CdHg, in proportions depending on the law of mass action. The e. m. f. formula is derived from this case and shown to give the observed values of e. m. f. very closely. The per cent. of the cadmium as CdHg is calculated. In the most dilute amalgams $^2/_3$ of the cadmium is combined to form CdHg.

The validity of the fundamental formula is discussed and its value is pointed out in determining the constitution of metallic solutions and as a means of investigating the present unknown factors influencing the vapor pressure of solutions.

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THE CALCULATION OF EQUIVALENT CONDUCTANCE AT INFINIT DILUTION.

BY STUART J. BATES.

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1. Introduction.

For the full interpretation of the results of any investigation upon the properties of solutions of electrolytes, it is necessary to know the concentrations, both of the ions and of the undissociated molecules with a considerable degree of accuracy. The calculation of these concentrations is based upon the degree of ionization, γ. This is most satisfactorily given by the relation,

$$\gamma = \frac{\Lambda}{\Lambda_0} f\left(\frac{\eta}{\eta_0}\right),$$

where Λ is the equivalent conductance of the solution in question, Λ_0 the equivalent conductance of an infinitly dilute solution of the electrolyte and $f(\eta/\eta_0)$ is some function of the relative viscosity of the solution which in sufficiently dilute solution may be taken as unity.

Evidently if the concentrations of the various constituents are to be accurately known, the value of Λ_0 must be determined with considerable precision. Thus an error of but 0.1% in the value of this constant for potassium chloride at 18° causes an error of over 1.7 per cent. in the value calculated for the concentration of the unionized molecules at 0.01 normal, and an error of over 4.7% at 0.001 normal. Hence it is of importance to examin various methods of calculating Λ_0 values, and to discuss, with the aid of the available experimental data, the most probable values for these constants.

2. Methods Commonly Employed.

Since the law of mass action does not hold in the case of strong electrolytes, theory affords no satisfactory method or formula which may be employed for calculating the corresponding Λ_0 values. The methods used have been empirical; in many cases they were suggested by the law of mass action and are modifications of the formula given by it.

Kohlrausch and A. A. Noyes, together with their associates, have produced a large proportion of the best conductivity data. Each of these groups of men has calculated the Λ_0 values of the salts which they investigated and the resulting values are those generally accepted for these constants.[1]

Methods of Kohlrausch.—This investigator employed algebraic equations for this calculation. At first[2] he used the two formulas .

$$\Lambda_0 = \Lambda + PC^{0.5}, \tag{1}$$

and

$$\Lambda_0 = \Lambda + Q\Lambda^{1.5}C^{0.5}, \tag{2}$$

C being the concentration of the solution whose equivalent conductance is Λ, and Λ_0, P and Q being constants to be determined from the data. Later[3] he employed the three-constant empirical equation

$$\Lambda_0 = \Lambda + KC^{0.5}\Lambda^p. \tag{3}$$

The two former equations were applied to the data up to 0.002 normal only, the latter to the data for solutions as concentrated as 0.1 normal. The Λ_0 values obtained by means of equation (3) are those usually accepted for these constants.[4]

Graphic Method of A. A. Noyes.—This method "consists in plotting the values of $1/\Lambda$ for concentrations up to 0.02 normal as abscissas against those of $(C\Lambda)^{n-1}$ as ordinates, the values of $(n-1)$ being varied until a straight line is obtained (or as nearly a straight line as possible); and reading from this plot by extrapolation to $C\Lambda = 0$, the value of $1/\Lambda_0$."[5] The method corresponds to the empirical formula

$$\Lambda_0 = \Lambda + KC^{n-1}\Lambda^n, \tag{4}$$

i. e., to Storch's equation:[6]

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[1] Various other methods have been suggested for determining Λ_0 values but it is not necessary to consider them in detail. Thus Drucker (*Z. Elektrochem.*, **13**, 81 (1907)) and Wegscheider (*Z. physik. Chem.*, **69**, 603 (1909); *Monatsh.*, **30**, 411 (1909)) have proposed choosing values for these constants such that in dilute solution, strong electrolytes approximately obey the law of mass action. Such results, however, involve the rejection of Kohlrausch's data for very dilute solutions and have not come into general use. See also Drucker, Tarle and Gomez, *Z. Elektrochem.*, **19**, 8 (1913).

[2] *Wiss. Abh. Phys. Tech. Reichsanstalt*, **3**, 155 (1900).

[3] *Sitzungber. königl. preuss. Akad.*, 1900, 1002; *Z. Electrochem.*, **13**, 333 (1907).

[4] Landolt-Börnstein-Meyeroffer's Tabellen, p. 744.

[5] Noyes and Falk, THIS JOURNAL, **34**, 462 (1912).

[6] *Z. physik. Chem.*. **19**, 13 (1896), also Bancroft, *Ibid.*, **31**, 188 (1899).

$$C_i^n/\dot{C}_u = K \qquad (5)$$

C_i and C_u being the concentrations of the ions ($C\gamma$) and of the undissociated molecules [$C(1-\gamma)$], respectively. This equation has been found to express with a considerable degree of accuracy, the relation between the degree of ionization and the concentration of strong electrolytes over a considerable concentration range. It has been found not only for uni-univalent salts but also for those of different valence types that the values of n which gives the "best" straight line varies within the rather narrow limits 1.4 to 1.6. For any given salt it varies slightly with the concentration; in general n increases as the concentration decreases.[1]

Example.—In Fig. 1 this graphic method has been applied to the data of Bray and Hunt[2] for NaCl at 25°. Interpolation curves have been drawn for the following values of n: 2.00, 1.60, 1.50, 1.45 and 1.35.

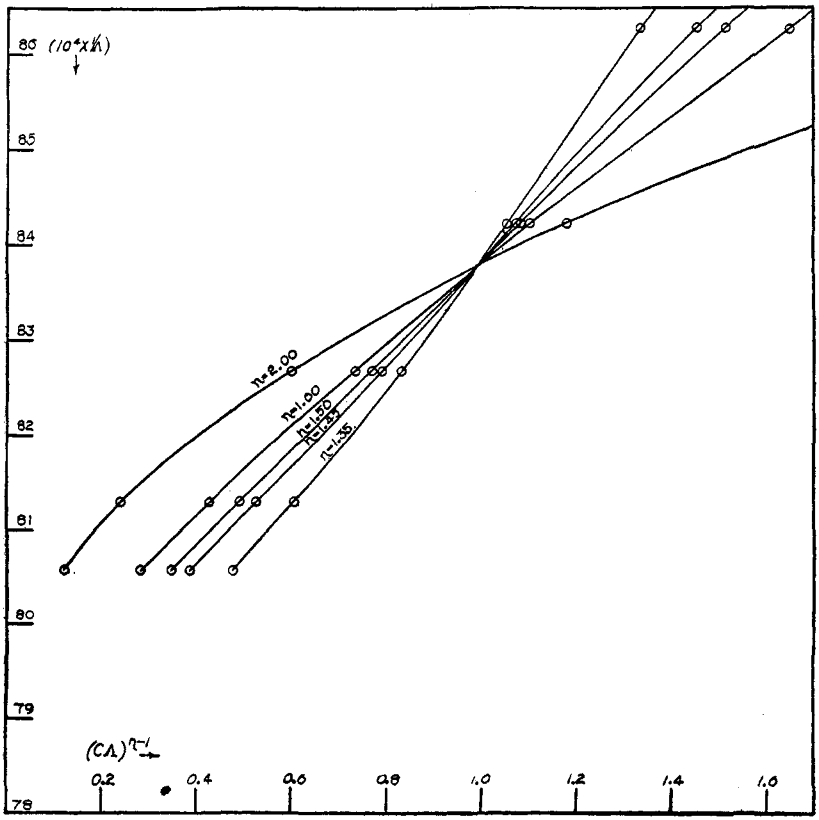

Fig. 1.

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[1] Noyes, *et al.*, *Pub. Car. Inst.*, **63**, 337 (1907); Noyes and Falk, THIS JOURNAL, **34**, 480 (1912), Table XIV.

[2] THIS JOURNAL, **33**, 781 (1911).

The five points on each curve correspond to the data for 0.001, 0.002, 0.005, 0.01 and 0.02 normal solutions, respectively. All of the curves pass through the same point where $C\Lambda = 1$, and when extrapolated they must meet on the $1/\Lambda$ axis. The problem is to determin the position of this point $(1/\Lambda_0)$. The method of Noyes locates this point where the curve which appears to be most nearly linear cuts the axis. In the figure the curve chosen is that for which $n = 1.45$.[1]

General Equation.—It will be readily seen that the four relations (equations 1–4) which have been extensively used for determining Λ_0 values, are special cases of the general form:

$$\Lambda_0 = \Lambda + KC^k\Lambda^l, \qquad (6)$$

where $1 > k > 0$ and $l \gtreqless 0$.

The substitution of Λ/Λ_0 for γ in the expression for the so-called "ionization constant" $(C\gamma)^2/C(1-\gamma)$ gives $\frac{C(\Lambda/\Lambda_0)^2}{C(1-\Lambda/\Lambda_0)}$. If the expression for Λ_0 given by equation (6) be substituted in this function, the expression $\frac{C^{1-k}\Lambda^{1-l}}{K(1+KC^k\Lambda^{l-1})}$ is obtained. This evidently approaches zero as the concentration decreases, since k is less than unity. Hence in employing any of the methods of calculating Λ_0 values, which have been referred to above, it is implicitly assumed that the so-called "ionization constant" of a strong di-ionic electrolyte is zero, at zero concentration. While this function undoubtedly decreases with the concentration, we are scarcely justified in employing for any *extrapolation*, into this region of very dilute solutions, where we believe the mass law to be at least more nearly obeyed, any method which assumes that the "ionization-constant" approaches zero as a limit. The fact that the four-constant empirical equation,

$$\frac{(C\Lambda/\Lambda_0)^2}{C(1-\Lambda/\Lambda_0)} = K + D\left(C\frac{\Lambda}{\Lambda_0}\right)^m,$$

recently proposed by Kraus, has been found to hold over a very considerable concentration range[2] supports the view that, as the concentration decreases, the "ionization constant" approaches a finite limit rather than the value zero.[3]

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[1] *Loc. cit.*, p. 785.

[2] THIS JOURNAL, 34, 484 (1912); *Trans. Am. Electrochem. Soc.*, 21, 143 (1912).

[3] The assumption which is contained in equation (6) may be also viewed from a different standpoint. It can be shown that each of the above equations (1–4) involves the assumption that the curve obtained by plotting values of C or $C\Lambda$ against values of Λ or $1/\Lambda$ when extrapolated does not cut the Λ or $1/\Lambda$ axis, but merely approaches it tangentially, the point of contact being that chosen for Λ_0 or $1/\Lambda_0$. For example, in the case of the curve obtained by plotting values of $C\Lambda$ against those of $1/\Lambda$ the slope of the tangent to the curve at any point is given by $\frac{d(1/\Lambda)}{d\,(C\Lambda)}$ which is $\frac{-\Lambda^{-2}d\Lambda}{Cd\Lambda + \Lambda dC}$.

Variation of the Exponent n with the Concentration.—If we substitute in equation (4) values of Λ and C corresponding to three concentrations (such as 0.0001, 0.0002 and 0.0005 normal), we may solve the resulting equations for any or all of the three parameters Λ_0, K and n. It is thus possible to determin accurately the manner in which the value of n, which gives the linear relation demanded by equation (4), changes from one concentration range to another.

This calculation was performed for a number of salts, using the data contained in the compilation of Noyes and Falk.[1] Table I gives the re-

TABLE I.

Milli-equivalents per liter. 18°.	KCl.	KNO_3.	NaCl.	$Pb(NO_3)_2$.
0.1, 0.2 and 0.5	1.64	1.70	1.67	1.76
0.2, 0.5 and 1.0	1.57	1.45	1.54	1.46
0.5, 1.0 and 2.0	1.45	1.45	1.48	1.50
1.0, 2.0 and 5.0	1.46	1.61	1.47	1.55
2.0, 5.0 and 10.0	1.45	1.52	1.44	1.60
5.0, 10.0 and 20.0	1.40	1.50	1.41	1.60
10.0, 20.0 and 50.0	1.41	1.52	1.34	1.57
0.1 to 20.0	1.48	1.53	1.50	1.58
25°.	NaCl.	KI.	Tl_2SO_4.	$PbCl_2$.
1.0, 2.0 and 5.0	1.47	1.45	1.59	1.56
2.0, 5.0 and 10.0	1.51	1.46	1.60	1.77
5.0, 10.0 and 20.0	1.38	1.46	1.67	1.66
10.0, 20.0 and 50.0	1.34	1.36	1.51	1.69
0.0 to 20.0	1.45[2]	1.45	1.58	1.65

The differentiation of equation (6) with respect to C and Λ gives the equation

$$d\Lambda + Kk\Lambda^{l}C^{k-1}dC + KlC^{k}\Lambda^{l-1}d\Lambda = 0,$$

hence

$$dc = -\frac{1 + KlC^{k}\Lambda^{l-1}}{Kk\Lambda^{l}C^{k-1}}\,d\Lambda.$$

The combination of this relation with the expression for the slope of the tangent gives, after canceling out $d\Lambda$ and multiplying numerator and denominator by $-Kk\Lambda^2$, the relation

$$\frac{d(1/\Lambda)}{d(C\Lambda)} = \frac{Kk}{Kl\Lambda^2C + \Lambda^{3-l}C^{1-k} - Kk\Lambda^2C}.$$

As $C\Lambda$, and hence C, approach zero, Λ becomes Λ_0. Since each term in the denominator of the above expression contains C to a positive power (k is less than unity), all the terms in the denominator become zero with $C\Lambda$. That is in the limit the slope of the tangent becomes infinit, or when $C\Lambda = 0$, the curve becomes parallel to the $1/\Lambda$ axis. Thus it is assumed that when the curve indicated by $n = 2.00$ in Fig. 1 is extrapolated, it touches, but does not cross the $1/\Lambda$ axis.

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[1] THIS JOURNAL, 34, 454 (1912). Unless otherwise stated the data employed for all of the calculations presented in this paper were taken from this source. Where possible, the viscosity correction has been applied.

[2] 1.0 to 50.0.

sults. The first column gives the three concentrations in milli-equivalents per liter, from which n was calculated. In the bottom row is given the value of n adopted by Noyes and his associates as giving the best straight line for the concentration range indicated.

In view of the great and often erratic variation of n with the concentration, it is evidently impossible to obtain a value for n which will give a straight line through more than three points; neither is it possible to assert, within rather considerable limits, that one value of n gives a better straight line than does another.[1] Any "straight" line through four or more points, obtained by employing an intermediate or average value for n, must in reality contain one or more points of inflexion. The value found for Λ_0 depends greatly upon the choice of a value for n, and since there is uncertainty in the latter there is also uncertainty in the former. In fact, the value obtained for Λ_0 depends much more upon the value of n employed than it does upon the particular concentration range which is used for the extrapolation.

It would appear that in general the value of n continues to increase as the concentration decreases, and that hence the assumption that n does not change appreciably below about 0.01 normal is not justified. This has been suspected, and it was recognized that if it were true, then the Λ_0 values usually accepted are too large.[2]

3. Determination of the Exponent n in Storch's Equation.

Graphic.—The value of n corresponding to any given concentration may be rather readily determined by a graphic method. The differentiation of equation (5) gives the relation

$$nC_i^{n-1}dC_i = KdC_u. \qquad (7)$$

The elimination of K between equations (5) and (7) gives $n\ dC_i/C_i = dC_u/C_u$, *i. e.*,

$$nd \log C_i = d \log C_u. \qquad (8)$$

Hence if we plot values of $\log C_u$ as abscissas against values of $\log C_i$ as ordinates, the slope of the tangent to the curve at any given point is the value of n for the corresponding concentration.

Algebraic.—The substitution of two sets of data in equation (5) and the elimination of K from the two resulting equations, gives the relation

$$\frac{C_{1i}^n}{C_{1u}} = \frac{C_{2i}^n}{C_{2u}}.$$

From this it follows that

$$n \log \frac{C_{1i}}{C_{2i}} = \log \frac{C_{1u}}{C_{2u}}, \qquad (9)$$

whence n may be readily calculated. An expression which is, however,

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[1] See figure.

[2] Hunt, THIS JOURNAL, 33, 800 (1911).

more convenient in practice is obtained by substituting $C\Lambda/\Lambda_0\ \eta/\eta_0$ for C_i and $C(1 - \Lambda/\Lambda_0\ \eta/\eta_0)$ for C_u. When simplified, the relation is

$$n \log \frac{C_1\Lambda_1\ \eta_1/\eta_0}{C_2\Lambda_2\ \eta_2/\eta_0} = \log \frac{C_1(\Lambda_0 - \Lambda_1\ \eta_1/\eta_0)}{C_2(\Lambda_0 - \Lambda_2\ \eta_2/\eta_0)}. \qquad (10)$$

The value of n thus obtained really corresponds to some concentration, C_3 between C_1 and C_2. Its value will be between those corresponding to these two concentrations. For most data the algebraic method is sufficiently exact, since at low concentrations the value of C_u is uncertain and hence n cannot be obtained by either method with a high degree of accuracy, while at higher concentration n changes but slowly with the concentration.

If n is calculated from experimental data which are not quite consistent, it is found to be irregular. In such cases the graphic method is preferable, since a smoothed curve may be drawn and hence regular values of n read off. The curve obtained by plotting values of log C_u against values of log C_i is valuable in judging the reliability of conductivity data. This follows from the fact that we may thus, in one curve, obtain conveniently and regularly spaced points corresponding to solutions from 0.0001 to 1.0 normal.

In Table II are found values of n calculated by means of equation (10). For the strong electrolytes two sets of values are given. Those in the left-hand columns were calculated by employing the Λ_0 values given in the compilation of Noyes and Falk, while for the right-hand column somewhat smaller values, obtained in a manner described below, were used.

For comparison, values of n are given for the intermediate electrolyte, phosphoric acid, and for the weak electrolyte, acetic acid. Here it is necessary to calculate n from but one value of Λ_0, for a considerable error in this constant would not materially affect the values found for n.

The conductivity data for phosphoric acid are due to Noyes and Eastman.[1] In solutions of this acid the law of mass action is evidently more nearly obeyed at moderate concentrations than it is in the case of strong electrolytes. The conductivity and viscosity data for acetic acid were determined by Rivett and Sidgwick.[2] The algebraic method gave somewhat irregular values for n; below about 0.2 normal some of these were greater and some less than 2, the value required by the law of mass action. The graphic method was hence applied to this data; a smooth curve was drawn and the tangents read off. Below about 0.15 normal the curve was linear within the experimental error and gave n equal to 2. Above this, the curve deviated from the linear position in such a manner that the tangent became greater. Hence acetic acid above about 0.15 normal

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[1] *Carnegie Publ.*, **63**, 262 (1907).

[2] *J. Chem. Soc.*, **97**, 732 (1910).

TABLE II.—VALUES OF n FOR DIFFERENT Λ_0 VALUES AND CONCENTRATION RANGES.

	NaCl.		TlCl.		$LiNO_3$.		KIO_3.	
Λ_0 =	108.9.	108.45.	131.4.	130.80.	95.1.	94.85.	98.5.	98.15.
0.0001 and 0.0002...	1.41	1.74	1.39	1.78	1.49	1.65	1.44	1.67
0.0002 and 0.0005..	1.49	1.72	1.51	1.78	1.50	1.61	1.48	1.63
0.0005 and 0.001...	1.48	1.61	1.53	1.68	1.47	1.54	1.48	1.58
0.001 and 0.002....	1.48	1.56	1.56	1.66	1.47	1.51	1.50	1.57
0.002 and 0.005....	1.48	1.51	1.60	1.67	1.46	1.49	1.49	1.54
0.005 and 0.01.....	1.47	1.50	1.61	1.65	1.46	1.48	1.48	1.51
0.01 and 0.02......	1.45	1.47	..	..	1.43	1.45	1.49	1.51
0.02 and 0.05......	1.42	1.44	..	..	1.44	1.45	1.47	1.49
0.05 and 0.1.......	1.41	1.42	..	..	1.43	1.43	1.47	1.48
0.1 and 0.2........	1.37	1.38	..	..	1.39	1.39	1.43	1.44
0.2 and 0.5........	1.33	1.33	..	..	1.37	1.37	..	..
0.5 and 1.0........	1.27	1.27	..	..	1.37	1.37	..	..
	K_2SO_4.		$Pb(NO_3)_2$.		$MgSO_4$.			
Λ_0 =	133.0.	131.9.	122.6.	121.9.	114.4.	112.9.		
0.0001 and 0.0002..	1.39	1.67	1.52	1.76	1.53	1.73	..	..
0.0002 and 0.0005..	1.46	1.65	1.60	1.76	1.58	1.71	..	..
0.0005 and 0.001...	1.46	1.59	1.55	1.64	1.61	1.68	..	..
0.001 and 0.002....	1.50	1.59	1.54	1.59	1.61	1.66	..	..
0.002 and 0.005....	1.51	1.57	1.54	1.58	1.60	1.64	..	..
0.005 and 0.01.....	1.50	1.54	1.55	1.57	1.58	1.60	..	..
0.01 and 0.02......	1.49	1.52	1.56	1.58	1.54	1.55	..	..
0.02 and 0.05......	1.46	1.49	1.57	1.58	1.49	1.49	..	..
0.05 and 0.1.......	1.40	1.41	1.57	1.57	1.40	1.40	..	..
0.1 and 0.2........	1.37	1.38	1.57	1.57	1.32	1.32	..	..
0.2 and 0.5........	1.29	1.29	1.60	1.60	..	..	..	..
0.5 and 1.0........	1.16	1.16	1.62	1.62	..	..	..	..
	H_3PO_4.						CH_3COOH.	
Λ_0 =	338.0.					Λ_0 =	392.4.	
0.0002 and 0.002...	2.02	..	..	..	0.0 to 0.1		2.00	..
0.002 and 0.01.....	1.97	..	..	..	0.2		2.02	..
0.01 and 0.0125....	1.88	..	..	..	0.3		2.04	..
0.0125 and 0.05....	1.87	..	..	..	0.5		2.07	..
0.05 and 0.08......	1.81	..	..	..	0.75		2.12	..
0.08 and 0.1.......	1.72	..	..	..	1.0		2.20	..
	..	..	..	..	1.5		2.45	..
	..	..	..	..	2.0		2.80	..

deviates from Ostwald's Dilution Law, but in a manner *opposit* to that found for strong electrolytes.[1]

4. Calculations of Limiting Values for Λ_0.

Although theory affords no satisfactory method for calculating Λ_0 values it does enable us to determin limits between which these constants lie.

Lower Limit.—We may calculate the lower limit for Λ_0 from the data

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[1] A further presentation of the relation between n and the concentration, and between n and the type of electrolyte is unnecessary for the present purpose. It is hoped to discuss the significance of n more fully in a future communication.

corresponding to the most dilute solutions by assuming that from this concentration range down to an infinitly dilute solution, Ostwald's Dilution Law holds. In the case of salts which dissociate into but two ions this is graphically equivalent to extrapolating linearly from the lowest point of the curve obtained by plotting $1/\Lambda$ against $C\Lambda$. This limit may be readily calculated algebraically by putting n in equation (4) equal to the number of ions (2, or 3, etc.) into which the salt dissociates, substituting the data (C and Λ) corresponding to the two most dilute solutions and solving for Λ_0. The lower limits thus calculated for a number of salts are given in column 2, Table IV.

Upper Limit.—It is generally recognized that the undissociated molecules are more "abnormal" than are the ions. With decreasing concentration, the behavior of both approaches that of the "normal" solute.[1] This is confirmed by the fact that with decreasing concentration (at least down to 0.001 normal) n increases (see Table II), thus becoming more nearly equal to the value required by the mass action law.

If in the calculations of n, the Λ_0 values given by Kohlrausch or those calculated by the graphic method of A. A. Noyes, be employed it is found that in general n rises to a maximum in dilute solution and then decreases (Table II). Such a behavior can be explained only by assuming that down to a certain concentration the ions and the undissociated molecules approach more closely the "normal" condition, but that one or the other or both again deviate more widely from this condition as the concentration approaches zero.

If, however, somewhat smaller Λ_0 values be employed, it is found that in general the exponent n increases continuously. As an upper limit for Λ_0 we may therefore choose the highest value which can be employed for this constant without causing the corresponding values of the exponent n to pass through a maximum. That is, we will assume that neither the ions nor the undissociated molecules are more "abnormal" in more dilute solution than they are in the lower part of the concentration range whose conductance has been determined.

This upper limit for Λ_0 is determined by a process of approximation as follows: A value for Λ_0 is substituted in equation (10) and the resulting equation corresponding to the two most dilute solutions (as 0.0001 and 0.0002 normal) is then solved for n. This is then repeated for the next pair of solutions (as 0.0002 and 0.0005 normal) and so on, thus obtaining a set of three or four values of n, corresponding to the value chosen for Λ_0. If the values for n thus obtained show a maximum, a smaller value is then chosen for Λ_0, while if they show no maximum one slightly greater is taken. This process is repeated until a value is found for Λ_0, such that the corresponding values determined for n showed no maximum,

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[1] Bray, THIS JOURNAL, 33, 1673 (1911); Lewis, *Ibid.*, 34, 1631 (1912).

yet a slightly greater value would cause the exponent to exhibit this maximum.

Example.—For KCl at 18°, the lower limit of Λ_0 was calculated to be 129.30. The upper limit was determined as described above. Different values of Λ_0 for which the corresponding values of n were calculated are given in the top row of Table III. The concentrations in moles per liter are given in the first column and the values of n in the succeeding columns.

TABLE III.—DEPENDENCE OF n UPON THE VALUE CHOSEN FOR Λ_0.

	Λ_0 = 129.60.	129.56.	129.54.
0.0001 and 0.0002	1.59	1.624	1.643
0.0002 and 0.0005	1.61	1.631	1.642
0.0005 and 0.001	1.59	1.605	1.612
0.001 and 0.002	1.54	1.554	1.559

The value 129.60 causes n to show a distinct maximum, the value 129.56 a slight maximum while the value 129.54 no longer causes this behavior. The upper limit of Λ_0 is then represented with sufficient exactness by 129.55.

In columns 2 and 3 of Table IV are found the upper and lower Λ_0 limits, respectively, for a number of salts. In a few cases it was discovered that no value of Λ_0 could be found which would cause a regular decrease in n. This evidently indicates an irregularity in the experimental data. It was usually found in such cases that by rejecting the conductance data for the most dilute solution, the values found for n were normal.[1] The resulting upper limit for Λ_0 is then somewhat higher than would otherwise be the case. The presence of brackets around a value in column 3 indicates that this irregularity was discovered in the corresponding data.

The more dilute the solutions are for which we have accurate conductivity data, the smaller will be the difference between the upper and lower limits of Λ_0. Thus for KCl at 18°, with data down to 0.0001 normal, the limits are 129.30 and 129.55, a difference from the mean of 0.10 per cent. If the data for KCl were available to 0.001 normal only, or if the data were considered reliable to but this concentration, then the limits would be 128.25 and 130.2, a difference from the mean of 0.7%. If these constants are to be known with a certainty greater than about 0.1% it is necessary that accurate conductivity data be determined for solutions more dilute than 0.0001 normal. An investigation is at present in progress in this laboratory[2] which it is expected will test the validity of the present arbitrary application of the "water correction" and will

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[1] It is not at all surprising to find that in some cases the conductance given for the most dilute solution is not quite consistent with the rest of the data. For many of the 0.0001 normal solutions, which Kohlrausch investigated, the arbitrary "water correction" is 10% of the measured conductance.

[2] Washburn and Bell, THIS JOURNAL, **35**, 177 (1913).

lead to the determination of data for solutions more dilute than 0.0001 normal.

5. Empirical Methods.

Theory then appears to be incapable of determining Λ_0 values more definitly than to indicate limits between which they must lie. However, from empirical methods it is possible to form an idea of the portion of this region in which the correct values probably lie.

From an empirical standpoint "the best that can be done is to base this extrapolation on the assumption that the functional relation between equivalent conductance and concentration which is found empirically to hold at higher concentrations continues to hold down to zero concentration."[1] On this basis a graphic method is developed below, which enables us to determin rather closely the value of Λ_0 most consistent with the experimental data.

The method consists in superimposing two curves, each obtained by plotting C as abscissas against Λ as ordinates in such a manner that two points of the one curve coincide with two of the other. Thus in the case of the salts whose conductances Kohlrausch investigated down to 0.0001 normal, one curve, A, is obtained by plotting the values for the four concentrations, 0.0001, 0.0002, 0.0005 and 0.001 normal. The second curve B is drawn through points corresponding to the seven solutions below 0.01 normal, whose conductances are given. For curve B the unit of the abscissas is one-tenth as large as for curve A, while the origin for the ordinates is so chosen that the point corresponding to 0.001 normal falls on the point 0.0001 normal of curve A, (M), and the unit of the ordinates is so chosen that the point 0.002 normal of curve B also falls on the point 0.0002 normal of curve A (N).

In Fig. 2 are plotted the data for KCl at 18°.[2] It will be noticed that the curves almost coincide and that the lower curve A is that corresponding to the most dilute concentration range. These were found to be general characteristics.

Another curve C not shown in the figure, was drawn by choosing the unit for the abscissas but one-tenth as large as those for curve B. The point M then corresponded to 0.01 normal and N to 0.02 normal. Curve B thus crossed C at M and at N. Between M and the Λ axis, B passed through three points which lay below those on curve C; those points on B to the right of N also lay below curve C. Curve A bears to B, the same relation that B does to C, it lies below B to the right of N, crosses B at N and again at M, and hence on the assumption upon which this extrapolation is to be based, when produced from M to the axis, A will again lie below B. If

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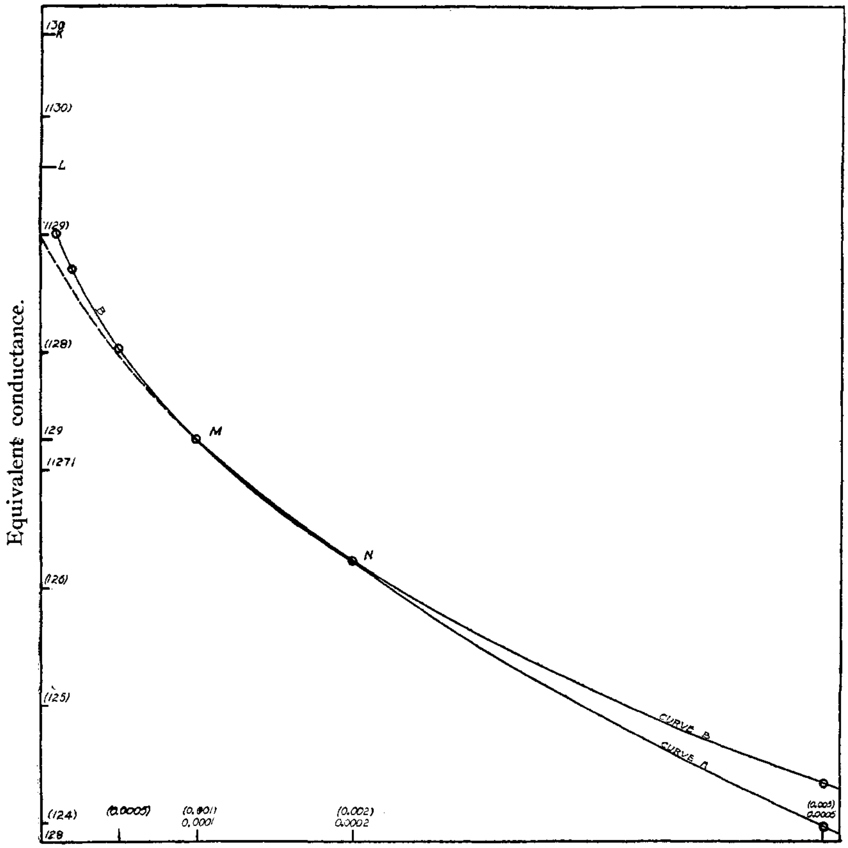
[1] Noyes and Falk, THIS JOURNAL, 34, 457 (1912).

[2] In order to present the graph on a suitable scale curves A and B included but three and six points, respectively.

now we determin the approximate point at which curve B cuts the axis and calculate the value of Λ_0, which this point would represent, were it on curve A, then this value will be an upper limit for Λ_0.



Concentration.

The coördinates in brackets refer to Curve B, the others to Curve A.

Fig. 2.

A more "probable" value for this constant may be obtained by producing curve A by the aid of a spline, in such a manner that the extrapolated portion of this curve and the portion of curve B directly above it, bear about the same relation to one another as do the interpolated portions of these two curves. Thus in Fig. 2, curve A, has been extrapolated (indicated by the broken line) to the point corresponding to the "probable" value. The upper limit (graphic) is indicated by L. In the case of KCl, at 18° at all events, it has been found that the method of Kohlrausch and that of A. A. Noyes give the same value for Λ_0, the uncertainty in the result being less than 0.1%.[1] However, the acceptance of this value means that the curve A, when extrapolated, cuts the axis at the point indicated by K.

The uncertainty in the "probable" value may be assumed to be about one-half of the difference between this value and the upper limit. These "probable" values are likely to be too high rather than too low.[2]

Columns 4 and 5 of Table IV give the graphic upper limit and the "probable" value, respectively, for a number of salts. The presence of brackets indicates either that one of the curves was irregular, or that curve A lay above curve B. In such cases the value which is given is that which appeared to be a reasonable upper limit. It will be noticed that in every case thus discovered, the algebraic calculation of the upper limit had already indicated an irregularity in the experimental data. In fact, at low concentrations, the latter method indicates inconsistencies in the data, if these amount to more than a few hundredths of one per cent. Hence the algebraic method of calculating the upper limit is of particular value when applied to very accurate data. Inconsistent data gives limits which are rather wide apart. In such cases the empirical methods are of more importance.

6. Adjusted Values and Ion Conductances.

In Table IV are brought together the Λ_0 values which have been obtained by a number of different methods. The conductivity data from which they were calculated are those contained in the compilation of Noyes and Falk.[3] The experimental data, for all the uni-univalent salts except $KBrO_3$ and those for a large proportion of the other salts are due to Kohlrausch and his associates.

The Λ_0 values in the first column are taken from Table VIII of Noyes and Falk's article. For the uni-univalent salts these values were determined by Kohlrausch (recalculated to 1911 atomic weights by Noyes and Falk); the remainder of the values were determined by the graphic method of A. A. Noyes. The values in this column were adjusted by Noyes and Falk in accordance with Kohlrausch's Law of the Independent Migration of Ions.

The lower and upper limits determined by the consideration of the exponent *n* in Storch's equation (see Section (4)) are given in the second and third columns, respectively. The fourth and fifth columns give, respectively, the results of the determinations of the upper limit and the "probable" value for Λ_0 by the graphic method described above. Values

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[1] Washburn and MacInnes, This Journal, 33, 1697 (1911).

[2] The application of this method is not as laborious at it may appear. For any given salt, the necessary calculations may be performed, the graph drawn and the Λ_0 value determined in from 20 to 25 minutes.

[3] *Loc. cit.* Table VIII.

adjusted in accordance with Kohlrausch's Law of the Independent Migration of Ions, are given in the last column. Except in the case of the "probable" valves, the figures have been rounded off to the nearest twentieth or tenth of a unit. As was explained above, a value enclosed in brackets indicates that the experimental data are irregular, but that the value given appears to be an upper limit for Λ_0. In a few cases (as KNO_3) it was

TABLE IV.—VALUES OF Λ_0 AT 18° DETERMINED BY VARIOUS METHODS.

		Theoretical limits.		Graphic values.		Adjusted value.
		Lower.	Upper.	Upper limit.	Probable.	
NaCl	108.9	108.30	108.50	108.60	108.46	108.45
KCl	130.0	129.30	129.55	129.65	129.49	129.50
LiCl	98.8	98.25	98.45	98.60	98.44	98.45
CsCl	133.5	132.50	132.75	132.75	132.64	132.65
TiCl	131.4	130.65	130.80	130.90	130.78	130.80
KBr	132.2	131.35	131.50	131.65	131.50	131.50
KI	131.1	130.00	[130.4]	130.25	130.16	130.15
KSCN	121.2	120.30	[120.7]	[120.8]	....	120.6
KF	111.2	110.60	[110.9]	[110.95]	....	110.85
NaF	90.1	89.55	89.90	89.95	89.90	89.80
$NaNO_3$	105.2	104.80	[105.3]	[105.3]	....	104.85
KNO_3	126.3	125.70	125.90	126.10	125.93	125.90
$LiNO_3$	95.1	94.60	94.90	95.00	94.83	94.85
$TlNO_3$	127.7	126.95	[127.3]	127.25	127.21	127.20
$AgNO_3$	115.8	115.45	[115.8]	[116.2]	....	115.7
$KClO_3$	119.6	118.90	119.05	119.2	119.07	119.05
$KBrO_3$	112.1	111.10	[113.0]	112.9	112.2	112.2
$NaIO_3$	77.4	76.95	77.10	77.20	77.10	77.10
KIO_3	98.5	97.95	98.25	98.25	98.14	98.15
LiO_3	67.3	66.90	[67.2]	67.15	67.08	67.10
$BaCl_2$	120.9	117.5	120.75	123.6	120.5	120.0
$CaCl_2$	117.4	115.40	116.6	116.55	116.35	116.7
$MgCl_2$	111.4	109.60	110.5	110.65	110.49	110.5
$PbCl_2$	126.3	120.35	[125.5]	127.0	125.3	125.5
$Ba(NO_3)_2$	117.2	115.55	116.7	116.8	116.46	116.45
$Sr(NO_3)_2$	113.7	111.95	113.3	113.3	113.11	113.1
$Ca(NO_3)_2$	113.7	112.15	113.7	113.7	113.4	113.1
$Mg(NO_3)_2$	107.7	103.15	108.5	107.75	106.7	106.9
$Pb(NO_3)_2$	122.6	121.0	121.9	122.4	122.1	121.9
K_2SO_4	133.0	130.9	132.0	132.2	131.87	131.9
Na_2SO_4	111.9	109.65	[112.5]	[112.7]	....	110.9
Li_2SO_4	101.8	98.2	101.2	101.8	100.7	100.8
Tl_2SO_4	134.4	128.4	135.0	135.5	133.4	133.2
Ag_2SO_4	122.5	117.3	122.0	121.6	121.0	121.6
$K_2C_2O_4$	127.5	125.2	[125.9]	[125.5]	....	125.5
$MgSO_4$	114.4	111.7	113.0	113.8	112.9	112.9
$ZnSO_4$	115.5	111.7	113.2	114.0	113.0	113.0
$CdSO_4$	114.9	112.1	113.8	114.7	113.7	113.7
$CuSO_4$	114.4	112.1	113.5	114.5	113.7	113.5
MgC_2O_4	109.0	102.0	[108.5]	118.0	108.0	106.5

found that the "probable" value graphically determined was greater than the upper limit indicated by the theoretical method; in such cases the latter was employed in adjusting the values.

The values determined by the theoretical and by the empirical methods show good agreement. Of the "probable" values founded upon the data of Kohlrausch, only three fall outside of the limits theoretically determined. On the other hand, of the corresponding values in column 1, all but two ($AgNO_3$ and $Ca(NO_3)_2$) fall outside of these limits; for these this value coincides with the upper limit. It will be seen that the final or adjusted values in the last column are smaller than those generally accepted. The average percentage difference for uni-univalent salts is about 0.4, for uni-bivalent about 0.7, and for bi-bivalent about 1.7. As regards the length of the *extrapolated* portion of the curve, however, these differences often amount to 40 to 50%.

It is important to compare the "probable" values with one another by means of Kohlrausch's Law of the Independent Migration of Ions. The difference between the mobilities of any two ions at infinit dilution should be independent of the particular salts from which it is determined. The data in the following table covers all cases in which it is possible to calculate this difference in three or more ways from uni-univalent salts whose conductances Kohlrausch determined down to 0.0001 normal. Brackets indicate that the value is uncertain, due to irregularity in the experimental data for one or both of the salts:

TABLE V.

	$\Lambda_K - \Lambda_{Na}$.		$\Lambda_{Cl} - \Lambda_{NO_3}$.
KCl-$NaCl$	21.03	$NaCl$-$NaNO_3$	(3.2)
KNO_3-$NaNO_3$	(20.6)	KCl-KNO_3	3.57
KIO_3-$NaIO_3$	21.04	$LiCl$-$LiNO_3$	3.61
KF-NaF	(21.0)	$TlCl$-$TlNO_3$	3.57
Mean	21.03	Mean	3.58

	$\Lambda_K - \Lambda_{Li}$.		$\Lambda_{Cl} - \Lambda_{IO_3}$.
KCl-$LiCl$	31.05	$NaCl$-$NaIO_3$	31.36
KNO_3-$LiNO_3$	31.09	KCl-KIO_3	31.35
KIO_3-$LiIO_3$	31.06	$LiCl$-$LiIO_3$	31.36
Mean	31.07	Mean	31.36

It will be seen that the agreement is entirely satisfactory. In fact the "probable" values are in better agreement than are the unadjusted values which Kohlrausch calculated by means of equation (3) from the same experimental data.[1]

The extrapolation for the Λ_0 values is, in the case of salts containing one or more bivalent ions, much longer than in the case of the uni-uni-

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[1] *Sitz. ber. königl. Preuss. Akad.*, 1900, 1002; 1902, 581.

valent salts, hence the mobilities of the bivalent ions may not be as accurately determined as may those of the univalent ions.

The mobilities at 18° of some of the more important ions are given in Table VI. Those of others may be readily calculated from those given and from the adjusted values in Table IV. The mobilities in Table VI were calculated almost entirely from the data of Kohlrausch, 0.496 being employed as the cation transference number for KCl.[1]

TABLE VI.—MOBILITIES OF IONS AT 18°.

Li	33.20	F	46.6
Na	43.20	Cl	65.25
K	64.25	NO_3	61.65
Tl	65.55	IO_3	33.90
Mg	45.25	SO_4	67.65

7. Summary.

1. The equations used by Kohlrausch and the method employed by A. A. Noyes and his associates for determining Λ_0 values have been discussed. It is shown that all of these methods involve the assumption that the expression $(C\gamma)^2/C(1-\gamma)$, for the so-called "ionization constant," becomes zero at zero concentration. From a graphic standpoint this is equivalent to the assumption that none of the four curves obtained by plotting values of C or of $C\Lambda$ against values of Λ or of $1/\Lambda$ cross the Λ or $1/\Lambda$ axis; they touch the axis tangentially at the point chosen as Λ_0 or as $1/\Lambda_0$.

2. A graphic and an algebraic method for determining the value at any given concentration of the exponent *n* in Storch's equation have been developed.

3. The manner in which *n* for weak, medium and strong electrolytes changes with the concentration has been compared. In all cases with decreasing concentration *n* becomes more nearly equal to the value required by the law of mass action.

4. It is shown that lower and upper limits, between which the value of Λ_0 must be, may be determined. In the case of the uni-univalent salts for which data was determined by Kohlrausch for solutions as dilute as 0.0001 normal, the difference between the limits is about 0.2%, that is, accepting the experimental data as correct, the uncertainty in the Λ_0 values of these salts is not over 0.1%. The lower limit is determined by assuming that the law of mass action holds from the lowest part of the concentration range whose conductance has been determined, down to infinitly dilute solutions. The upper limit is the largest value which may be taken for Λ_0 which will not necessitate the assumption that the ions, the undissociated molecules, or both, are more abnormal in very dilute solution than they are in the lowest part of the concentration range

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[1] Noyes and Falk, THIS JOURNAL, **33**, 479 (1912).

whose conductance has been determined. In general, the values obtained by the methods of Kohlrausch and of Noyes are greater than this upper limit.

5. An empirical graphic method is described by means of which an upper limit and a "probable" value for Λ_0 may be determined.

6. The limiting values and the "probable" values have been calculated for a number of the more common salts. These show good agreement. The "probable" values were adjusted by means of Kohlrausch's Law of the Independent Migration of Ions. The resulting Λ_0 values are smaller than those generally employed.

URBANA, ILLINOIS.

THE BASIC PROPERTIES OF OXYGEN. II.

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In a previous communication[1] we have shown that organic compounds containing oxygen unite readily with the halogens and halogen hydrides yielding compounds stable at low temperatures, which differ in many respects from molecular aggregates containing water or alcohol of crystallization. Following Friedel, these combinations are explained by ascribing to oxygen a higher valency than two, and, except in a few cases, the assumption of oxygen as a tetravalent element suffices. The constitutions of the compounds are not definitly fixed since their molecular weights have not as yet been determined with sufficient accuracy. In future papers we hope to discuss this problem and to determin not only the molecular weights but the ions present in solution.

While there is no doubt that compounds of the acids and ethers separate from their cooled solutions, the question of the existence of compounds in solution or in the molten state has not been investigated. We have endeavored to solve this problem by means of conductivity measurements, an account of which is given here with the freezing-point curves of several systems which we have determined for comparison with the conductivity results.

Few systems have had their resistances measured from pure solvent to pure solute and these only in aqueous solutions. Kohlrausch[2] and others have examined sulfuric acid in all concentrations; Veley and Manley[3] nitric acid, and Hill[4] hydrofluoric acid. Apart from the object we had in view, a comparison of water and other solvents over wide concentrations is not without interest. For this purpose only hydrochloric acid is available, since oxonium compounds separate from solutions of

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[1] THIS JOURNAL, 34, 1273 (1912).

[2] *Wied. Ann.*, 17, 69 (1882); *Pogg. Ann.*, 159, 233 (1876).

[3] *Phil. Trans.*, (*A*) 191, 365 (1898).

[4] *Proc. Roy. Soc. London*, (*A*) 83, 130 (1909).