[CONTRIBUTION NO. 175 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Conductances of Aqueous Solutions of Some Rare Earth Chlorides at 25°[1]

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

The equivalent conductances of aqueous solutions of the chlorides of lanthanum, cerium, praseodymium, neodymium, samarium, europium, erbium and ytterbium have been measured in the concentration range from 0.0004 to 0.1 *N*. The anticipated uniform change in properties with atomic number was not found for the first four members of the series, but beyond these the behavior was as expected. This behavior may be associated with differences in the coördination numbers of the rare earth ions for water molecules.

Introduction

The rare earth metals and their compounds, due to their unique atomic structure, offer one of the best keys to a better understanding of the theories of physical chemistry and the theories of the solid state. Each of the rare earths have three electrons normally either in valency shells or in the conduction bands of the metals. Since most of the physical and practically all of the chemical properties of a substance are determined by the interactions and configurations of the outermost electrons of the atom, the rare earths have remarkably similar properties. For this reason they have been difficult to obtain pure in the past owing to the enormous amount of work involved in separating them. In general, as one progresses across the rare earth series, the increasing charge on the nucleus is offset by adding electrons usually in the 4f subshell. These 4f electrons are shielded from the influence of the neighboring ions by the completed 5s 5p shells, and therefore play a very small part in the chemical properties of the solid states of these atoms. These electrons do, however, play an important role in the physical properties such as the absorption spectra and the magnetic properties of the solids or solutions. The sharp energy states arising from various configurations of these inner electrons can be observed by means of absorption spectra, and it is found that external fields, due to surrounding molecules and ions, cause a splitting of these levels which depends upon the symmetries and the strengths of these fields. They therefore act as indicators of what is happening to the atom or ion in the fields of a solution or solid even though these fields have very little influence on its actual chemical properties.

It is interesting that in checking any of the recent theories of physical chemistry or of the solid state against experimental data, it is possible in the case of the rare earths to observe data for a series of compounds in which the predominating variable is the radius of the atom or ion. The rare earths form similar series of compounds in which the size of the rare earth ion or atom decreases in a definite way as the charge on the nucleus increases. Usually when one compares data against theory for atoms elsewhere in the periodic table, other variables such as crystal symmetry, valence state, bond angles, etc., change simultaneously with ionic or atomic radius, but for the rare earths these factors are essentially constant or progress in a manner which may be predicted from smaller ionic or atomic size. Further, the external electronic configurations of scandium, yttrium, lanthanum and actinium are identical with those of the rare earths, and with this series it is possible to observe the effects of ionic or atomic radius changes which result from the successive addition of completed shells of electrons.

This paper is the first of a series dealing with dilute solutions of the rare earth chlorides and deals with conductance. A great deal of work has appeared in the literature dealing with the experimental data of aqueous solutions and the theories which apply to them.[2] In the various theories which have attempted to account for this data, many simplifying assumptions have been made. It should be helpful, in determining just where these assumptions break down, to have available accurate data for various rare earth salts in solution. Some of the properties of such solutions should be very sensitive to one assumption as concentration increases while insensitive to others. Correspondingly, other properties would be sensitive to a second assumption, but not sensitive to the first.

The conductances of solutions of lanthanum chloride,[3a,b] and of lanthanum sulfate[4] have been measured with high accuracy, but other salts have not been studied with sufficient care. In this paper, data are presented for the chlorides of lanthanum, cerium, praseodymium, neodymium, samarium, europium, erbium and ytterbium. The data for lanthanum chloride are in agreement with those of the previously mentioned investigators (see Fig. 2) and serve as a check upon the experimental technique.

Experimental

Preparation of Solutions.—The rare earth oxides used for preparation of the chlorides were purified by the ion-exchange method. Purities of the oxide samples were determined by emission spectrography using techniques developed at Iowa State College.[5] The limit of detection of rare earths was about 0.02 to 0.03%. That for common elements was about 0.01%. In all cases the samples were further purified by two precipitations with doubly recrystallized oxalic acid from solutions approximately one normal in hydrochloric acid. Ignitions were made in platinum. The purities of the rare earths may be described as: lanthanum: no other rare earths or thorium detected; trace of calcium observed; cerium: no other rare earths, thorium or common elements detected; praseodymium: no other rare earths or thorium detected; faint traces of magnesium and calcium observed; neodymium: no other earths or thorium detected; faint trace of magnesium observed; samarium:

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

(2) See author index of *C. A.* for publications by such authors as N. Bjerrum, P. Debye, H. Falkenhagen, H. Harned, E. Hückel, J. Kirkwood, C. Kraus, V. LaMer, D. MacInnes, L. Onsager, B. Owen, G. Scatchard and T. Shedlovsky.

(3) (a) G. Jones and G. F. Bickford, THIS JOURNAL, **56**, 602 (1934); (b) L. G. Longsworth and D. A. MacInnes, *ibid.*, **60**, 3070 (1938).

(4) I. L. Jenkins and C. B. Monk, *ibid.*, **72**, 2695 (1950).

(5) V. A. Fassel and H. A. Wilhelm, *J. Opt. Soc. Am.*, **38**, 518 (1948); V. A. Fassel, *ibid.*, **39**, 187 (1949).

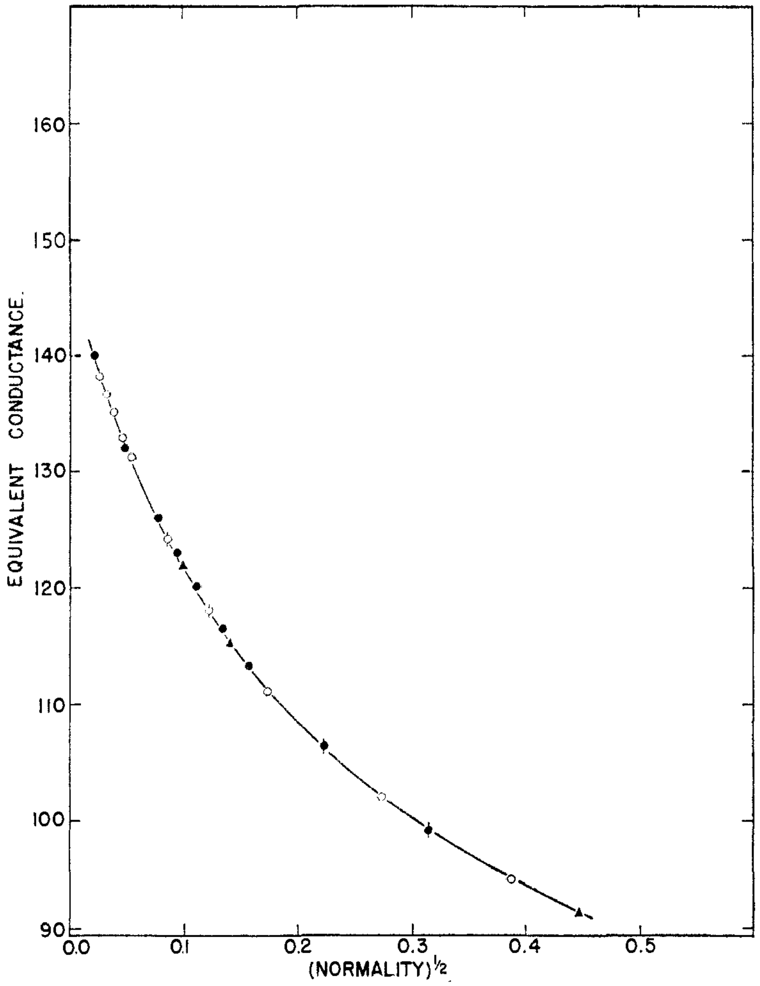

Fig. 1.—Comparison of conductances of lanthanum chloride solutions obtained by various investigations: ●, Ames Laboratory; ○, Jones and Bickford; ▲, Longsworth and MacInnes; ⧳ and ⦶ data coincide.

0.020 ± 0.002% Eu_2O_3; no other rare earths detected; faint trace of calcium observed; europium: traces of Dy_2O_3, Gd_2O_3, Nd_2O_3 and Yb_2O_3 of the order of magnitude of 0.03%; Sm_2O_3 and Y_2O_3 in the neighborhood of 0.1%; traces of several common elements detected; ytterbium: no other element detected.

Freshly ignited rare earth oxides were dissolved in an excess of redistilled hydrochloric acid. Purified chlorine gas was bubbled through the solutions, and they were boiled vigorously to remove any possible bromine contamination. The solutions were used for the measurement of the voltage of concentration cells as well as for conductance measurements. It was therefore necessary to assure the absence of bromide ions which have a deleterious effect upon silver–silver chloride electrodes. Each solution was then evaporated to a thick sirup on a hot-plate. Further drying was accomplished by evaporating under vacuum at about 80° until the remaining chloride crystals appeared flaky in composition. Final drying was accomplished by heating slowly in a hydrogen chloride atmosphere to a final temperature of 300 to 400°. The hydrogen chloride, generated by dropping concentrated sulfuric acid into concentrated hydrochloric acid was dried by passing it in succession through a sulfuric acid bubbler, a Dry Ice–acetone cold trap, and a calcium chloride tube immersed in Dry Ice–acetone. In the final drying step it was found essential to halt the temperature at several points to prevent melting of the crystals; oxychloride was formed, which was not reconverted to chloride upon further heating, if the crystals were allowed to melt at any stage. Since the hexahydrates melt at about 80°, the first halt was made below this temperature and the heating was continued until no water was evolved in the hydrochloric acid stream. The next halt was made in the vicinity of 100°, and the final halt was made at about 160°. The furnace could then be rapidly heated to the final temperature. After the drying had been completed, the apparatus was flushed with helium at the high temperature until no hydrogen chloride could be detected in the exit gas. The sample was then cooled and bottled.

Stock solutions of each rare earth chloride were prepared by dissolving weighed amounts of anhydrous chloride in conductance water in a sealed system so as to prevent the possible loss of hydrochloric acid formed by hydrolysis. These solutions were then diluted to volume with conductance water in calibrated Pyrex flasks at 25°. The test solutions were prepared by dilution, using calibrated glassware. The solutions so prepared were clear; the *p*H values measured with a Beckman model G *p*H meter were from 6.4 to 6.6; and normalities calculated from the weights of chloride added agreed within 0.1% in all cases with those obtained by determination of the rare earth content by oxalate precipitation and ignition. The rare earth chlorides proved to be strong electrolytes, and when prepared in this way they show no tendency to hydrolyze. They should thus be an ideal set of salts with which to test the properties of 3–1 electrolytes in aqueous solutions.

Reagent grade potassium chloride was purified by two recrystallizations from conductance water. It was then dissolved in conductance water; the solution was saturated with chlorine and boiled vigorously; and the potassium chloride was precipitated by saturating the solutions with hydrogen chloride. After one more recrystallization from conductance water the potassium chloride was fused in a nitrogen atmosphere in platinum dishes. Solutions were prepared by dissolving the weighed potassium chloride in conductance water and diluting to volume at 25°.

Apparatus.—The conductivity bridge and accessories were in accord with the specifications recommended by Jones and Josephs.[6] It was purchased from the Leeds and Northrup Company and it has been described by P. H. Dike.[7] The unit was capable of an accuracy of 0.02%. The conductivity cells were commercially available types (Leeds and Northrup catalog numbers 4911, 4914 and 4915). They were platinized before use by the procedure recommended by Jones and Bollinger.[8] These cells were used for the work, since they require the use of a smaller amount of solution than necessary for larger cells. They were of such dimensions that a slight Parker effect was observed, and they were thus calibrated at a number of points using potassium chloride solutions. The data of Shedlovsky[9] for potassium chloride were used as standards.

The constant temperature bath maintained the temperature constant at 25° within ± 0.02° during measurements.

Results

The conductance data for the rare earth chloride solutions are given in Table I. The conductances of lanthanum chloride have previously been determined with high accuracy by Jones and Bickford[3a] and by Longsworth and MacInnes.[3b] The measurements were repeated in this investigation as a check upon the preparation of solutions and the measuring technique. The agreement of the three sets of data is shown in Fig. 1. Values of Λ_0 were obtained by extrapolation using the Onsager limiting law in the manner discussed by Harned and

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(6) G. Jones and R. C. Josephs, This Journal, **50**, 1049 (1928).

(7) P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

(8) G. Jones and D. M. Bollinger, This Journal, **57**, 280 (1935).

(9) T. Shedlovsky, *ibid.*, **54**, 1411 (1932).

TABLE I

CONDUCTANCES OF AQUEOUS SOLUTIONS OF RARE EARTH CHLORIDES AT 25°[a]

		Equivalent conductance, mho. cm.$^{-1}$							
C	$\sqrt{C}$	$LaCl_3$	$CeCl_3$	$PrCl_3$	$NdCl_3$	$SmCl_3$	$EuCl_3$	$ErCl_3$	$YbCl_3$
0.0000	0.0000	146.1	146.2	146.0	146.6	144.9	144.2	142.3	141.5
.0002	.01414	142.3	142.3	142.3	142.5	140.9	140.2	138.4	137.6
.0004	.02000	140.6	140.6	140.5	140.8	139.2	138.6	136.8	135.9
.0007	.02646	138.8	138.8	138.7	139.0	137.4	136.8	135.0	134.2
.0010	.03162	137.4	137.4	137.3	137.5	135.9	135.4	133.6	132.8
.0020	.04472	133.9	133.9	133.8	134.0	132.6	132.1	130.4	129.6
.0040	.06325	129.5	129.5	129.4	129.6	128.3	127.8	126.1	125.3
.0070	.08367	125.2	125.2	125.1	125.4	124.2	123.7	122.0	121.2
.0100	.1000	122.1	122.1	122.0	122.2	121.1	120.6	118.9	118.1
.0200	.1414	115.6	115.6	115.5	115.7	114.8	114.2	112.8	112.0
.0400	.2000	108.8	108.8	108.7	108.9	108.0	107.4	106.2	105.4
.0700	.2646	102.7	102.7	102.6	120.9	102.1	101.7	100.4	99.8
.1000	.3162	99.0	99.0	98.9	99.1	98.5	98.2	96.9	96.4

[a] The data of this table are smoothed values. Anyone desiring the exact data for the experimental points may obtain them from the authors upon request.

Owen.[10] Plots of Λ'_0 *vs.* concentration for the rare earths studied are shown in Fig. 2. In computing the Λ_0 values from the Onsager equation the value of λ_0 for chloride ion was taken as 76.34. The extent to which the measurements agree with the Onsager equation is indicated in Fig. 1, which shows the Onsager limiting slope. This agreement is typical of all salts studied.

The rare earths, beginning with neodymium, show a progressive decrease in conductance (see Fig. 3) in spite of the fact that there is a progressive decrease in the crystallographic ionic radius for these elements. This fact suggests that the hydration of the ions plays a predominant role in determining the limiting mobility. The lack of a regular decrease among the first four elements is somewhat anomalous since the rare earth series would be expected to show a regular change in properties over the whole series. A possible explanation, in view of the apparent importance of the hydration of the ions is that as the ion becomes larger with lower atomic number, a second coördination number may become possible so that an equilibrium may be set up between two kinds of hydrated ions having different coördination numbers. A change of this type would undoubtedly give rise to a change in the effective radius of the hydrated ion and in the amount of water dragged with the ion in motion. Crystallographic evidence indicates that a change in the hydration of rare earth salts in crystal form occurs in the neighborhood of neodymium; for example: $Pr_2(SO_4)_3 \cdot 9H_2O$, $Nd_2(SO_4)_3 \cdot 8H_2O$; $PrCl_3 \cdot 7H_2O$, $NdCl_3 \cdot 6H_2O$. In addition, X-ray evidence by Rundle and co-workers[11] shows that two coördination numbers exist for the lanthanum ions in the same crystal; part of the ions are coördinated with 9 oxygens and the remainder are coördinated with 12 oxygens. It is expected that

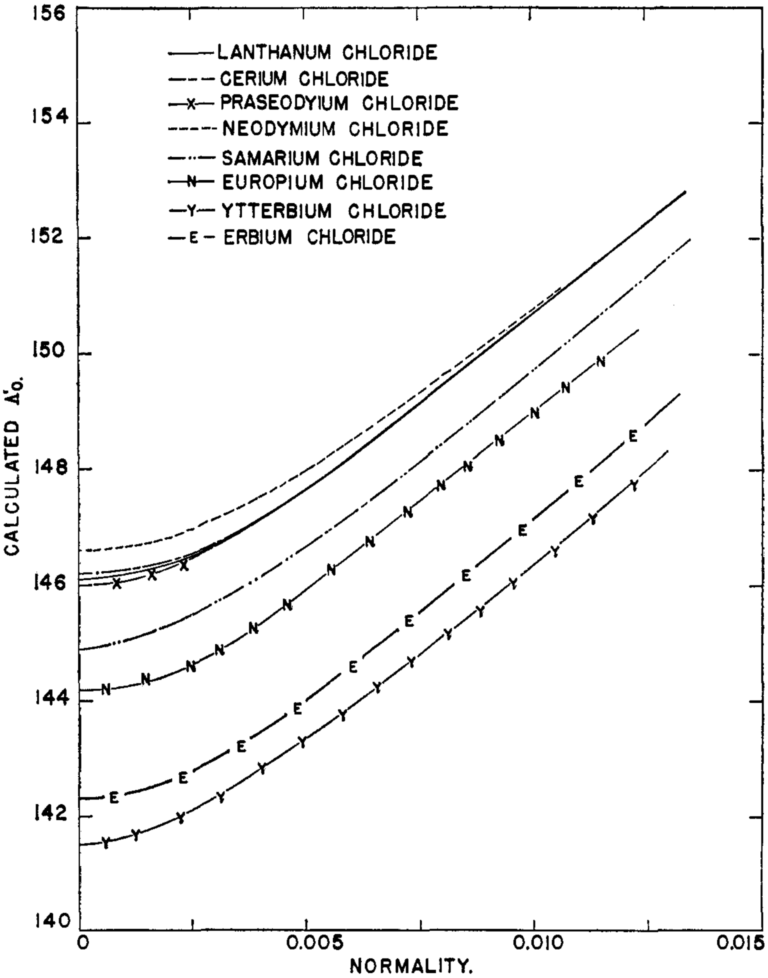

Fig. 2.—Comparison of the limiting conductance of rare earth chloride solutions at 25°.

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[10] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 152.

[11] E. Hunt, Doctors Thesis, Iowa State College, 1950.

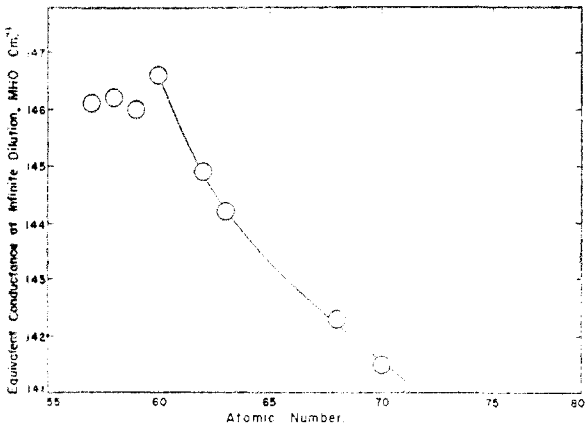

Fig. 3.—Variation of equivalent conductances at infinite dilution with atomic number for rare earth chloride solutions

$Nd_2(SO_4)_3 \cdot 8H_2O$ will show only one coördination number. At the present time there is insufficient evidence for conclusions to be made. Any speculations or deductions as to the causes of deviations from the Onsager law, etc., are being reserved for later papers after data for transference numbers, activity coefficients, partial molal volumes, heats of dilution and other properties have been obtained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Study of the Diffusion of Urea in Water at 25° with the Gouy Interference Method[1]

BY LOUIS J. GOSTING AND DAVID F. AKELEY

The variation with concentration of the diffusion coefficient, D, of urea in water has been measured in the concentration range from 0 to 4 molar. These values of D are self-consistent to within about 0.1%, and it was established that the results obtained are differential diffusion coefficients. As the Gouy interferometer measures the optical path difference between the two solutions forming each diffusion boundary, refractive index data for the system were also obtained.

Measurements with the Gouy interference method of the diffusion coefficients, D, of sucrose[2] and glycine[3] in water have shown the method to yield values which are self-consistent to within 0.1%, while a more recent investigation[4] of the diffusion of potassium chloride yielded data which were equally consistent with the results that Harned and Nuttall obtained with their conductance method.[5] At higher potassium chloride concentrations where the conductance method could not be used, the values of D obtained by Stokes[6] with an improved diaphragm cell are in good agreement with data from the Gouy method. Since the accuracy of the Gouy method thus appears to be well established, it may now be used with confidence to investigate the variation of D with concentration for different systems in order to test present theories and to provide a basis for future theoretical work on this transport process. This paper reports results of measurements on the urea–water system.

Experimental

Our measurements were made with the same equipment[2,3,7] used for the sucrose and glycine diffusion studies, except that a twin double-slit[4] was utilized to form an improved reference pattern for the diffusion pictures. The diffusion reference correction, δ, and the refractometer reference correction, δ', were each obtained by averaging measurements of 3 to 5 separate sets of photographs in each experiment, but the value of δ used for each experiment was taken from a smoothed plot of all δ values *versus* the concentration.

A Wratten 77A filter served to isolate the green line of an AH4 mercury lamp used to illuminate the source slit. The optical distance, b,[8] from the center of the diffusion cell to the emulsion of the photographic plate was found to be 304.5_2 cm.; while the cell thickness, a, along the optic axis, was shown to be 2.486_2 cm. by direct measurement with a traveling microscope and also with a special inside caliper.

In most experiments diffusion took place from a solution containing C_2 moles per liter into a more dilute solution of concentration C_1, rather than into water. All initial boundaries were sharpened by withdrawing from 90 to 140 ml. of liquid at a rate of about 4 ml. per minute from the cell through a two-pronged stainless steel capillary adjusted to the level of the optic axis. The second when sharpening was stopped was taken as the start of the diffusion; then the capillary was withdrawn from the cell. From 10 to 15 Gouy fringe photographs were taken over a period of about four hours in each experiment, and, using the Airy integral refinement[2] of the "quarter-wave approximation,"[9] apparent diffusion coefficients, D', were calculated from measurements of fringe minima numbered 1 through 8. To correct for slight but unavoidable imperfections in each initial boundary, D' was plotted against the reciprocal of the observed time for each experiment.[10] The intercept and slope of this line were determined by the method of least squares to give the correct diffusion coefficient, D, and the starting time correction, Δt. Values of Δt ranged from 3.4 to 7.7 seconds, while the mean deviation of points from the straight lines varied from 0.024 to 0.056%.

During all experiments the bath temperature was maintained constant to within ± 0.002°. Since the mean temperature of each experiment was always within 0.005° of

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(1) Presented before the Division of Physical and Inorganic Chemistry at the XIIth International Congress of Pure and Applied Chemistry, New York City, September, 1951.

(2) L. J. Gosting and M. S. Morris, THIS JOURNAL, **71**, 1998 (1949).

(3) M. S. Lyons and J. V. Thomas, *ibid.*, **72**, 4506 (1950).

(4) L. J. Gosting, *ibid.*, **72**, 4418 (1950).

(5) H. S. Harned and R. L. Nuttall, *ibid.*, **71**, 1460 (1949).

(6) R. H. Stokes, *ibid.*, **72**, 2243 (1950); **73**, 3527 (1951).

(7) L. J. Gosting, E. M. Hanson, G. Kegeles and M. S. Morris, *Rev. Sci. Instruments*, **20**, 209 (1949).

(8) Here $b = \sum_i l_i/n_i$, where l_i is distance along the optic axis in each medium, i, of refractive index n_i, relative to air as unity.

(9) G. Kegeles and L. J. Gosting, THIS JOURNAL, **69**, 2516 (1947).

(10) L. G. Longsworth, *ibid.*, **69**, 2510 (1947).