

to the brown dioxide. Both the trivalent hydroxide and the dioxide are dissolved by long heating with a solution of potassium cyanide in contact with air, and give the octacyanide. The fact, too, that in the presence of nitrogen a solution of  $K_3MoCl_6$  and potassium cyanide react, when heated, to form  $K_4Mo(CN)_8$  was made clear after it was noted that  $K_3MoCl_6$  in alkaline solution, when heated in the absence of oxygen, reacts with the water, the molybdenum being oxidized and hydrogen being evolved.

CAMBRIDGE, MASSACHUSETTS

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

## AN EQUATION FOR ELECTROLYTIC CONDUCTANCE

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Debye and Hückel<sup>1</sup> have proposed a theory for the effect of the ionic atmosphere on the mobilities of ions. According to that theory the decrease in equivalent conductance should be proportional to the square root of the concentration, a relation which was first found empirically by Kohlrausch. The theoretical calculations for the decrease of ionic mobility with increasing concentration consider two effects. In the first place, when an ion moves through a solution under the influence of an applied electric field, it tends to disturb the surrounding ionic atmosphere, which then exerts an opposing electric force. In the second place, the ions comprising the ionic atmosphere produce a counter current of solvent which also retards the motion of the central ion.

However, Onsager<sup>2</sup> has pointed out that in calculating the first or so-called ionic effect, Debye and Hückel neglected to take into account the influence of the Brownian movement of the ions, and also used a treatment which is valid only if the negative and positive ions have equal mobilities. Furthermore, he has shown that the second or electrophoretic effect could be calculated in a manner which does not involve the ionic radii. Onsager's treatment likewise confirmed the square-root relationship between the equivalent conductance decrease and concentration, and, what is very important, the proportionality factor in his theoretical expression can be readily calculated from well-known constants.

Although Onsager's equation has been shown to be in close agreement with measurements at very low concentrations, it is strictly valid only as a limiting expression. This is so because in the derivation of the simple equation, only the first approximations were retained in the mathematical

<sup>1</sup> Debye and Hückel. *Physik. Z.*, **24**, 305 (1923).

<sup>2</sup> Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

treatment, and also the simple physical picture assumed in the derivation may be inadequate for finite concentrations.

Numerous empirical equations have been proposed to correlate conductance measurements with concentration, and to serve for extrapolations of equivalent conductances at infinite dilution. An empirical formula suitable for the latter purpose should, if the recent theoretical deductions are correct, reduce in the limit of zero concentration to the Onsager equation.

Recently Ferguson and Vogel<sup>3</sup> and Lattey<sup>4</sup> have proposed conductance formulas, which, however, do not appear to be satisfactory for the purpose of extrapolation. These formulas have been criticized by Davies and others.<sup>5</sup>

In this paper an equation is suggested which is an empirical extension of Onsager's limiting expression, containing only one additional (empirical) constant. It agrees with measurements up to a concentration of about one-tenth normal, and yields Onsager's equation in the limit.

### The Onsager Equation

Onsager's equation for the mobility of an ion is

$$l = l^0 - \left[ \frac{(0.9838)(10^6)}{(DT)^{3/2}} w l^0 + \frac{28.95 Z}{(DT)^{1/2} \eta} \right] \sqrt{(Z_1 + Z_2)C} \quad (1)$$

$l^0$  is the mobility at infinite dilution

$D$  is the dielectric constant of the solvent

$T$  is the absolute temperature

$\eta$  is the viscosity of the solvent

$Z$  is the charge carried by the ion (absolute value)

$C$  is the equivalent concentration

$Z_1$  and  $Z_2$  are the charges carried by the anions and cations

$l_1^0$  and  $l_2^0$  are the mobilities at infinite dilution of anions and cations

$$w = Z_1 Z_2 \frac{2q}{1 + \sqrt{q}}; \quad q = \frac{Z_1 Z_2 (l_1^0 + l_2^0)}{(Z_1 + Z_2)(Z_2 l_1^0 + Z_1 l_2^0)}$$

The first term in the brackets takes account of the ionic effect, and the second term of the electrophoretic effect, both of which decrease the mobility of the ions. For the equivalent conductance,  $\Lambda$ , of a uni-univalent electrolyte the expression

$$\Lambda = \Lambda_0 - \left[ \frac{5.78 \times 10^5}{(DT)^{3/2}} \Lambda_0 + \frac{58.0}{(DT)^{1/2} \eta} \right] \sqrt{2C} \quad (2)$$

in which  $\Lambda_0$  is the equivalent conductance at zero concentration, is thus obtained.

Since, as has already been noted, all higher terms have been neglected in the derivation of this equation, it is, strictly speaking, a limiting formula. The effect of retaining higher terms, however, would be such as to decrease

<sup>3</sup> Ferguson and Vogel, *Phil. Mag.*, **50**, 971 (1925); **4**, 1, 233, 300 (1927); **5**, 199 (1928).

<sup>4</sup> Lattey, *ibid.*, **4**, 831 (1927).

<sup>5</sup> Davies. "The Conductivity of Solutions," John Wiley and Sons, Inc., New York, 1930, pp. 81-85, 113; *Trans. Faraday Soc.*, **27**, 597 (1931).

the rate at which  $\Lambda$  falls off with concentration according to the above equation. This is in accord with the facts for strong electrolytes, and Debye and Hückel and also Onsager have used an additional empirical term, linear with concentration, for purposes of extrapolating for  $\Lambda_0$  from measurements of dilute solutions. However, this extension is valid only to concentrations of several thousandths normal. If, on the other hand, the electrolyte had a tendency to associate as the concentration is increased, the observed deviations from the values predicted by Equation 2 would be in the opposite direction.

For convenience let us rewrite Equation 2 in simpler form

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta) \sqrt{C} \quad (3)$$

where  $(\alpha\Lambda_0 + \beta) = A$  is the limiting theoretical slope. Solving for  $\Lambda_0$  we obtain

$$\Lambda_0 = \frac{\Lambda + \beta \sqrt{C}}{1 - \alpha \sqrt{C}} \quad (4)$$

which is, of course, only another way of writing the Onsager equation.

For solutions in water at 25°  $\alpha$  is 0.2274 and  $\beta$  is 59.79, using the recent data of Drake, Pierce and Dow<sup>6</sup> and of Wyman<sup>7</sup> for the dielectric constant of water, and the values given in the "International Critical Tables" for the other constants. At 18°  $\alpha$  is 0.225 and  $\beta$  is 50.3.

### An Extension of the Onsager Equation

In examining the conductivity of numerous strong uni-univalent electrolytes it was found that values of  $\Lambda_0$  as calculated from Equation 4 are not constant over any appreciable concentration range. Thus the data do not follow the limiting Onsager equation. However, I have observed that these computed values, which will be designated by  $\Lambda'_0$ , plotted against the first power of the concentration, usually give straight lines up to about 0.1 normal. On this basis the correct  $\Lambda_0$  value for each electrolyte is the intercept of the  $\Lambda'_0$  vs.  $C$  line at  $C = 0$ . Figure 1 shows plots of  $\Lambda'_0$  vs.  $C$  for aqueous solutions of a number of strong electrolytes at 18°. The data are taken from the "International Critical Tables" and from the results of Kohlrausch and his co-workers. Figure 2 shows the same relationship for solutions of several electrolytes at 25°, the data for which have been obtained in this Laboratory with an improved conductivity technique.<sup>8</sup> If the slope of these lines is represented by  $B$ , we have the following conductance equation

$$\Lambda_0 = \frac{\Lambda + \beta \sqrt{C}}{1 - \alpha \sqrt{C}} - BC \quad (5)$$

instead of the limiting equation (4).

<sup>6</sup> Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

<sup>7</sup> Wyman, *ibid.*, **35**, 623 (1930).

<sup>8</sup> Shedlovsky, *THIS JOURNAL*, **54**, 1411 (1932).

It is an interesting fact that for many electrolytes the slopes  $B$  of these lines have values not far from the magnitude of  $A = \alpha \Lambda_0 + \beta$ , in Onsager's limiting equation (Equation 3).

An examination of Equation 5 shows that it approaches the limiting equation of Onsager asymptotically.  $\alpha$  and  $\beta$  are the theoretical constants

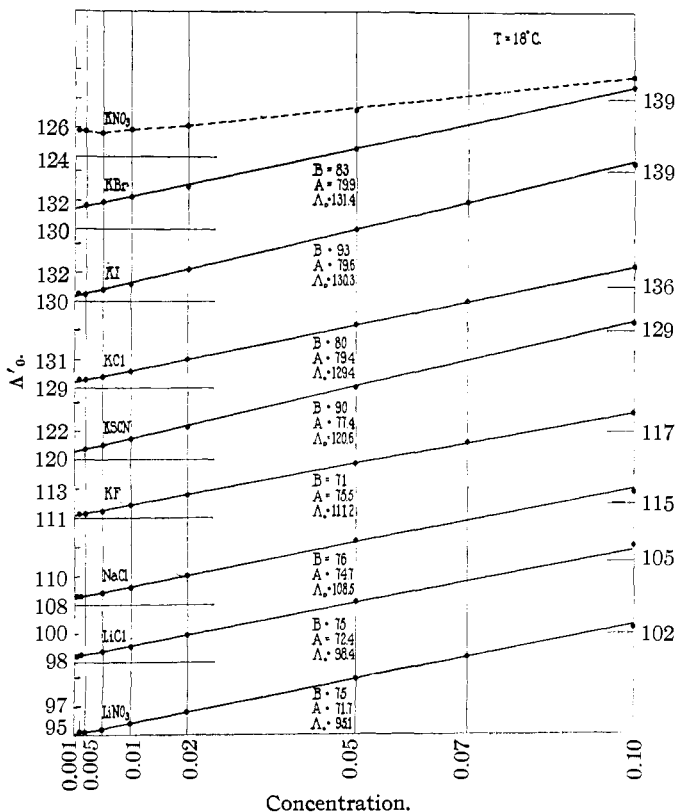


Fig. 1.

of Onsager's equation. It should be noted that Equation 5 is not equivalent to the addition of a linear term in the direct expression for equivalent conductance; *i. e.*,  $\Lambda = \Lambda_0 - (\alpha \Lambda_0 + \beta) \sqrt{C} + BC$ , which, as mentioned above, has been used by Onsager for extrapolating  $\Lambda_0$  from measurements at concentrations below 0.01 normal. The expression just given rearranges to

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

instead of Equation 5, in which the term  $BC$  is added to  $\Lambda_0$  instead of to  $\Lambda$ .

The substances which conform to Equation 5 (Figs. 1 and 2) belong to the class of strong electrolytes, which according to the modern theory

of solutions are considered to be essentially entirely ionized. It is found that for these cases  $A$  is generally somewhat smaller than  $B$  but within 15% of it.

However, in the plot for potassium nitrate, represented by the dotted curve in Fig. 1, the linear relationship between  $\Lambda'_0$  and  $C$  of Equation 5 does not hold. Similar behavior is exhibited by the chlorates and iodates, and

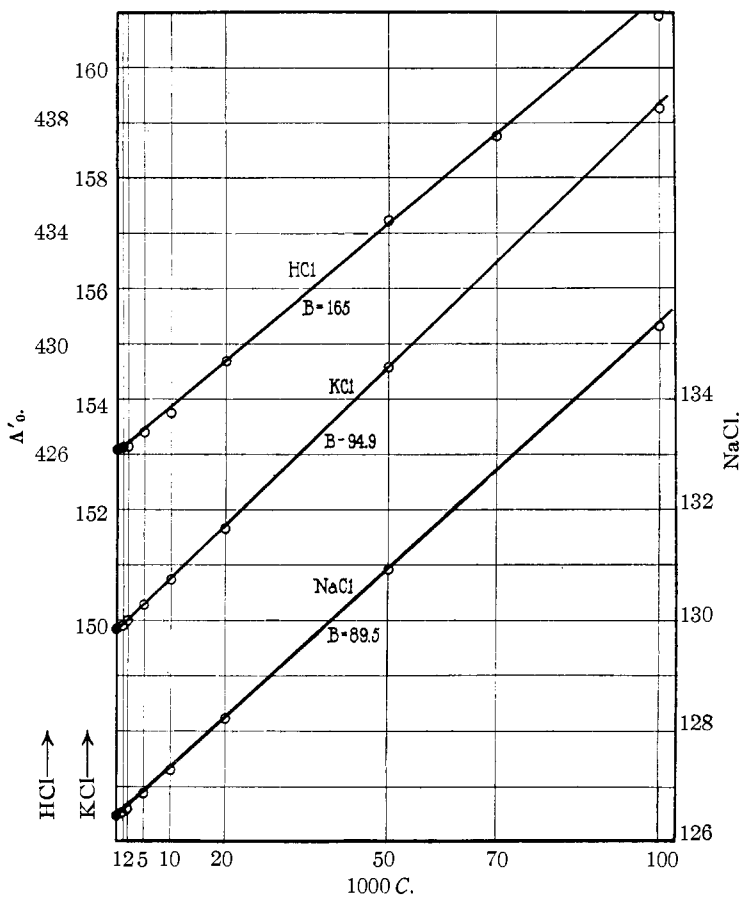


Fig. 2.

by thallium salts. We may tentatively assume that Equation 5, with  $B$  near to or larger than  $A$ , represents the behavior of strong uni-univalent electrolytes. On this basis the substances resembling potassium nitrate behave in a manner which would result from association. Equation 5 may also be useful as a guide in calculating degrees of dissociation.

It is often more convenient to deal with an expression explicit in  $\Lambda$ . For this purpose Equation 5 can be rearranged in the form

$$\Lambda = \Lambda_0 - A \sqrt{C} + BC(1 - \alpha \sqrt{C}) \quad (6)$$

where  $A = \alpha \Lambda_0 + \beta$ .

Table I shows a comparison between the observed values of the equivalent conductance,  $\Lambda$ , and those calculated from Equation 6 for the solutions of salts at 18° corresponding to the linear plots in Fig. 1. The agreement is within the limits of experimental error for these data.

TABLE I  
EQUIVALENT CONDUCTANCE (18°). COMPARISON OF OBSERVED AND COMPUTED VALUES

C	LiNO <sub>3</sub>		LiCl		NaCl		KF	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
0	95.1		98.4		108.5		111.2	
0.001	92.9	92.9	96.2	96.2	106.2	106.3	108.9	108.9
.002	92.0	92.0	95.3	95.3	105.3	105.3	108.0	107.9
.005	90.4	90.3	93.7	93.6	103.6	103.5	106.2	106.2
.01	88.6	88.6	91.9	91.8	101.7	101.7	104.4	104.3
.02	86.5	86.4	89.6	89.6	99.4	99.4	102.0	101.9
.05	82.6	82.7	85.9	85.9	95.4	95.5	97.7	97.7
.07	81.1	81.1	..	..	...	...	95.9	96.0
.10	79.4	79.2	82.7	82.8	92.0	91.8	94.0	94.0
A	71.7		72.4		74.7		75.5	
B	75		77		76		71	
C	KSCN		KCl		KI		KBr	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
0	120.6		129.4		130.3		131.4	
0.001	118.3	118.4	127.0	127.1	127.9	128.0	129.0	129.1
.002	117.3	117.4	126.0	126.0	126.9	127.0	128.0	128.0
.005	115.5	115.5	124.2	124.2	125.1	125.1	126.2	126.1
.01	113.7	113.7	122.2	122.2	123.3	123.2	124.2	124.1
.02	111.4	111.3	119.8	119.7	120.8	120.8	121.7	121.6
.05	107.6	107.5	115.5	115.5	116.9	117.0	117.5	117.5
.07	106.0	106.1	113.6	113.6	115.4	115.5	...	...
.10	104.5	104.5	111.7	111.8	113.8	113.8	113.9	114.0
A	77.4		79.4		79.6		79.9	
B	90		80		93		83	

Table VI of the following paper shows the same comparison for our own measurements at 25° on solutions of potassium chloride, sodium chloride and hydrochloric acid.<sup>8</sup>

Equation 6 is consistent with the theoretical prediction of Onsager<sup>2</sup> that the first higher order term in his derivation, were it not neglected, would be linear in concentration and opposite in sign to the square root term.

Lattey's equation,<sup>4</sup> which is  $\Lambda = \Lambda_0 - (A'\sqrt{C})/(1 + B'\sqrt{C})$  (in which  $\Lambda_0$ ,  $A'$  and  $B'$  are adjustable constants), when applied to data on strong uni-univalent electrolytes does not necessarily approach Onsager's limiting equation. In fact Lattey's  $A'$  is usually found to be appreciably greater than the theoretical limiting slope,  $A = \alpha \Lambda_0 + \beta$ . Also, as an extrapola-

tion formula it gives values for  $\Lambda_0$  which appear to be too high, if Onsager's expression is valid for sufficiently low concentrations.

The equation proposed in this paper is an extension of Onsager's theoretical equation. It has been found to be valid up to a concentration of about tenth normal. As an extrapolation formula for most strong uni-univalent electrolytes it gives values of  $\Lambda_0$  from data at concentrations which can be measured readily. These  $\Lambda_0$  values will agree with values obtained from Onsager's equation applied to measurements on sufficiently dilute solutions.<sup>9</sup>

### Summary

An equation is proposed for the relation between the equivalent conductance of strong uni-univalent electrolytes and the concentration. It has been found to agree with measurements up to about 0.1 normal in aqueous solutions. Besides theoretically calculable constants and the limiting conductance,  $\Lambda_0$ , it contains only one additional constant, and reduces to the limiting Onsager equation.

<sup>9</sup> The author has made some preliminary tests of Equation 5 on strong uni-univalent electrolytes. It appears to hold in a perfectly analogous manner for these cases if the concentrations are expressed as "ionic strengths." The application of the equation to this and higher valence types will be communicated at a later date to THIS JOURNAL.

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## THE ELECTROLYTIC CONDUCTIVITY OF SOME UNI- UNIVALENT ELECTROLYTES IN WATER AT 25°

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### Introduction

It has appeared important to obtain accurate values for the electrolytic conductance of solutions of a number of electrolytes. Besides providing a test for the conductivity relationships predicted by the modern theory of ionic solutions, such measurements make possible the calculation of the degrees of dissociation of certain weak electrolytes, as is shown in another paper.<sup>1</sup> Also, when combined with determinations of transference numbers, they give values for individual ionic mobilities. This will be the subject of a communication from this Laboratory in the near future.

With the alternating current bridge method, which has been almost universally used since Kohlrausch for measuring electrolytic conductance, a sensitivity of one part in 100,000 in the resistance readings can be readily attained. Due to various sources of error, some of which will be men-

<sup>1</sup> MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).