N*. The numbers for the first five earths are about the same, while a regular decrease with increasing atomic number seems to occur for elements beyond samarium. The data for samarium chloride are slightly higher than anticipated from the conductance data,[2] while the other earths lie in the expected order. The plots of data for all but ytterbium were linear functions of the square root of concentration in the range studied; however, the slopes of the lines were not in agreement with the Onsager limiting values (see Fig. 2). This behavior is in agreement with the previous observation of Longsworth and MacInnes[3] for lanthanum chloride. The plot for ytterbium curved downward at high dilution, but this effect may have been due to the greater difficulty in measurements for this salt.

Introduction

As pointed out in the first article of this series,[2] the rare earths and their salts provide an excellent group of elements with which to study the points at which the simplifying assumptions introduced into the theories of physical chemistry and of solids break down. Such an examination of the theories requires the use of a wide variety of accurate data which it is the intention of the present series of papers to provide. This paper deals with the determination of the transference numbers in aqueous solution of the chlorides of lanthanum, cerium, praseodymium, neodymium, samarium, europium, erbium and ytterbium in the concentration range from 0.007 to 0.1 *N*.

Only one measurement of the transference numbers of a rare earth salt has apparently been made with the precision afforded by modern methods. Longsworth and MacInnes[3] measured those for lanthanum chloride in aqueous solutions using the

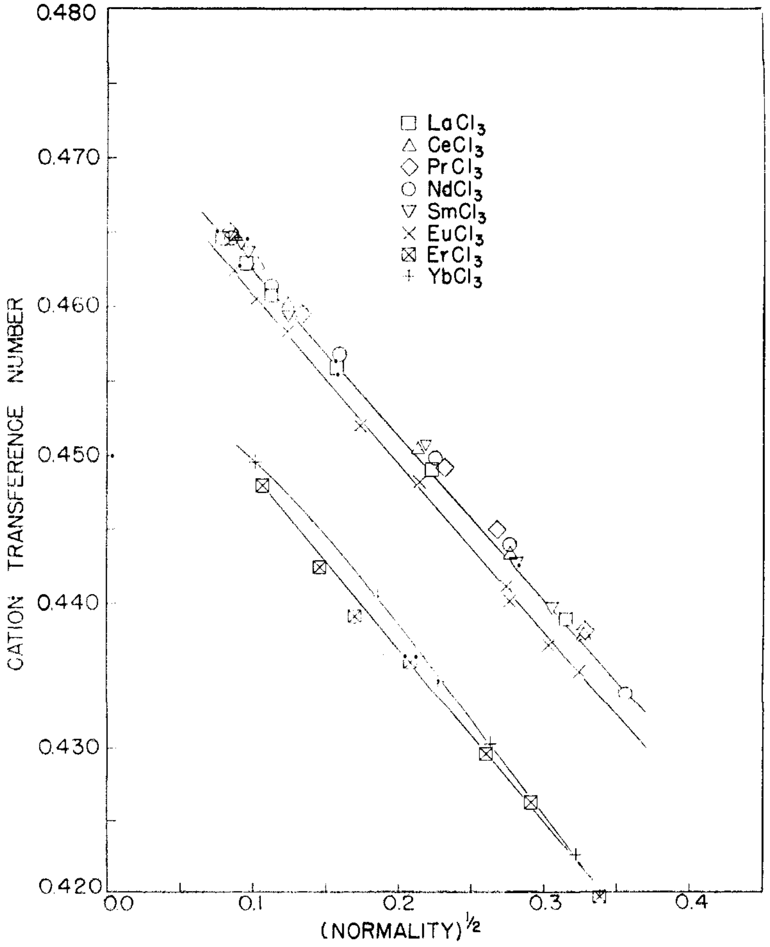

Fig. 1.—Cation transference numbers of rare earth chlorides.

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[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**, 2055 (1952).

[3] L. G. Longsworth and D. A. MacInnes, *ibid.*, **60**, 3070 (1938).

TABLE I

CATION TRANSFERENCE NUMBERS OF RARE EARTH CHLORIDES IN AQUEOUS SOLUTIONS AT 25°

Each experimental value is the mean of about 20 timings. When two numbers are given these were determined on completely independently prepared cells.

$LaCl_3$			$CeCl_3$			$PrCl_3$			$NdCl_3$		
N	Uncor. $T+$	Cor. $T+$	N	Uncor. $T+$	Cor. $T+$	N	Uncor. $T+$	Cor. $T+$	N	Uncor. $T+$	Cor. $T+$
0.09933	0.4391	0.4389	0.1075	0.4381	0.4378	0.1077	0.4384	0.4382	0.1274	0.4340	0.4338
	.4391			.4380			.4386			.4341	
.04967	.4491	.4490	.07675	.4437	.4433	.07177	.4449	.4450	.07642	.4440	.4439
	.4491			.4432			.4455			.4439	
.02483	.4558	.4559	.04605	.4509	.4505	.05383	.4495	.4494	.05095	.4501	.4498
.01242	.4601	.4606		.4500			.4494			.4495	
	.4604		.01535	.4599	.4602	.01794	.4594	.4596	.02547	.4568	.4569
.009030	.4624	.4629		.4601			.4593			.4565	
.006209	.4638	.4645	.01075	.4626	.4629	.007177	.4646	.4652	.01274	.4609	.4613
				.4628						.4610	
			.007675	.4647	.4650				.007642	.4643	.4645
										.4637	

$SmCl_3$			$EuCl_3$			$ErCl_3$			$YbCl_3$		
0.09486	0.4401	0.4399	0.1056	0.4357	0.4353	0.1152	0.4198	0.4196	0.1038	0.4228	0.4224
	.4405		.09198	.4375	.4371	.08470	.4264	.4263	.06919	.4306	.4303
.07905	.4432	.4430	.07665	.4404	.4401	.06776	.4297	.4296		.4304	
	.4434		.07539	.4417	.4414	.04320	.4360	.4360	.05189	.4346	.4347
.04743	.4507	.4507	.04599	.4484	.4484	.02880	.4390	.4391		.4349	
	.4508			.4485		.02118	.4423	.4425	.03460	.4408	.4405
.01581	.4595	.4598	.03016	.4520	.4520	.01152	.4476	.4480		.4401	
	.4598		.01533	.4585	.4586				.01038	.4494	.4495
.009486	.4637	.4637		.4584						.4490	
	.4630		.01056	.4605	.4607						
.007905	.4644	.4648	.007665	.4620	.4624						

direct moving boundary technique. Their measurements were repeated in this work as a check upon the performance of the apparatus and the preparation of the solutions. Good agreement was observed between the two sets of data (see Fig. 2).

Experimental

Preparation of Solutions.—The rare earth chloride solutions were prepared in the manner previously described.[2]

The lithium chloride indicator solution was prepared by dissolving C.P. lithium carbonate in redistilled hydrochloric acid and flushing out carbon dioxide with nitrogen. The acid was carefully added until the *p*H of the solution reached exactly 6.6 as recommended by Scatchard and Prentiss.[4] The normality of this stock solution was determined by weighing lithium as the sulfate. Solutions to be used as indicators were prepared from the stock solution by dilution. Conductance water was used for all solutions.

Description of the Apparatus.—A modification of the apparatus of Longsworth and MacInnes[5] was used for the transference measurements. This technique was selected because it is precise and convenient, and also because the above investigators[3] have applied their method with excellent results to the determination of the transference numbers of lanthanum chloride. In place of the glass disc shearing assembly of Longsworth and MacInnes, a stopcock of the hollow high vacuum type was used to produce the boundary. This device was more conveniently constructed and operated than was the glass disc apparatus; the use of a stopcock in an analogous manner had been shown to be entirely satisfactory by Allgood, LeRoy and Gordon.[6] An electronic current supply was used in place of the mechanical unit used by Longsworth and MacInnes. This substitution seems to be preferred by recent investigators,[7] and it is more compact and less fragile. The unit employed was able to maintain

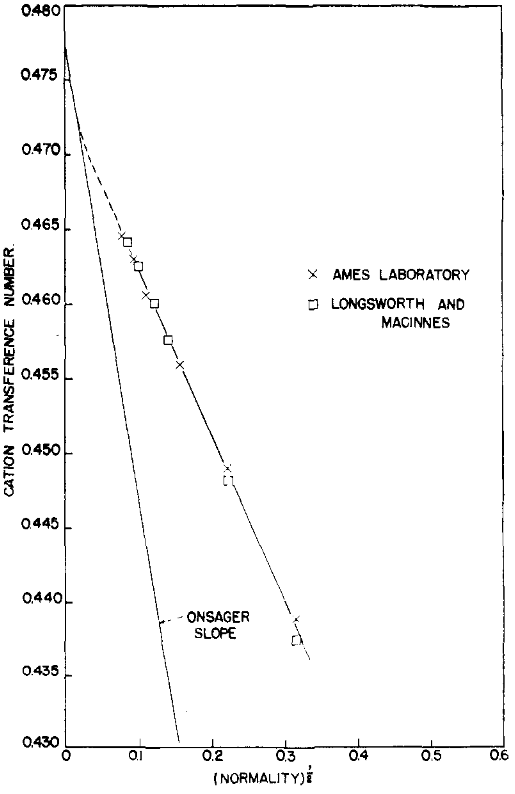

Fig. 2.—Comparison of transference numbers of $LaCl_3$.

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(4) G. Scatchard and S. S. Prentiss, *ibid.*, **55**, 4355 (1933).

(5) L. G. Longsworth and D. A. MacInnes, *Chem. Revs.*, **11**, 171 (1932).

(6) R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940).

(7) D. J. LeRoy and A. R. Gordon, *ibid.*, **6**, 398 (1938); *ibid.*, **7**, 314 (1939); R. W. Allgood, D. J. LeRoy and A. R. Gordon, *ibid.*, **8**, 418 (1940); *ibid.*, **10**, 124 (1942); *ibid.*, **11**, 172 (1943); B. Collie and G. S. Hartley, *Trans. Faraday Soc.*, **30**, 657 (1934); P. Bender and D. R. Lewis, *J. Chem. Education*, **24**, 454 (1947).

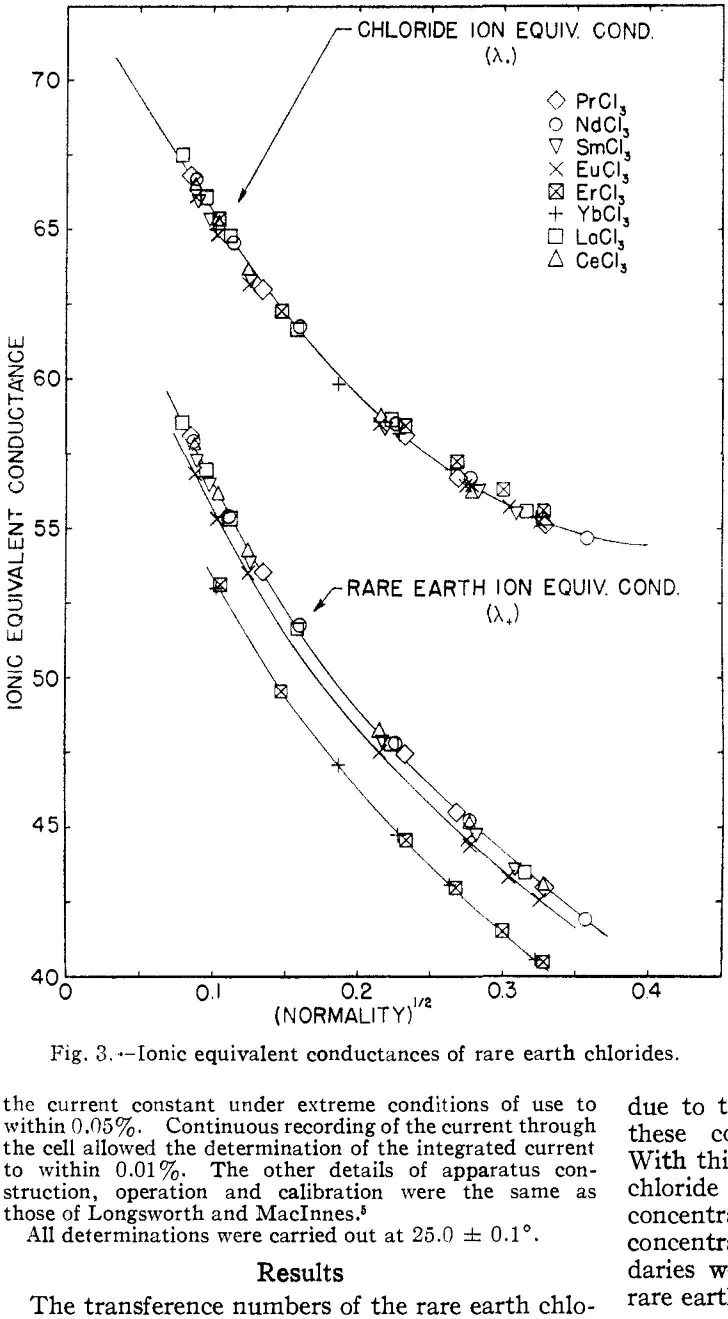

Fig. 3.—Ionic equivalent conductances of rare earth chlorides.

the current constant under extreme conditions of use to within 0.05%. Continuous recording of the current through the cell allowed the determination of the integrated current to within 0.01%. The other details of apparatus construction, operation and calibration were the same as those of Longsworth and MacInnes.[5]

All determinations were carried out at 25.0 ± 0.1°.

Results

The transference numbers of the rare earth chloride solutions are given in Table I. The data are also plotted in Fig. 1. The transference numbers of lanthanum chloride solutions have been previously determined with high accuracy by Longsworth and MacInnes.[3] The measurements on this salt were repeated in this investigation as a check upon the preparation of solutions and the measuring technique. The agreement is shown in Fig. 2. A further check upon the apparatus employed was obtained by determining the transference numbers of potassium chloride solutions. These were in excellent agreement with previously determined values.[8] The volume corrections and solvent corrections were made in the usual way.[5] The densities employed in making the former correction are listed in Table II, and the conductances used for the latter correction are reported elsewhere.[2]

The cation transference numbers for the first five rare earths are about the same within experimental error, although samarium and lanthanum are slightly lower than neodymium, praseodymium and cerium. Following samarium the transference numbers decrease with increasing atomic number. The behavior is consistent with the conductances of the salts except in the case of samarium chloride. For this salt the transference numbers are about equal to those of lanthanum chloride while the samarium chloride conductance is slightly lower than that of lanthanum chloride. Figure 3 is a plot of the ionic conductances of the rare earth chlorides which were obtained from the relationship $\lambda_i = T_i\Lambda$. The chloride ionic conductances for all salts lie very close to the same line although the points for samarium, europium and ytterbium seem to be lower at higher dilutions. The rare earth ionic conductances fall in the order expected from the conductances of their salts.

The transference numbers of all salts but ytterbium seem to be linear functions of the square root of the concentration; however, in the range measured there was no indication that the slope would rise to the Onsager limiting value (see Fig. 2). Since the conductances of the salts approach the limiting slope even at concentrations up to 0.01 N,[2] this behavior is somewhat anomalous. The same relationship was observed by Longsworth and MacInnes[3] for lanthanum chloride. The transference number plot for ytterbium appears to curve downward at high dilution. This effect might be due to the somewhat lower precision possible for these concentrations with ytterbium chloride. With this salt the refractive indices of the lithium chloride and ytterbium solution in the Kohlrausch concentration ratio appeared to become equal at concentrations below 0.01 N, so that the boundaries were much less visible than for the other rare earths.

TABLE II

DENSITIES OF AQUEOUS SOLUTIONS OF RARE EARTH CHLORIDES AT 25°

Element	Density,[a] ρ =
Lanthanum	$0.99707 + 0.2293C_m$
Cerium	$.99707 + .228C_m$
Praseodymium	$.99707 + .231C_m$
Neodymium	$.99707 + .235C_m$
Samarium	$.99707 + .240C_m$
Europium	$.99707 + .242C_m$
Erbium	$.99707 + .247C_m$
Ytterbium	$.99707 + .265C_m$

[a] The densities of $LaCl_3$ solutions were taken from data of Jones and Stauffer.[9] Other relations were obtained from measurements of densities over the range from 0.001 to 0.1 normal with a 50-ml. pycnometer. C_m is the molar concentration.

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(8) L. G. Longsworth, THIS JOURNAL, **54**, 2741 (1932).

(9) G. Jones and R. E. Stauffer, *ibid.*, **62**, 335 (1940).

While some speculations have been made with regard to the explanation of the observed transference numbers of the rare earth chlorides, a further discussion will be reserved until more data on other properties have been studied.

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Activity Coefficients of Rare Earth Chlorides in Aqueous Solutions at 25°

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The activity coefficients of the chlorides of lanthanum, cerium, praseodymium, neodymium, samarium, europium, erbium and ytterbium in aqueous solutions have been measured by means of concentration cells with transference. The data agree well with the Debye–Hückel theory, although a small deviation begins about 0.1 normal. The magnitudes of the Debye–Hückel å values exceed the sums of the crystallographic ionic radii of rare earth ions and chloride ion by about the diameter of one water molecule; thus, they are reasonable values for the distances of closest approach.

Introduction

This paper is the third in a series intended to provide a wide range of information on the properties of the rare earth elements and their compounds. As discussed in the first article of the series,[2] such information should be of considerable value in the study of the various factors which enter into the modern theories of physical chemistry. The present paper deals with the activity coefficients of the chlorides of lanthanum, cerium, praseodymium, neodymium, samarium, europium, erbium and ytterbium. The coefficients were measured with concentration cells with transference, using the transference numbers reported in the second paper of the present series.[3] The method involving concentration cells with transference was used because of the precision of the method, and because the unavailability of rare earth reversible electrodes makes the use of cells without transference impractical.

Very few activity data have been obtained for 3–1 electrolytes. The work already done upon salts of this type has been summarized by Harned and Owen.[4] MacInnes and Shedlovsky[5] have determined the activity coefficients of lanthanum chloride with high precision, but theirs was the only work on salts of this type which was carried into sufficiently dilute solutions to allow satisfactory extrapolation. Values for lanthanum chloride were redetermined in this Laboratory as a check on the experimental technique and apparatus. The agreement between the two sets of data is good (see Fig. 2).

Experimental

The solutions employed in this work were prepared as described in the first paper of this series.[2]

The silver–silver chloride electrodes were prepared in accordance with the directions of Harned.[6] Silver oxide was prepared by adding hot dilute sodium hydroxide solution to a hot dilute solution of silver nitrate. The resulting precipitate was washed thoroughly 30 to 40 times by stirring it up in a large volume of boiling conductance water and decanting. To prepare the electrodes, silver oxide paste was liberally applied to freshly cleaned platinum spirals or gauze. These electrodes were ignited at 400° until pure white and spongy; they were then chloridized electrolytically in 1 *N* hydrochloric acid. The electrodes were prepared in batches of about 30. After the electrolysis they were immersed in a 0.1 *N* solution of potassium chloride, and allowed to stand 24 hours with all electrodes connected together electrically. The potassium chloride used for this purpose must be specially purified as recommended by Pinching and Bates.[7] After the equilibration period, the potentials of the electrodes were compared, and all electrodes were rejected which differed from the mean by more than 0.02 mv. In using the electrodes for measurement, they were first rinsed with conductance water, then with the solution to be studied. They were then soaked in the test solution for at least one hour, the solution was changed, and they were soaked at least one more hour in fresh solution before they were introduced into the cell. To compensate for differences of the order of 0.01 mv. between electrodes, all measurements were repeated with the electrodes reversed, and the average voltage was taken as the true cell voltage. In a typical set of four voltage readings for a given pair of solutions the average deviation was about 0.002 mv. and the maximum deviation about 0.003 mv.

The liquid-junction cell employed consisted of two electrode compartments joined by a stopcock of the hollow high-vacuum type. Each electrode compartment was equipped with two 10/30 standard taper female ground-glass joints into which the electrodes could be inserted. The electrodes were sealed into short extensions of 10/30 male ground joints. The more dilute solution was always placed in the compartment joined to the center opening of the stopcock. This compartment was provided with a small trap as a safeguard against the entry of the stronger solution. When the junctions were established by opening the stopcock, the potentials remained constant within one or two microvolts for periods as long as 8 hours. A Rubicon type B precision

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[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**, 2055 (1952).

[3] F. H. Spedding, P. E. Porter and J. M. Wright, *ibid.*, **74**, 2778 (1952).

[4] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publishing Corp., New York, N. Y., 1950, pp. 426–429.

[5] D. A. MacInnes and T. Shedlovsky, THIS JOURNAL, **61**, 200 (1939); T. Shedlovsky, *ibid.*, **72**, 3680 (1950).

[6] H. S. Harned, *ibid.*, **51**, 416 (1929).

[7] G. D. Pinching and R. G. Bates, *J. Research Natl. Bur. Standards*, **37**, 311 (1946).