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

Transference Numbers and Ion Mobilities of Some Electrolytes in Deuterium Oxide and its Mixtures with Water

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

Introduction

In previous publications from this Laboratory, transference data obtained by the method of moving bundaries,[1] of many of the strong electrolytes have been reported. These data are of value, in the first place, in the accurate determination of the activities of electrolytes from potential measurements on concentration cells with transference[2,3] and, in addition, they may be combined with conductance measurements to give ionic mobilities as functions of the concentration.[4] It is our program to extend such measurements to other solvents. Heavy water is of particular interest since, of the variables entering into modern solution theory, its viscosity is the only property in which it differs appreciably from normal water.[5] Moreover, we believe that the data to be presented in this paper will eventually be of service in explaining the abnormal mobilities of the hydrogen and deuterium ions.

Experimental Procedure

Since the moving boundary method for the determination of transference numbers normally requires only small volumes of solution it is quite suitable for work with limited amounts of material. With the apparatus previously described[1] and using autogenic boundaries only 15 ml. of solution was required for a determination. This quantity was further reduced to 10 ml. by redesigning the electrode chamber as shown in cross section in Fig. 1. The function of the inner cup A is to keep the products of the electrode reaction, $AgCl + \epsilon^- = Ag + Cl^-$, from altering the composition of the solution at the boundary in the graduated tube T. The silver-silver chloride cathode was in the form of a flat spiral resting on the bottom of the inner cup so that the concentrated chloride solution which forms at this electrode during an experiment tends to remain in place. Moreover, by constricting the lower end of the glass tube B the solution in the bottom of the cup tends to remain cooler than in the upper part and thus further restricts convection.

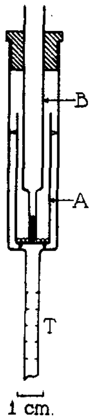

Fig. 1.— Modified electrode chamber.

The conductivity cell used was of the pipet type. The electrodes were truncated hollow cones of platinum, the outer surfaces of which are completely sealed to the glass, as described by Shedlovsky.[6] It had a capacity of 4 ml. and a constant of 16.482 on the basis of a specific conductance of 0.012856[7] for 0.1 demal potassium chloride at 25°. With the solutions whose conductances were measured in this cell the error due to the Parker effect[8] was never greater than 0.03%, which was about the accuracy with which the concentrations of the solutions were known.

Densities were determined with the aid of a pycnometer similar to that described by Smith and Wojciechowski.[9] The volume of the pycnometer was 8.5 ml. and the capillary neck, marked with a single graduation, had an internal diameter of 1.4 mm. The pycnometer was filled with the aid of a hollow stainless steel needle. It was supported in a thermostat at 25° on a framework which also carried, outside the glass wall of the thermostat, a microscope whose position could be shifted and read with a micrometer screw. When observation with the microscope indicated that the meniscus had stopped moving, its position relative to the graduation was read to 0.001 cm. Weighings were then made with a duplicate pycnometer as counterpoise. An air density of 0.0012 was used in the reduction of all weights to vacuum. It may be noted that the densities of light and heavy water result in appreciably different vacuum corrections.

The samples of sodium and potassium chlorides were purified by recrystallization and fused prior to weighing. In the preparation of the hydrogen-deuterium chloride solutions constant boiling hydrochloric acid, whose concentration was checked at intervals by conductance measurements, was added to the solvent from a small weight buret. The solvent was distilled under its own vapor pressure from an alkaline permanganate solution at 40° into a receiver at 0°. If precautions were taken to prevent ebullition, a single distillation was sufficient to give water having a specific conductance less than 10^{-6} mhos and no water was used as solvent having a conductance greater than that value. About 20 ml. of each solution was prepared. The moving boundary cell, conductivity cell and pycnometer, previously cleaned and dried, were filled without rinsing.

Experimental Results

The experimental results consist (a) of a study of the transference numbers and conductances of 0.05 normal solutions of potassium chloride in a wide range of mixtures of hydrogen and deuterium oxides, (b) similar measurements on

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(1) MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932).

(2) Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

(3) MacInnes and Brown, *Chem. Rev.*, **18**, 335 (1936).

(4) MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

(5) Jones and Fornwalt, *J. Chem. Phys.*, **4**, 30 (1936).

(6) Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

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

(8) Parker, *ibid.*, **45**, 1366, 2017 (1923).

(9) Smith and Wojciechowski, *Roczniki Chem.*, **16**, 104 (1936).

TABLE I

TRANSFERENCE NUMBERS AND CONDUCTANCES OF 0.05 NORMAL SOLUTIONS OF KCl IN MIXTURES OF D_2O AND H_2O AT 25°

1 Concn.	2 N_{D_2O}	3 d^{25}_4	4 Λ	5 T_+	6 T_+ computed equation (1)	7 λ_{Cl}	8 λ_{Cl} computed equation (2)
0.04997	0.9935	1.10614	110.51	0.4939	0.4939	55.93	55.93
.05007	.7521	1.08027	115.33	.4932	.4929	58.45	58.46
.05002	.4959	1.05277	120.89	.4916	.4919	61.46	61.43
.04999	.2471	1.02610	126.86	.4909	.4909	64.58	64.60
.05000	.0002	0.99942	133.37	.4899	.4899	68.03	68.03

0.05 normal solutions of hydrogen–deuterium chloride and (c) measurements of three strong electrolytes over a range of salt concentrations in nearly pure deuterium oxide.

(a) Solutions of Potassium Chloride in H_2O-D_2O Mixtures.—The results of measurements of solutions of potassium chloride in H_2O–D_2O mixtures are recorded in Table I. The concentrations, in equivalents per liter of solution at 25°, are given in the first column. The mole fraction of deuterium oxide in the solvent, N_{D_2O}, is recorded in the second column. This was computed directly from the weights of hydrogen and deuterium oxides or from the measured density of the mixture, using the relation[10]

$$N_{D_2O} = \frac{9.2351\ \Delta S}{1 - 0.0327\ \Delta S}$$

in which $\Delta S = (d^{25}_4/0.99705_5) - 1$, obtained from recent measurements made in this Laboratory. Columns 3, 4 and 5 of Table I contain, respectively, the observed density of the solution, the equivalent conductance and the cation transference number. The data for normal water in this and later tables are from earlier work from this Laboratory.[6,11] The necessary small solvent and volume corrections[1] have been applied to the transference data. In making the volume corrections the molal volumes of the electrolytes were assumed to have the same values in the mixtures as in water, an assumption that is justified by existing density data of solutions in deuterium oxide.

The transference numbers given in Table I for 0.05 normal solutions of potassium chloride in H_2O–D_2O mixtures vary linearly with the mole fraction, N_{D_2O}. Values of T_+ computed from the relation

$$T_+ = 0.4899 + 0.0040\ N_{D_2O} \qquad (1)$$

are recorded in column 6 of Table I and agree with the observed values within the experimental error. Theory,[11] and the experimental results given below in Table III, both indicate that transference numbers of potassium chloride change but little with salt concentration so that the variation with N_{D_2O} given by equation (1) is valid for solutions at infinite dilution. It may be shown readily that this variation of the transference number with change of solvent is contrary to the assumptions underlying the Walden rule,[12] *i. e.*, $\Lambda_0\eta$ = constant, in which η is the viscosity of the solvent. Since the ions are assumed to move independently and Stokes' law is assumed to apply to each, then for a binary electrolyte $\lambda_0{}^+\eta = k^+$ and $\lambda_0{}^-\eta = k^-$, in which $\lambda_0{}^+$ and $\lambda_0{}^-$ are the limiting ion conductances and k^+ and k^- are constants. From these relations $T_0{}^+ = \lambda_0{}^+/(\lambda_0{}^+ + \lambda_0{}^-) = k^+/(k^+ + k^-)$. Thus it is a corollary of the Walden rule that the limiting transference number should be independent of the solvent, which, as has been shown from the data in Table I and equation (1), is not true for solvents as similar as hydrogen and deuterium oxides.

The conductances of the chloride ion constituent, which is common to all of the electrolytes considered in this paper, are recorded in the seventh column of Table I. These data may be represented adequately by the relation

$$\lambda_{Cl}(0.05\ N\ \mathrm{KCl}) = 68.03 - 14.46\ N_{D_2O} + 2.30\ N^2_{D_2O} \qquad (2)$$

as is indicated by the agreement between the values of columns 7 and 8.

(b) Solutions of Hydrogen-Deuterium Chloride in H_2O-D_2O Mixtures.—The results of measurements on 0.05 normal solutions of hydrogen-deuterium chloride in several H_2O–D_2O mixtures are recorded in Table II. In the computation of N_{D_2O} for these solutions account was taken of the water added in the form of constant boiling hydrochloric acid but the very slight change in N_{D_2O} due to the reaction[13]

$$2H^+ + D_2O = 2D^+ + H_2O \qquad (3)$$

was ignored. The observed conductances and

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[10] Longsworth, THIS JOURNAL, **59**, 1483 (1937).

[11] Longsworth, *ibid.*, **54**, 2741 (1932).

[12] Walden, *Z. physik. Chem.*, **55**, 207 (1906). See also Ulich, *Fortschr. Chem., Physik physik. Chem.*, **18**, 567 (1926).

[13] Korman and La Mer, THIS JOURNAL, **58**, 1396 (1936).

TABLE II

TRANSFERENCE NUMBERS AND CONDUCTANCES OF 0.05 NORMAL SOLUTIONS OF HCl–DCl IN MIXTURES OF D_2O AND H_2O AT 25°

1 Concn.	2 N_{D_2O}	3 d^{25}_4	4 Λ	5 $\Lambda(0.05\ N)$	6 T_+	7 T_+ compd.	8 ΔT_+
0.05464	0.9853	1.10400	290.96	291.68	0.8081	0.8077	−0.0002[a]
.05086	.9007	1.09481	295.50	295.64	.8065	.8073	+ .0008
.04966	.8082	1.08499	301.19	301.11	.8072	.8076	+ .0004
.05049	.5990	1.06243	317.37	317.46	.8094	.8101	+ .0007
.05013	.4052	1.04167	338.12	338.14	.8146	.8147	+ .0001
.05073	.1972	1.01931	366.33	366.47	.8217	.8216	− .0001
.05000	.0002	0.99798	399.08	399.08	.8292	.8292	.0000

[a] T_+ obsd. = 0.8079 at C = 0.050.

transference numbers are recorded in columns 4 and 6, respectively. Since the concentrations of some of the solutions differed from 0.05 it was desirable to adjust the conductances to this concentration. This was done with more than sufficient accuracy with the aid of the Shedlovsky equation,[14] the coefficient B of that equation being set equal to $(\alpha\Lambda_0 + \beta)$. The adjusted values are recorded in column 5 of Table II. If these equivalent conductances are plotted against the mole fraction of the solvent, N_{D_2O}, the resulting curve sags below the straight line connecting the limiting values in the pure solvents, an observation also made by Baker and La Mer[15] on 0.02 normal solutions of hydrogen and deuterium chlorides. Assuming that the chloride ion conductances of these solutions are normal, values of T_+, column 7, were computed by means of the relation

$$1 - T_+ = \frac{\lambda_{Cl}(0.05\ N\ \text{KCl})}{\Lambda(0.05\ N\ \text{HCl–DCl})} + 0.003$$

in which λ_{Cl} is given by equation (2), Λ is taken from column 5 of Table II and the small constant term corrects for the slight difference in the chloride ion conductance in potassium and hydrogen chloride solutions. The agreement between the observed and computed values of T_+ is sufficiently close to justify the assumption on which the equation just given is based.[16] The cation constituents of the hydrogen–deuterium chloride solutions must therefore be responsible for the large deviations from linearity mentioned above.

Baker and La Mer[15] explain, qualitatively, the irregular behavior of the cation constituents of hydrogen–deuterium chloride solutions as follows. They accept the hypothesis, treated theoretically in several recent papers,[17] that the high mobilities of the hydrogen and deuterium ions in hydrogen and deuterium oxides, respectively, are due in a large measure to symmetrical transitions of the type

$$H_3O^+ + H_2O = H_2O + H_3O^+$$
$$D_3O^+ + D_2O = D_2O + D_3O^+$$

In H_2O–D_2O mixtures, however, the foregoing transitions are partially replaced by unsymmetrical, and hence less probable, transitions of which the following is an example

$$D_3O^+ + H_2O = D_2O + DH_2O^+$$

Since the total number of possible transitions in a mixture is essentially the same as in the pure solvent, any decrease in the probability of certain types of transitions will be accompanied by a corresponding decrease in the apparent mobility of the hydrogen and deuterium ions. Our transference number measurements in these mixtures are compatible with this hypothesis since it attributes all abnormalities to the cation constituents and permits the chloride ion to be normal. Of the various hypotheses that may be advanced in explanation of the observed cation conductances of hydrogen–deuterium chloride in H_2O–D_2O mixtures, one which our data definitely excludes is that the negative deviations are due to ion association. With this hypothesis the chloride ion conductance in these mixtures would be less than in other chloride solutions at the same

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(14) Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

(15) Baker and La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

(16) The differences at N_{D_2O} = 0.9, 0.8 and 0.6 are probably outside of the experimental error and may be due to the complex nature of the cation constituents in these mixtures. It was observed that the boundaries became less sharp as they moved and in some cases a progressive separation into two boundaries was observed. A possible explanation is as follows. More hydrogen than deuterium ions leave the region immediately ahead of the boundary. Thus the equilibrium indicated by equation (3) must be displaced to the left to compensate for the loss of hydrogen ion. The resulting shift in the composition of the solvent in the neighborhood of the boundary may therefore account for the complications observed at these boundaries. A computation indicates that although a measurable accumulation of deuterium oxide occurs behind the boundary it is of no practical importance.

(17) Hückel, *Z. Elektrochem.*, **34**, 546 (1928); Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933); Wannier, *Ann. Physik*, **24**, 545, 569 (1935).

concentration of electrolyte and mole fraction of deuterium oxide and this is not observed.

(c) **Solutions of Sodium, Potassium and Deuterium Chloride in Heavy Water.**—Transference number and conductance measurements on solutions of three chlorides in nearly pure deuterium oxide are reported in Table III. These data may be interpreted with the aid of a quantity, λ_0', defined by the relation

$$\lambda_0' = (\lambda + \beta\sqrt{C})/(1 - \alpha\sqrt{C})$$

in which α and β are constants of the Onsager theory and have the values 0.2323 and 24.53, respectively, for D_2O at 25°.[5,18] Values of λ_0' for the four ion constituents of the electrolytes of Table III are plotted as ordinates against the concentration as abscissa in Fig. 2. As in water[4] λ_0' is found to be a linear function of the concentration for each ion species, *i. e.*

$$\lambda_0' = \lambda_0 + bc$$

and this relation may be used to obtain values of the ion conductance at zero concentration, λ_0. Values of λ_0 and b, as computed by the method of least squares, are recorded in Table IV. The average value of λ_0 for the chloride ion from the three chlorides of Table III is 62.79 with an average deviation from the mean of 0.07%. It is of interest that the values of b for this constituent show a parallel but somewhat smaller variation than is found with the data for water solutions.

TABLE III

TRANSFERENCE NUMBERS AND CONDUCTANCES OF SOME ELECTROLYTES IN HEAVY WATER AT 25°

1 Salt	2 Concn.	3 N_{D_2O}	4 d^{25}_4	5 Λ	6 T_+
KCl	0.02013	0.9935	1.10485	114.53	0.4940
	.04997	.9935	1.10614	110.51	.4939
	.09985	.9935	1.10843	106.87	.4939
NaCl	.02013	.9935	1.10473	95.50	.3922
	.04996	.9938	1.10596	91.74	.3901
	.09735	.9938	1.10791	88.36	.3877
HCl–DCl	.02129	.9889	1.10382	297.80	.8055
	.05464	.9853	1.10400	290.96	.8081
	.10182	.9773	1.10391	286.24	.8105

The values of λ_0 recorded in Table IV are limiting ion conductances in an H_2O–D_2O mixture for which N_{D_2O} = 0.9935. This value for the mole fraction of deuterium oxide is based upon the density data for the pure material given by Selwood, Taylor, Hipple and Bleakney.[19] In view of the existing uncertainty[20] as to the density of pure deuterium oxide, it is not desirable at present to extrapolate our ion conductances to their values for the pure solvent. The extrapolation will, in any event, be a very short one and can be made readily from the data of this paper when the density of pure deuterium oxide has been determined.

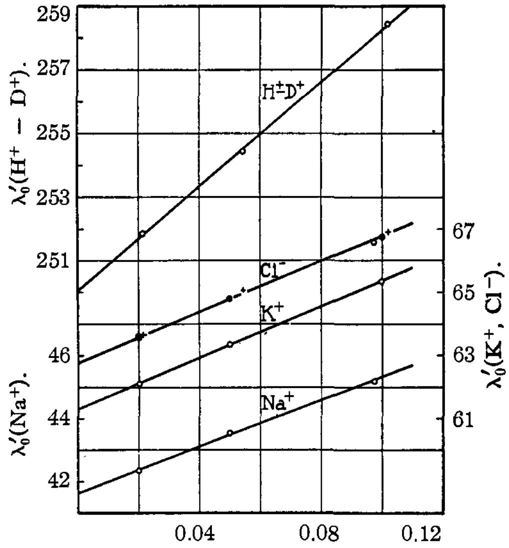

Fig. 2.

TABLE IV

LIMITING ION CONDUCTANCES IN HEAVY WATER AT 25°

Salt	Ion	b	λ_0
KCl	K^+	40.33	61.31
NaCl	Na^+	36.73	41.64
HCl–DCl[a]	H^+–D^+	82.18	250.05
KCl	Cl^-	40.19	62.74
NaCl	Cl^-	38.27	62.86
HCl–DCl[a]	Cl^-	40.64	62.79
		Average	62.79

[a] In the computation of λ_0' for the ion constituents of the hydrogen–deuterium chloride solutions it was necessary to correct the observed conductances to their values for N_{D_2O} = 0.9935. These small corrections were made as follows. The conductance data of Table II may be represented by the empirical equation $\Lambda(0.05\ N\ \text{HCl–DCl}) = 399.11 - 179.5\,N_{D_2O} + 71.8\,N_{D_2O}^2$ with an average deviation of 0.05%. Assuming that the value of $d\Lambda/dN_{D_2O}$ obtained by differentiating this expression is also valid at concentrations in the neighborhood of 0.05 N, the value of the necessary correction, $\Delta\Lambda$, was computed from the relation $\Delta\Lambda = (-179.5 + 143.6\,N_{D_2O})(0.9935 - N_{D_2O})$.

It is of interest that our data for the chloride ion constituent of potassium chloride give the

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(18) Müller, *Physik. Z.*, **36**, 1009 (1935).

(19) Selwood, Taylor, Hipple and Bleakney, THIS JOURNAL, **57**, 642 (1935).

(20) Tronstad, Nordhagen and Brun, *Nature*, **136**, 515 (1935).

nearly identical values of 1.1221 and 1.1218 for the ratio $\lambda_{Cl}(C = 0)/\lambda_{Cl}(0.05\ N\ KCl)$ in light and heavy water, respectively. La Mer and Chittum[21] have shown recently from theory and experiment that the salt conductance ratio Λ_0/Λ_c is very nearly constant for these two solvents and their mixtures. We thus have

$$\lambda_0(N_{D_2O}) = (\lambda_0/\lambda_c)_{H_2O}\,\lambda_c(N_{D_2O}) \qquad (4)$$

in which λ_c and λ_0 are the conductances of a given ion constituent at concentration C and at infinite dilution, respectively. Substitution in equation (4) of the value for $\lambda_c(N_{D_2O})$ given for the chloride ion by equation (2) and 1.1221 for the ratio $(\lambda_0/\lambda_c)_{H_2O}$ gives

$$\lambda_0(Cl^-) = 76.34 - 16.23\ N_{D_2O} + 2.58\ N^2_{D_2O}$$

a relation that may be used in determining the limiting transference number of any chloride in any H_2O–D_2O mixture for which the limiting salt conductance is known.

The authors wish to thank Professor La Mer and Dr. Chittum of Columbia University for many helpful suggestions concerning experimental technique.

Summary

Transference and conductance measurements on solutions of several electrolytes in deuterium oxide and its mixtures with water have been made. The investigation included 0.05 N solutions of potassium and hydrogen–deuterium chlorides in a wide range of H_2O–D_2O mixtures. The conductance of the chloride ion constituent from these two chlorides varies nearly linearly with the mole fraction of deuterium oxide in the mixed solvent. The hydrogen–deuterium component, on the other hand, shows wide variations from linearity, thus indicating a complex conductance mechanism.

Measurements have also been made on solutions of sodium, potassium and hydrogen–deuterium chlorides at several concentrations in nearly pure ($N_{D_2O} = 0.9935$) deuterium oxide. From these data limiting values of the ion conductances have been computed for heavy water.

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[21] La Mer and Chittum, THIS JOURNAL, **58**, 1642 (1936).

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X-Ray Studies on the Hydrous Oxides. VIII. Gallium, Indium and Thallic Oxides[1]

BY W. O. MILLIGAN AND HARRY B. WEISER

The composition of precipitated alumina prepared and aged under varying conditions has been established with considerable certainty as a result of numerous dehydration and X-ray diffraction studies.[2] The present paper is concerned with the composition of the precipitated oxides of other members of the aluminum family about which but little authentic information was available.

A. Hydrous Gallium Oxide

A review[2] (pp. 120–121) of the earlier work on precipitated gallium oxide leads to the conclusion that the freshly formed gel is a hydrous oxide amorphous to X-rays, and not a hydrate. If the fresh gel is dissolved in ammonia and reprecipitated by dilution, a granular product is obtained which gives a definite X-ray diffraction pattern different from that of the anhydrous oxide. This material must be either a definite hydrate or a new modification of the oxide. Havestadt and Fricke[3] found that the composition may be represented by the formula $3Ga_2O_3 \cdot 5H_2O$ both when dried at 100° and when dried over phosphorus pentoxide at room temperature, but this evidence is insufficient to establish the existence of a definite hydrate.

Goldsmidt, Barth and Lunde[4] found that the precipitated oxide gave a distinctive X-ray diffraction pattern up to a temperature of 350° but when heated to 420–440° it gave a new pattern[5] similar to that from α-Al_2O_3; hence this product was designated as α-Ga_2O_3. Heating to 650° gave a second modification of gallium

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[1] Preliminary results were reported at the New York Meeting of the American Chemical Society, April, 1935.

[2] *Cf.* Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, Inc., New York City, 1935, pp. 90–100.

[3] Havestadt and Fricke, *Z. anorg. allgem. Chem.*, **188**, 357 (1930); *cf.* Fricke and Blencke, *ibid.*, **143**, 183 (1925); Fricke, *Z. Elektrochem.*, **30**, 393 (1924).

[4] Goldsmidt, Barth and Lunde, *Skrifter Norske Videnskaps-Akad. i. Oslo, I. Mat.-Natur. Klasse*, No. 7, 24 (1925).

[5] *Cf.* Zachariasen, *ibid.*, No. 4, 18 (1928).