in Table II any one of the five solutes may be used as standard.

Summary

A modification for precision work of the isotonic apparatus and method of Sinclair and Robinson is described.

The isotonic concentrations at 25° of aqueous solutions of sodium chloride, potassium chloride, sulfuric acid, sucrose, urea and glycerol have been determined from 0.1 *M* sodium chloride to the saturated solution or to a saturated solution of sodium chloride.

The solubilities in water at 25° of sodium chloride, potassium chloride, sucrose and urea have been determined in the same apparatus by a new and convenient method.

The most precise determinations of the chemical potential of water in solutions of non-volatile solutes have been compared critically by means of these isotonic measurements, and a standard curve for the osmotic coefficients of each substance has been based on all the measurements with any of these substances.

CAMBRIDGE, MASS. RECEIVED AUGUST 4, 1938

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

Transference Numbers of Lanthanum Chloride at 25° by the Moving Boundary Method

BY L. G. LONGSWORTH AND D. A. MACINNES

Introduction

In recent publications from this Laboratory Brown and MacInnes[1] and Shedlovsky and MacInnes[2] have shown that transference numbers, and electromotive forces of concentration cells, may be used in determining activity coefficients of salt solutions. The salts studied in this manner have been the chlorides of hydrogen, sodium, potassium and calcium. The results were found to be in close accord with the Debye–Hückel theory. In addition transference numbers are of utility in interpreting the results of conductance measurements according to the recent developments of the interionic attraction theory. The extension of the studies to solutions of lanthanum chloride appeared to be of interest. Since this salt is of a highly unsymmetric valence type, the data obtained should afford a severe test of the interionic attraction theory in relation to both activity coefficients and conductances. This paper describes the determination of the transference numbers of lanthanum chloride by the moving boundary method and gives data on these numbers at 25° in the concentration range 0.0075 to 0.5 normal.

Description of the Apparatus

Of the apparatus used in determining transference numbers by the moving boundary method the cell was the same as that used in recent investigations in this Laboratory and has been described fully.[3] The constant current device has, however, been much simplified, as shown in Fig. 1. In this figure a portion, B, of the storage battery, A-B, furnishing current to the moving boundary cell, C, is shunted by a potential divider, the point of contact, T, being shifted by winding resistance wire from one of the insulated cylinders, DD′, to the other. In series with this and the cell C is a decade resistance box, R, with the range 10 to 11,110 ohms, which is shunted by the galvanometer, G, and the Hulett cell, X, which is, essentially, a heavy-duty Weston unsaturated standard cell. The needle of the galvanometer carries a vane, V, of aluminum foil which serves to intercept the light to the photo-tube, PJ 23. The photoelectric current operates a thyratron, FG 57, whose plate circuit includes the electromagnet E which controls the addition of potential by the divider, DD′, by drawing the pulley P_1 against the constantly rotating disk F. On release the pulley P_2 causes an adjustment in the reverse direction. For use with continuously increasing resistance, as in the present case, P_2 may be removed.

In operation the resistance R is set at such a value that a drop of 1.0189 v., the potential of the Hulett cell, results from the passage of the current. The advantages of this arrangement over that previously described[3] are: (1) a thyratron has replaced a vacuum tube and two mechanical relays and (2) a Hulett cell and a resistance box have replaced a Weston standard cell, standard resistances, potentiometer and storage battery. The precision and convenience of the apparatus have been increased since it is no longer necessary to adjust the potentiometer current at intervals during a transference number determination. As a matter of fact, the device will operate for an indefinitely long period with an accuracy of 0.01% or better.

The frequency control of the local a. c. power supply is

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[1] Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

[2] Shedlovsky and MacInnes, *ibid.*, **58**, 1970 (1936); **59**, 503 (1937).

[3] MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932).

now of sufficient precision to warrant replacement of our original timing device by a counter driven by a synchronous motor.

Preparation of the Solutions

Lanthanum chloride from two sources was used in this investigation. Preliminary treatment of both samples included precipitation with recrystallized oxalic acid, ignition to the oxide, solution in distilled hydrochloric acid and precipitation as $LaCl_3 \cdot 7H_2O$ with hydrogen chloride gas at 0°. One sample was obtained from a German source and the second was prepared for us under the direction of Professor B. S. Hopkins of the University of Illinois. Spectroscopic examination and conductance measurements showed that the two samples were practically identical. Spectroscopic comparison with a cerium-free sample kindly given us by Professor G. Jones of Harvard and with samples to which known amounts of cerium had been added indicated that our material contained less than 0.03% of cerium and was free of other impurities. Since cerium has nearly the same mobility and equivalent weight as lanthanum the presence of this amount of cerium in our salt has no appreciable effect on either the transference or the conductance measurements. We are indebted to Dr. G. I. Lavin of these Laboratories for the spectrographic analysis of our material.

Several methods of preparing lanthanum chloride for weighing were used and the results are summarized in Table I. As much of the water of hydration as possible was removed at a low temperature in a vacuum desiccator, using "Drierite" and continuous pumping. The temperature of this desiccation is given in the first column of the table. The sample, either pure or mixed with ammonium chloride, was then placed in a Richards "bottling" apparatus and heated to a high temperature in a stream of dry hydrogen chloride gas. The treatment given the material is recorded in the second column of Table I. As is indicated in the third column, a minute trace of insoluble material, presumably the basic chloride, invariably remained when the *fused* salt was dissolved in water. Fusion with ammonium chloride, in the process of which the ammonium salt sublimes and is carried away by the stream of hydrogen chloride gas, did not prevent the formation of this basic chloride. When, however, the salt was heated to 600° the resulting solution was clear.[4] The agreement between the conductances of the various preparations as given in the last column of Table I indicates, barring improbable compensation, that the insoluble residue in the fused material and the residual water in that heated to 600° amount to less than 0.01%, which is the limit of error of the conductance measurements.

TABLE I

PREPARATION OF STOCK SOLUTIONS OF LANTHANUM CHLORIDE

Temp. of vacuum desiccation, °C.	Treatment in HCl atmosphere	Basic chloride residue	Equiv. conductance, $\Lambda_{0.1}$
140	Rapid fusion	Large	. . .
20	Slow fusion	Trace	99.02
20	Slow fusion with NH_4Cl	Trace	99.03
100 with NH_4Cl	Slow fusion with NH_4Cl	Trace	99.02
142	Slowly heated to 600°	None	99.04
100	Slowly heated to 600°	None	99.03

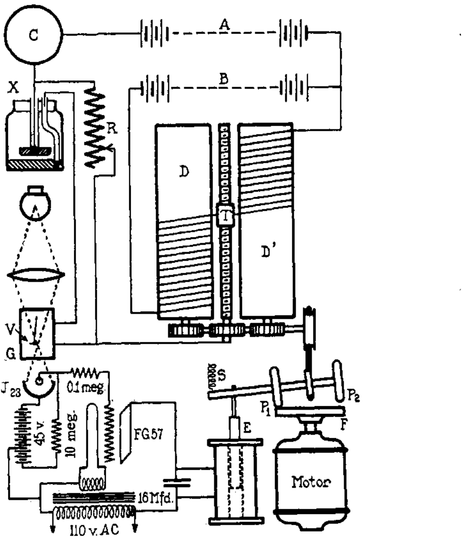

Fig. 1.

Lithium Chloride was prepared by dissolving, in hydrochloric acid, lithium carbonate that had been recrystallized from boiling water. This salt proved to be an excellent cation indicator for solutions of lanthanum chloride over the entire range of concentration studied.

Lanthanum bromate was prepared by the addition of an excess of solid silver bromate to a concentrated solution of lanthanum chloride. The trace of silver ion remaining in the solution of lanthanum bromate does not interfere with the use of this solution as anion indicator since the cation constituents migrate away from the boundary. Although the bromate ion is but slightly slower than the chloride ion it was found that satisfactory boundaries between solutions of their lanthanum salts could be obtained at 0.2 and 0.5 normal. Lanthanum bromate was used therefore to obtain confirmation of the results with lithium chloride as indicator.

Anion boundaries with lanthanum acetate were also tried but excessive heating in the indicator solution caused mixing at the boundary. Moreover, this salt appears to be appreciably hydrolyzed.

Experimental Results

The experimental results are given in Table II in which concentrations are expressed in equivalents per liter of solution at 25°. Values of the transference number obtained in individual determinations are recorded under "$T_{\pm}$ observed" and their average under "$T_{\pm}$ mean." These values are subject to two small corrections: for the conductivity of the solvent (1.5×10^{-6} mho), and for the volume changes in the closed side of the moving boundary cell, both of which are discussed in detail by MacInnes and Longsworth.[3] The

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[4] Jones and Bickford, THIS JOURNAL, **56**, 602 (1934).

TABLE II

TRANSFERENCE NUMBERS AND CONDUCTANCES OF AQUEOUS SOLUTIONS OF LANTHANUM CHLORIDE AT 25°

	T_+								T_-	
Concn. eq. per liter at 25°	0.0075	0.010	0.015	0.02	0.05	0.1	0.2	0.5	0.2	0.5
$T_\pm$ obsd.	.4636	.4620	.4600	.4575	.4486	.4387	.4261	.4020	.5742	.5986
	.4632	.4620	.4599	.4577	.4486	.4387	.4255		.5740	.5990
		.4619		.4577	.4487	.4388				
		.4620		.4576		.4387				
$T_\pm$ mean	.4634	.4620	.4599$_5$	.4576	.4486	.4387	.4258	.4020	.5741	.5988
Solvent corr.	.0008	.0006	.0004	.0003	.0002	.0001	.0000	.0000	.0000	.0000
Volume corr.	−.0001	−.0001	−.0002	−.0003	−.0006	−.0013	−.0025	−.0062	+.0025	+.0062
$T_\pm$ corr.	.4641	.4625	.4601	.4576	.4482	.4375	.4233	.3958	.5766	.6050
Λ	124.34	121.83	118.09	115.32	106.10	99.04	92.04	82.28		

volume change for both the anion and cation boundaries is

$$\Delta V = \frac{1}{3}\, T_+\, \overline{V}_{\text{LaCl}_3} + V_{\text{Ag}} - V_{\text{AgCl}}$$

in which $\overline{V}_{\text{LaCl}_3} = 0.01615 + 0.01733\sqrt{\text{molality}}$, $V_{\text{Ag}} = 0.0103$ and $V_{\text{AgCl}} = 0.0258$, all at 25°. These corrections are given in the fourth and fifth lines of Table II and the corrected transference numbers in the sixth line. The conductances of all solutions were measured on the bridge described by Shedlovsky[5] and are recorded in the last line of the table. A value of 0.012856[6] for the specific conductance of 0.1 demal potassium chloride was used in the determination of cell constants.

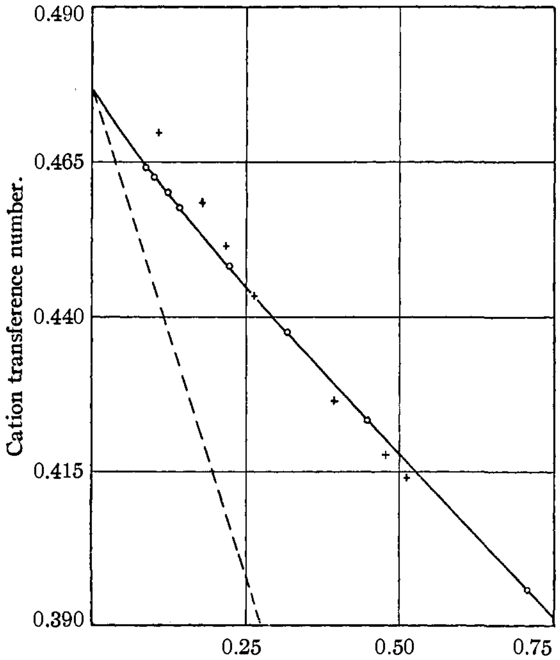

Fig. 2.

Discussion of the Results

In Fig. 2 the transference data for lanthanum chloride are plotted as ordinates against the square root of the concentration as abscissas. The values recently obtained with the Hittorf method by Jones and Prendergast[7] are indicated by the crosses while our results are plotted as circles. The differences between the results by the two methods, reaching a maximum of 0.007 for the most dilute solutions, are larger than those found in similar comparisons for lithium[8] and potassium chlorides[9] and are certainly outside the limit of error of the moving boundary measurements. That the Hittorf values for dilute solutions are not consistent with the results for other salts, and with Kohlrausch's law of independent ion mobilities, have already been pointed out by Hartley and Donaldson.[10] A test of the accuracy of our measurements is afforded by independent observation of both anion and cation boundaries with the same solution. The sum of the transference numbers thus obtained should be 1.0000. Thus from the data of Table II, $T_+ + T_- = 0.9999$ at 0.2 normal and 1.0008 at 0.5 normal. It may be noted that the conductances of Table II are in excellent agreement with the values published by Jones and Bickford.[4]

The smooth curve drawn through our data has been extrapolated to the value of 0.4768. This limiting cation transference number is based on the values of 76.34 and 145.9 for the limiting conductances of the chloride ion[11] and lanthanum chloride,[12] respectively. The dashed line in Fig. 2 is the limiting slope

$$\left(\frac{\mathrm{d}T_+}{\mathrm{d}\sqrt{C}}\right)_{C \to 0} = \frac{(z_+ + z_-)T_+^0 - z_+}{\Lambda_0}\,\beta\sqrt{z_+ + z_-} \quad (1)$$

derived by Longsworth[13] from the Onsager theory.[14] As in the case of calcium chloride the

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(5) Shedlovsky, This Journal, **52**, 1793 (1930).

(6) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

(7) Jones and Prendergast, *ibid.*, **58**, 1476 (1936).

(8) Longsworth, *ibid.*, **54**, 2741 (1932).

(9) MacInnes and Dole, *ibid.*, **53**, 1357 (1931).

(10) Hartley and Donaldson, *Trans. Faraday Soc.*, **33**, 457 (1937).

(11) MacInnes, Shedlovsky and Longsworth, This Journal, **54**, 2758 (1932).

(12) Shedlovsky, unpublished results.

(13) Longsworth, This Journal, **57**, 1185 (1935).

(14) Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

experimental curve of transference numbers for lanthanum chloride apparently merges with the limiting slope only at extreme dilutions. Assuming that the salt conductances have been extrapolated correctly, we are confronted with the anomaly that these conductances appear to obey the Onsager equations to somewhat higher concentrations than do the transference numbers, although the latter are merely ratios of ionic conductances. No satisfactory explanation for this anomaly has been advanced. A similar anomaly involving the activity coefficients will be discussed in a forthcoming paper from this Laboratory.[15]

In Fig. 3 we have plotted, as ordinates, the chloride ion conductances, $\lambda_{\mathrm{Cl}} = T_{\mathrm{Cl}}^{\mathrm{MCl}}\,\Lambda$, of lanthanum, calcium[13,16] and sodium chlorides[8,17] against the square root of the concentration as abscissas. The smooth curves through the experimental points are extrapolated to the limiting conductance of the chloride ion, 76.34, and the straight lines through this point are the limiting slopes given by the following Onsager equations

$$\left.\begin{aligned} \lambda_{\mathrm{Cl}}^{\mathrm{NaCl}} &= 76.34 - 47.2\sqrt{C} \\ \lambda_{\mathrm{Cl}}^{\mathrm{CaCl_2}} &= 76.34 - 74.0\sqrt{C} \\ \lambda_{\mathrm{Cl}}^{\mathrm{LaCl_3}} &= 76.34 - 99.1\sqrt{C} \end{aligned}\right\} \qquad (2)$$

The conductance of the chloride ion associated with a univalent cation exhibits the normal positive deviation from the limiting slope with increasing concentration. When associated with a divalent cation, however, the deviations in dilute solutions appear to be negative and still more pronounced negative deviations occur when the co-ion is trivalent as in lanthanum chloride. These negative deviations, due to the anomalous behavior of the transference numbers discussed in the preceding paragraph, do not appear to be indicative of intermediate ion formation since the salt conductances are normal.

The curves of Fig. 3 also serve to illustrate the large deviations from additivity of ion conductances when the valence of the co-ion is altered. In our study of the chloride ion conductance in solutions of uni-univalent chlorides, it was observed that this conductance was additive at concentrations below about 0.02 normal and depended only slightly upon the specific nature of the co-ion at higher concentrations. The magnitude of this dependence is indicated in Fig. 3 by the vertical line through each point for $\lambda_{\mathrm{Cl}}^{\mathrm{NaCl}}$. These lines were drawn to include, at each concentration, the values of λ_{Cl} for hydrogen, potassium and lithium chlorides. Marked deviations from additivity occur, however, when the valence of the co-ion is increased, as is shown by the divergence of the three curves of the figure.

Sherrill and Noyes[18] have assumed for the purpose of computation that ion conductances are additive at equal ionic strengths. This is equivalent to extending the concentration scale for a bi-univalent salt by the factor 1.5 and that for a tri-univalent salt by 2. Alteration of the concentration scales by these factors is, however, insufficient to bring the curves of Fig. 3 into coincidence. Although not strictly applicable at the concentrations for which transference data are available, the Onsager theory explains, qualitatively, this valence effect. Thus reference to equation (2) indicates that $\lambda_{\mathrm{Cl}}^{\mathrm{CaCl_2}}$ should equal $\lambda_{\mathrm{Cl}}^{\mathrm{NaCl}}$ when $C_{\mathrm{NaCl}} = (74.0/47.2)^2\, C_{\mathrm{CaCl_2}} = 2.45 C_{\mathrm{CaCl_2}}$. The corresponding factor for $C_{\mathrm{LaCl_3}}$ is 4.40. Even these factors are not large enough. The ones actually required are 3.3 for calcium chloride and 10 for lanthanum chloride. Thus the open circles and crosses of the upper curve of Fig. 3 are, respectively, the observed values of $\lambda_{\mathrm{Cl}}^{\mathrm{LaCl_3}}$ and $\lambda_{\mathrm{Cl}}^{\mathrm{CaCl_2}}$ plotted on such adjusted concentration scales. The transposed points fall on the $\lambda_{\mathrm{Cl}}^{\mathrm{NaCl}}$ curve with deviations of the same order as is observed among univalent chlorides, *i. e.*, deviations attributable to properties of the co-ion other than its valence. Although only those

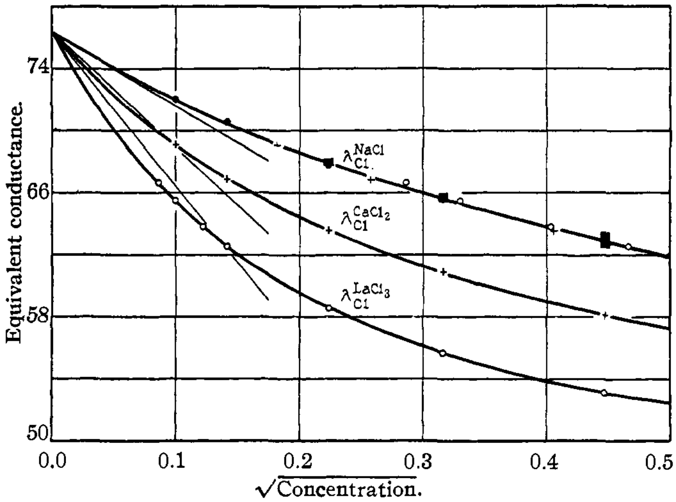

Fig. 3.

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(15) Shedlovsky and MacInnes, THIS JOURNAL, January (1939).

(16) Shedlovsky and Brown, *ibid.*, **56**, 1066 (1934).

(17) Shedlovsky, *ibid.*, **54**, 1411 (1932).

(18) Sherrill and Noyes, *ibid.*, **48**, 1861 (1926).

points on the two lower curves for which $\lambda_{Cl} > 62$ can be thus transposed, computations with the available data indicate that the curves may be thus superposed to higher concentrations.

Summary

Measurements of the transference numbers at 25° of aqueous solutions of lanthanum chloride by the method of moving boundaries have been made. The chloride ion conductances of these solutions have been compared with similar measurements of solutions of calcium chloride and sodium chloride. From this comparison an empirical rule for the effect of the valence of the co-ion on the chloride ion conductance has been obtained.

NEW YORK, N. Y. RECEIVED OCTOBER 15, 1938

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Electrolytic Conductivity of Zinc Sulfate and Copper Sulfate in Water at 25°[1]

BY BENTON BROOKS OWEN AND ROBERT W. GURRY[2]

Within the last decade the conductivities of a large number of electrolytes have been precisely redetermined at 25°. Most of these modern measurements have been confined to 1–1 and 2–1 valence types because they conform to the requirements of the inter-ionic attraction theory at experimentally accessible dilutions, and may therefore be readily extrapolated. The 3–1 electrolyte lanthanum chloride can possibly be satisfactorily extrapolated along the Onsager[3] slope, but no 2–2 electrolyte has yet been found amenable to this simple treatment. The extrapolation of the conductivities of zinc and copper sulfates is of particular interest because of the complications introduced by relatively large departures from the limiting slope and partial hydrolysis of the ions.

In the present research we have carefully measured the specific conductivity and *p*H of dilute solutions of these salts at 25°, and made what we believe to be adequate solvent and hydrolysis corrections. The results have been extrapolated by a number of methods fulfilling the requirements of the inter-ionic attraction theory, and which lead to essentially the same values of Λ_0. Zinc and copper sulfates are particularly well suited for this type of investigation because they can be highly purified, and their hydrolysis corrections are not too great to be estimated with sufficient accuracy. Furthermore, the supplementary thermodynamic and conductance data required in our calculations are available for these salts, and for the sulfate and hydrosulfate ions.

Materials and Technique

Merck reagent grade zinc sulfate heptahydrate was recrystallized twice from a mixture of highly purified methanol and water, and then twice from conductivity water. The last crystallization was accomplished by partial evaporation of the water at room temperatures with the necessary precautions against contamination by dust.

Merck reagent grade copper sulfate pentahydrate was recrystallized four times from conductivity water. The purified salt was crushed in an agate mortar and dried over a mixture of the penta- and trihydrates.

Stock solutions, 0.1 and 0.5 *m*, were prepared by weight and checked by gravimetric analysis. Vacuum corrections were applied throughout. Samples of the zinc sulfate solutions were evaporated at 95° and the salt dehydrated at 300° and weighed as $ZnSO_4$. The copper was determined electrolytically, with the last traces precipitated as sulfide and weighed as oxide. All duplicate analyses checked within 0.02% from the means.

The Dike[4] bridge was operated by a vacuum tube oscillator at 1000 cycles. It was calibrated against Bureau of Standard resistors with a d. c. source and a sensitive galvanometer. All measurements reported were made without shunts, and were reproducible to 0.002%.

The temperature was adjusted to 25 ± 0.005° with a platinum resistance thermometer certified by the Bureau of Standards, and thermoregulation within 0.005° was maintained during the course of the measurements.

The cells were the type B[5] generally employed in this Laboratory. The electrodes were lightly platinized. Cell constants were determined several times during the course of the measurements with 0.1 demal potassium chloride according to Jones and Bradshaw.[6] The cell constants, *l/a*, were 4.5221 for cell III and 3.7260 for cell IV. The specific conductivity of the water employed was usually less than 2×10^{-7} mho.

The *p*H values required for the solvent and hydrolysis corrections were obtained colorimetrically by the use of LaMotte indicator standards in the zinc sulfate solutions, and electrometrically with glass electrodes[7] in the copper

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[1] This communication embodies part of the experimental material contained in the thesis submitted by Robert W. Gurry to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy (1937).

[2] Present address: Research Laboratory, United States Steel Corp., Kearny, N. J.

[3] Onsager, *Physik. Z.*, **27**, 388 (1926).

[4] Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[5] Saxton and Meier, THIS JOURNAL, **56**, 1918 (1934).

[6] Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

[7] The authors are indebted to Professor Leslie F. Nims of the Department of Physiology for making these measurements.