

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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for the preparation of pure praseodymium, neodymium and samarium oxides, and Mr. Sigmund Jaffe for completing the measurements on erbium chloride. They also wish to thank Dr. V. A. Fassel and Mr. Harold Cook for spectrographic analyses of the oxide fractions. Finally, we wish to thank Dr. E. I. Fulmer for his interest and helpful advice.

AMES, IOWA

[CONTRIBUTION NO. 187 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]¹

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

BY F. H. SPEDDING, P. E. PORTER AND J. M. WRIGHT

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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 δ values exceed the sums of the crystallographic 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 Shedlovsky⁵ 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).

(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**, 2680 (1950).

Experimental

The solutions employed in this work were prepared as described in the first paper of this series.³

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

(6) H. S. Harned, *ibid.*, **61**, 416 (1929).

(7) G. D. Pinching and R. C. Bates, *J. Research Natl. Bur. Standards*, **67**, 811 (1948).

TABLE I
ACTIVITY COEFFICIENTS OF RARE EARTH CHLORIDE SOLUTIONS AT 25°

Each experimental value is the average of four independent measurements. γ_{\pm} = mean molal activity coefficient.

Molality	E.m.f., mv.	γ_{\pm}	Molality	E.m.f., mv.	γ_{\pm}	Molality	E.m.f., mv.	γ_{\pm}	Molality	E.m.f., mv.	γ_{\pm}
LaCl ₃			CeCl ₃			PrCl ₃			NdCl ₃		
0.03119	0.000	0.4319	0.04009	0.000	0.4078	0.03235	0.000	0.4283	0.03701	0.000	0.4180
.02494	2.567	.4556	.03207	2.545	.4302	.02587	2.582	.4512	.03024	2.562	.4406
.01247	10.828	.5318	.02405	5.907	.4594	.01293	10.864	.5271	.01512	10.761	.5157
.006234	19.538	.6082	.01603	10.711	.5035	.006462	19.544	.6049	.007559	19.375	.5881
.003117	28.652	.6824	.008015	19.292	.5795	.003230	28.663	.6798	.003779	28.419	.6624
.002493	31.636	.7067	.003205	31.248	.6788	.002583	31.649	.7042	.003023	31.357	.6880
.001248	41.392	.7661	.001603	40.833	.7438	.001291	41.397	.7652	.001512	40.963	.7533
.....0008015	50.745	.8012	.0006456	51.487	.8165	.0007559	50.934	.8093
SmCl ₃			EuCl ₃			ErCl ₃			YbCl ₃		
0.03646	-3.902	0.4105	0.03532	0.000	0.4159	0.03399	-4.591	0.4256	0.04004	-3.749	0.4043
.02675	0.000	.4451	.02522	3.850	.4506	.02832	-2.263	.4349	.02860	0.000	.4385
.02140	2.582	.4698	.01008	14.798	.5513	.02266	0.000	.4657	.02288	2.491	.4625
.01070	10.937	.5468	.005041	23.558	.6290	.01444	5.497	.5044	.01144	10.578	.5385
.007490	15.408	.5856	.003529	28.225	.6679	.01132	8.053	.5419	.008006	14.915	.5779
.003740	24.403	.6622	.002521	32.725	.7035	.009629	10.212	.5522	.004003	23.612	.6549
.002139	32.003	.7182	.001008	45.502	.7864	.005663	16.268	.6302	.002287	30.919	.7136
.001070	41.749	.7805003398	23.154	.6694	.001144	40.431	.7732
.....002266	28.401	.7141
.....001132	37.919	.7734

potentiometer equipped with a galvanometer having a sensitivity of 1.2×10^{-9} amp./mm. with an internal resistance of 16.4 ohms and a critical damping resistance of 8 ohms was used for the measurements. The cells were immersed in a water-bath at $25 \pm 0.02^\circ$ during the tests.

Results

The data obtained are summarized in Table I. The activity coefficients were calculated using the method of MacInnes and Shedlovsky⁵; the extra-

polarization for $\log y_{\pm, ref}$ was by means of the Debye-Hückel expression in the form

$$\log \frac{y_{\pm}}{y_{\pm, ref}} + A' \sqrt{C_m} = - \log y_{\pm, ref} - \delta B' \left[\log \frac{y_{\pm}}{y_{\pm, ref}} + \log y_{\pm, ref} \right] \sqrt{C_m}$$

in which $A' = 3.7446$; $B' = 0.8049 \times 10^{-8}$; C_m = molar concentration; y_{\pm} = mean molar activity coefficient of the solution of concentration C_m ; $y_{\pm, ref}$ = mean molar activity coefficient of the reference solution; and δ = Debye-Hückel distance of closest approach (in ångström units).

The methods of successive approximations and of least squares were employed in order to obtain the best straight line for extrapolation. The points for all salts fell on these straight lines within experimental error. Values of δ , computed from the slopes of these lines, are listed in Table II, together with the mean absolute differences between activity coefficients computed by the Debye-Hückel expression, $\log y_{\pm} = \frac{-A' \sqrt{C_m}}{1 + \delta B' \sqrt{C_m}}$, and the experi-

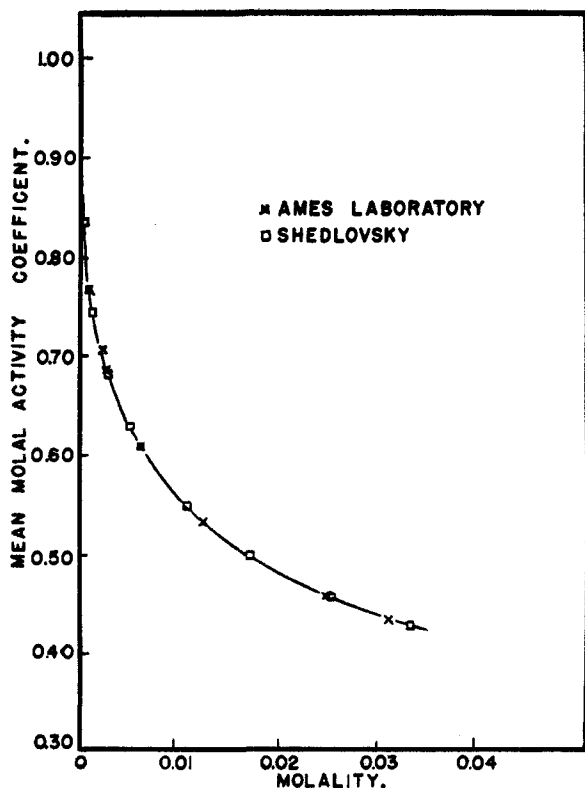


Fig. 1. Comparison of mean molal activity coefficients.

TABLE II

DISTANCES OF CLOSEST APPROACH FOR RARE EARTH CHLORIDE SOLUTIONS AND THE AVERAGE DIFFERENCES BETWEEN CALCULATED AND OBSERVED ACTIVITY COEFFICIENTS

Rare earth	δ (ångströms)	Average difference between calculated and observed activity coefficients
Lanthanum	5.75	0.0013
Cerium	5.75	.0024
Praseodymium	5.73	.0019
Neodymium	5.92	.0012
Samarium	5.63	.0009
Europium	5.60	.0005
Erbium	5.65	.0048
Ytterbium	5.65	.0011

mentally observed values. Standard methods were used to convert molarity to molality.

The activity coefficients for LaCl_3 have been previously determined by MacInnes and Shedlovsky⁵ with precision. The measurements were repeated in this paper as a check upon experimental technique. The agreement, shown in Fig. 1, is well within the experimental error.

Mason⁸ has used the isopiestic method to determine the osmotic coefficients of some rare earth chloride solutions. Using the data of Table I, these osmotic data may be used to extend the activity coefficients for these salts up to 2 molal.

The activity coefficients for the rare earth salts studied show very little variation and are plotted in Fig. 2. The data up to 0.1 *N* agree remarkably well with the Debye-Hückel theory, although evidence that a small deviation is beginning at the higher concentrations is indicated when the data of Mason⁸ are combined with our results. The magnitudes of the α values are quite reasonable for rare earth chlorides. They exceed the sums of the crystallographic ionic radii by an amount approximately equal to the diameter of a water molecule.

Acknowledgments.—The authors wish to thank the following members of Dr. Spedding's research group: Mr. Tom A. Butler and Mr. J. E. Powell for the preparation of pure praseodymium, neodymium and samarium oxides, and Mr. Sigmund Jaffe and Mr. I. S. Yaffe for completing the measurements on erbium chloride. They also wish to thank Dr. V. A. Fassel and Mr. Harold Cook for spectrographic analyses of the oxide fractions.

(8) C. M. Mason, *THIS JOURNAL*, **60**, 1638 (1938); *ibid.*, **63**, 220 (1941); R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

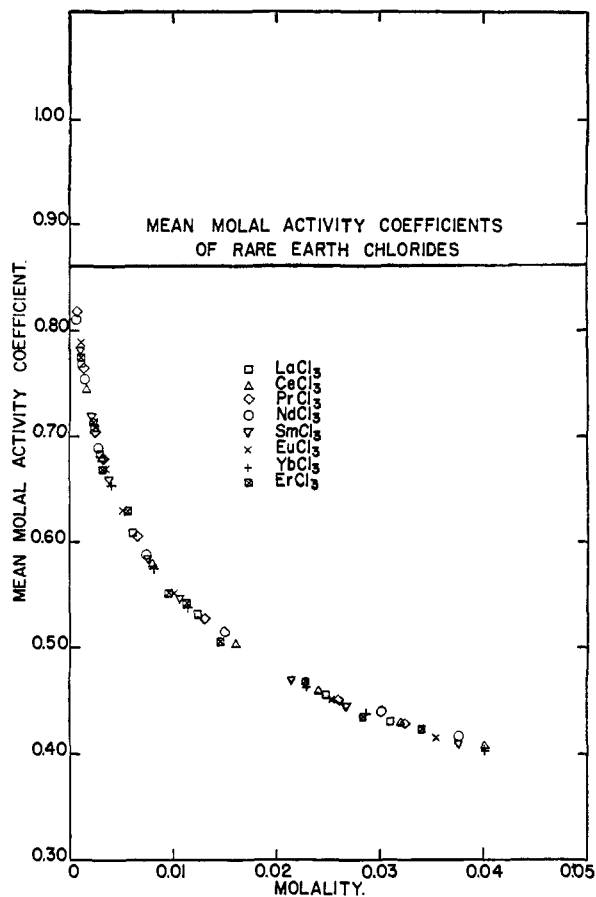


Fig. 2.—Mean molal activity coefficients of the rare earth chlorides.

Finally, we wish to thank Dr. E. I. Fulmer for his interest and helpful advice.

CONTRIBUTION NO. 188 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE¹

The Preparation of Rare Earth Metals

BY F. H. SPEDDING AND A. H. DAANE

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In order to prepare highly pure rare earth metals, a technique was devised whereby rare earth chlorides are reduced by calcium in tantalum crucibles; the resulting rare earth metal is vacuum cast in tantalum containers. Samarium, europium and ytterbium chlorides are reduced only to their stable divalent state and can thus be efficiently removed from rare earth mixtures by such metallurgical processing.

Introduction

Iowa State College has in progress several researches wherein it is hoped to obtain accurate data on properties of metals such as resistivity, thermal conductivity, magnetic susceptibility, vapor pressures, thermodynamic data, Hall coefficients, etc. It is hoped that the obtaining of such accurate data will prove extremely valuable in arriving at a better understanding of the nature of the metallic state. Due to their unique electronic structures, the rare earth metals seem to offer an ideal group of metals for such an investigation. It

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

has been pointed out elsewhere² that with this series, it is possible to get elements which only differ essentially from each other in the radius of the atoms and in their properties which depend on this radius. Therefore, accurate data over this series would permit a simpler theoretical treatment than would be possible for metals in general, since many variables could be held constant which would not be the case in metals from other parts of the periodic table.

(2) (a) F. H. Spedding, P. Porter and J. Wright, *THIS JOURNAL*, **74**, 2781 (1952); (b) F. H. Spedding, H. A. Wilhelm, W. H. Keller, D. H. Ahmann, A. H. Daane, C. C. Back and R. P. Brickson, *Ind. Eng. Chem.*, in press (1952).