In conclusion the author would like to express his sincere appreciation to Dr. D. A. MacInnes for many suggestions during the course of this work and for valuable criticism during the preparation of this paper.

Summary

Measurements of the transference numbers at 25° of aqueous solutions of potassium chloride, sodium chloride, lithium chloride and hydrochloric acid by the moving boundary method have been made. The results are given in Table X.

TABLE X

TRANSFERENCE NUMBERS AT 25° OF POTASSIUM CHLORIDE, SODIUM CHLORIDE, LITHIUM CHLORIDE AND HYDROCHLORIC ACID

Concn.	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2
KCl	$.490_5$	$.490_4$	$.490_4$	.4903	.4901	.4899	.4898	$.489_2$
NaCl	...	...	...	.3918	.3902	.3876	.3854	$.381_4$
HCl	...	...	...	$.825_1$	$.826_6$	$.829_2$	$.831_4$	...
LiCl	...	...	...	.3289	.3261	.3211	.3168	...

A correction for the conductance of the solvent, neglected by previous workers, has been found to be important when dilute solutions are measured.

An equation connecting the transference numbers with the concentration, which is useful for interpolation, and which gives a correct extrapolation to infinite dilution, is given.

NEW YORK, N. Y.

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

THE LIMITING EQUIVALENT CONDUCTANCES OF SEVERAL UNIVALENT IONS IN WATER AT 25°

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Data on the conductances of aqueous solutions of a number of binary electrolytes at concentrations ranging from 3×10^{-5} to 0.1 N are given in recent papers from this Laboratory,[1] and an article preceding this one describes the accurate determination of the transference numbers of four chlorides in the range 0.01 to 0.1 N.[2] With these data at hand we have been able to arrive at some definite conclusions concerning the equivalent conductances of ion constituents, and the values of the limiting ion mobilities.

Table I contains the assembled data on the equivalent conductances, Λ, of four chlorides and the corresponding transference numbers of the

[1] Shedlovsky, THIS JOURNAL, **54**, 1411 (1932); MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

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

chloride ion, T_{Cl}. These transference numbers are the directly determined values with the exception of those for lithium chloride, which have been brought to round concentrations by very short interpolations. From these data the equivalent conductances of the chloride ion constituents have been computed, and the results have been tabulated in the fourth column of the table.

TABLE I

EQUIVALENT CONDUCTANCES OF CHLORIDE ION CONSTITUENTS AT 25°

Concn.	Equivalent cond., Λ	Trans. no., T_{Cl}	Cond. of chloride ion constituent, $T_{Cl}\,\Lambda = \lambda_{Cl}$ Observed	Computed
		KCl		
0.01	141.32	0.5098	72.04	72.04
.02	138.34	.5099	70.54	70.54
.05	133.33	.5100	68.00	67.99
.10	128.90	.5102	65.76	65.76
		NaCl		
0.01	118.43	0.6081	72.01	72.03
.02	115.65	.6100	70.54	70.51
.05	110.88	.6122	67.88	67.89
.10	106.68	.6147	65.57	65.56
		HCl		
0.01	411.88	0.1748	71.99	72.08
.02	407.12	.1736	70.67	70.59
.05	398.97	.1708	68.14	68.11
.10	391.20	.1686	65.96	65.98
		LiCl		
0.01	107.29	0.6711	72.00	72.04
.02	104.62	.6739	70.50	70.51
.05	100.08	.6789	67.94	67.85
.10	95.83	.6832	65.47	65.48

If values of λ_{Cl} for the four chlorides at equivalent concentrations are compared it will be seen that they are very nearly the same at 0.01 and 0.02 N but show definite deviations from each other at 0.05 and 0.1 N. This is not in accord with the observations of Lewis[3] and MacInnes,[4] who found from less accurate data that the chloride ion conductance appeared to be independent of its univalent co-ion up to a concentration of 0.1 N.

The data in Table I may be used to discover how the conductance of the chloride ion constituent changes with the concentration. Shedlovsky[5] has proposed an empirical extension of Onsager's equation for the change of the equivalent conductance of a uni-univalent electrolyte with the concentration, C, having the form

[3] G. N. Lewis, THIS JOURNAL, **34**, 1631 (1912).

[4] MacInnes, *ibid.*, **43**, 1217 (1921).

[5] Shedlovsky, *ibid.*, **54**, 1405 (1932).

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} - BC \tag{1}$$

With a few exceptions this equation has been found to hold with high accuracy for uni-univalent electrolytes up to 0.1 N.

In Onsager's equation

$$\alpha = \frac{5.78 \times 10^{-5}}{(DT)^{3/2}} \text{ and } \beta = \frac{58.0\sqrt{2}}{\eta(DT)^{3/2}}$$

in which D is the dielectric constant, T the absolute temperature, and η the viscosity. The numerical coefficients depend upon universal constants. The extension of Onsager's equation consists of the term BC in which B is an empirical constant. For the equivalent conductance of an ion constituent $\lambda = T\Lambda$ the corresponding equation is

$$\lambda_0 = \frac{\lambda + 1/2\,\beta\sqrt{C}}{1 - \alpha\sqrt{C}} - bC \tag{2}$$

in which λ_0 is the limiting equivalent conductance of the ion species and b is an empirical constant.

To use Equation (2) it is convenient to compute values of

$$\frac{\lambda + 1/2\,\beta\sqrt{C}}{1 - \alpha\sqrt{C}} = \lambda_0' \tag{3}$$

and plot them against C. Figure 1 shows values of λ_0' for the chloride ion constituent plotted in this way. The result is a straight line for

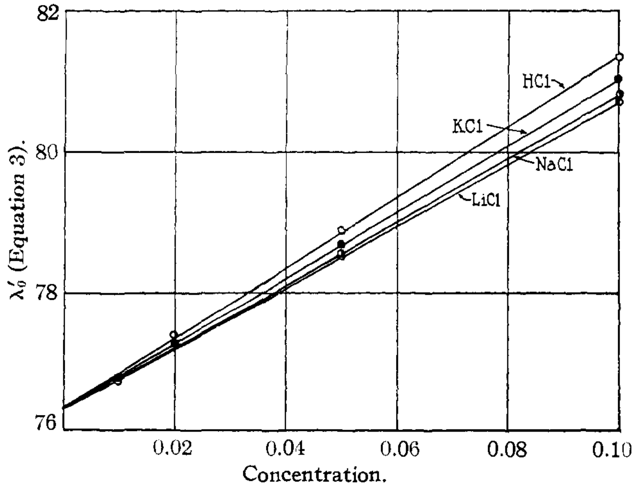

Fig. 1.

the λ_0' values from each of the electrolytes. The four lines converge and meet at a point at zero concentration. Equation (2) thus provides a method for obtaining the limiting conductance of the chloride ion, λ_{0Cl}.

The most probable values of that constant and of b for each electrolyte were found by applying the method of least squares to the equation

$$\lambda_0' = \lambda_0 + bC$$

The resulting constants are given in Table II.

TABLE II

COMPUTED VALUES OF THE LIMITING CONDUCTANCE AT 25° OF THE CHLORIDE ION

Substance	b	λ_0 for Cl ion
KCl	47.30	76.31
NaCl	45.00	76.32
LiCl	44.09	76.34
HCl	49.50	76.32
	Average	76.32

It will be observed that the values for the limiting chloride ion conductance thus obtained are, within about 0.02%, the same from all four chlorides. The close agreement of the data with Equation (1) is best shown by comparing in Table I the observed and computed values of λ_{Cl}, the latter having been obtained by using in that equation the appropriate values of the constants in Table II. The comparatively large difference between the computed and measured values for 0.05 N for lithium chloride possibly indicates that the behavior of this substance may be influenced by some secondary effect, particularly as the conductance values of this salt deviate from Shedlovsky's equation at a lower concentration than is observed for the other electrolytes under consideration. However, the agreement shows that Equation (2) for the chloride ion constituent holds as well as Equation (1) has been found to do for complete uni-univalent electrolytes.

A check on the mean value of λ_{0Cl} in Table II is given by the limiting conductance value for potassium chloride, $\Lambda_0 = 149.82$, obtained by Shedlovsky from his measurements on the most dilute solutions, and the limiting value of the transference number, $T_{0Cl} = 0.5094$, of that salt, as given by Longsworth in the paper preceding this one. The product of these two figures yields $\lambda_{0Cl} = 76.32$, agreeing exactly with the average value by the other method. Using the data from say 3×10^{-5} to 0.001 N an accurate extrapolation may be made of the conductance data by simply plotting the equivalent conductance values against the square root of the concentration. This does not involve the extension of the Onsager equation. The very close agreements just shown may be in some measure fortuitous, particularly as the transference numbers at the lower concentrations are not known to this high degree of accuracy.

It will be noted that the value $\lambda_{0Cl} = 76.32$ differs quite widely from that generally accepted for this constant. Noyes and Falk[6] give $\lambda_{0Cl} = 75.8$

[6] Noyes and Falk, THIS JOURNAL, 34, 454 (1912).

and the figures in the "International Critical Tables"[7] yield 75.1 if the value at 18° and the temperature coefficient there given are used. It is important to note that *the new value of the constant is not dependent on any one transference number as were the older figures, the same value within a very narrow range being obtained from data on four electrolytes and four series of determinations of transference numbers.*

From the λ_{0Cl} value just given and the limiting conductances, Λ_0, from the recent papers by Shedlovsky and MacInnes and Shedlovsky,[1] the limiting ion conductances of a number of ions may be computed from Kohlrausch's law of independent ion mobilities. The results, which are collected in Table III, are all on the basis that a "demal" solution of potassium chloride, containing 7.47896 g. of potassium chloride and 1000 g. of water (weighed in air) has a specific conductance value of 0.012852_4 at 25°.[8]

TABLE III

LIMITING ION CONDUCTANCES AT 25°

Cations		Anions	
K^+	73.50	Cl^-	76.32
Na^+	50.10	NO_3^-	71.42
H^+	349.72	CH_3COO^-	40.87
Ag^+	61.90		
Li^+	38.68		

These constants will be added to from time to time as the work in this Laboratory proceeds. A more elaborate theoretical discussion of the results will also be given along with further data, some of which are already at hand.

Summary

A table is given of the limiting conductance at 25° of eight ion species, based on transference and conductance values obtained in this Laboratory. The extrapolations have been made with an extension of Onsager's equation, which reduces to that equation in the limit. Closely agreeing values of the limiting chloride ion conductance have been found from the use of conductance and transference data on four different chlorides.

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[7] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, p. 230.

[8] Parker and Parker, THIS JOURNAL, **46**, 332 (1924).