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THE FORM OF THE CONDUCTANCE FUNCTION IN DILUTE SOLUTIONS.

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Some years ago Kraus and Bray[1] showed that in the case of a large number of electrolytic solutions the mass-action law is approached as a limiting case.[2] In a series of papers which recently appeared in THIS JOURNAL, Washburn[3] has described a method of extrapolating for Λ_o which is based on this result. He adds, however, the arbitrary assumption that at high dilutions the function $C\Lambda^2/\Lambda_o(\Lambda_o-\Lambda)$ approaches its limiting value asymptotic to a line parallel to the C-axis. While he does not so state, he nevertheless implies that this method of approach is the only one compatible with the assumption that the mass-action law is a limiting form of a more general function. He applies his method of extrapolation to conductance measurements carried out under his direction by Weiland[4] and reaches certain conclusions which he believes to be decisive. These conclusions are obviously dependent upon the assump-

[1] THIS JOURNAL, **35**, 1315 *et seq.* (1913).

[2] They did not discuss in detail the precise manner in which the limiting form is approached, but this may be inferred from their equation.

[3] THIS JOURNAL, **40**, 128 (1918).

[4] *Ibid.*, **40**, 131 (1918).

tions made and it is the purpose of this paper to examine these assump-
tions in order to determine whether or not the conclusions derived there-
from are valid.

The method which Washburn employs is a graphical one involving two
graphs, one between the equivalent conductance and the concentration,
the other between the function $C\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda)$ and the concentration.
In order to make clear what it implies, it will be necessary to examine
these two graphs. Let us assume for the moment that we have a binary
electrolyte which obeys the mass-action law. We have then

$$\frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} = K, \tag{I}$$

where C is the concentration, Λ is the equivalent conductance, Λ_0 is the
limiting value which the conductance approaches as the concentration
becomes indefinitely small, and K is the mass-action constant. If we
have a very dilute solution of a highly ionized electrolyte, the ratio Λ/Λ_0
approaches unity. In any case its variation becomes negligible in com-
parison with the difference $\Lambda_0 - \Lambda$. If we introduce this simplifying
condition in Equation I, we have

$$\frac{C\Lambda}{\Lambda_0 - \Lambda} = K, \tag{II}$$

or

$$C\Lambda = K\Lambda_0 - K\Lambda. \tag{III}$$

From Equation III we have

$$d\Lambda/d(C\Lambda) = -1/K, \quad \text{(IV)} \qquad d^2\Lambda/d(C\Lambda)^2 = 0. \quad \text{(V)}$$

This means that, if we plot values Λ against those of $C\Lambda$ for a dilute
solution, the graph begins on the axis of Λ at the value Λ_0 and proceeds
downward toward the axis of $C\Lambda$ as a straight line, the slope being given
by the constant value $-1/K$, from which it follows that K is equal to
the cotangent of the acute angle which the line makes with the Λ-axis.
If we employ the concentration C in the place of the specific conductance
$C\Lambda$, the graph will have the same form since Λ increases only very slowly
in comparison with $\Lambda_0 - \Lambda$ and C. The slope will then be given by the
expression $-\Lambda_0/K$.[1] What has been said with regard to the curve con-
necting $C\Lambda$ and Λ holds equally for a curve between C and Λ so long as
the concentration is sufficiently low.

The mass-action law does not hold in the case of strong electrolytes.
The function

[1] In the general case we have $d\Lambda/d(c\Lambda) = -\Lambda^2/K\Lambda_0{}^2$, and $d\Lambda/dc = -\Lambda^3/K(2\Lambda_0{}^2 -$
$\Lambda_0\Lambda)$. It is obvious that as Λ approaches the value Λ_0, the expressions for the differ-
ential coefficient approach the limiting values $-1/K$ and $-\Lambda_0/K$ respectively. If the
ionization of an electrolyte were 99%, neglecting the difference between the values of
Λ_0 and Λ in comparison with Λ_0 would scarcely cause an appreciable error in the posi-
tion of the tangent.

$$\frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} = K' \qquad\qquad \text{(VI)}$$

increases with increasing concentration. If we plot values of C or $C\Lambda$ along the x-axis, and values of Λ along the y-axis, the slope of the curve at any point is given by the equation

$$d\Lambda/d(C\Lambda) = -1/K' \qquad\qquad \text{(VII)}$$

Since K' increases with increasing concentration, it follows that the slope decreases with increasing concentration, $i.\ e.$, the curve bends away from the axis of C, or is convex toward this axis. This follows also from the sign of the second differential coefficient. We have

$$\frac{d^2\Lambda}{d(C\Lambda)^2} = \frac{1}{dK'/d(C\Lambda)} \qquad\qquad \text{(VIII)}$$

The second differential coefficient is positive, since, according to experiment $dK'/d(C\Lambda)$ is always positive. But this is the condition that the curve shall be convex toward the axis of $C\Lambda$. The continuous curve in Fig. 5 is of this type.[1] Generally the curve will have its greatest curvature at that point for which $dK'/d(C\Lambda)$ is greatest, that is, at that point where K' changes most rapidly.

Having established the geometrical properties of the curve in which C (or $C\Lambda$) and Λ are plotted as variables, let us examine the curve obtained when $K' = C\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda)$ and C (or $C\Lambda$) are plotted as variables. Let us assume the general function

$$K' = \frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} = F(C\Lambda) \text{ or } F(C), \qquad\qquad \text{(IX)}$$

assuming the solutions to be dilute. $F(C)$ is a purely empirical function whose nature can be obtained from a graph between K' and C. Let us assume values of C to be plotted as abscissas. We have then

$$dK'/dC = F'(C), \qquad\qquad \text{(X)}$$

and

$$d^2K'/dC^2 = F''(C). \qquad\qquad \text{(XI)}$$

Since, according to experience, K' increases with increasing concentration, it follows that $dK'/dC > 0$, $i.\ e.$, the curve rises as the concentration increases. As regards the second differential coefficient, we know that the curve is concave toward the axis of C up to $10^{-4}\ N$. It follows therefore, that throughout this region

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[1] From the geometrical relations it follows that $d\Lambda/d(C\Lambda) = \tan\Theta$, where Θ is the angle which the line from Λ_0 to the tangent point on the curve makes with the $C\Lambda$-axis. Therefore, we have $K' = \cot\varphi$ where φ is the angle which the line makes with the Λ-axis. This is evident from Fig. 4.

$$\frac{d^2K'}{dC^2} < 0. \tag{XII}$$

If this curvature continues to be maintained at lower concentrations than 10^{-4} N down to any desired value, then it follows that the tangent to the curve as it cuts the axis of K' makes with the C,Λ-axis an angle greater than zero. In other words, such a curve will not become asymptotic to a line parallel to the C-axis. Algebraically this is expressed by the equation

$$\lim_{C=0} \frac{dK'}{dC} > 0. \tag{XIII}$$

Whether or not the function, IX, will ultimately suffer a reversal in the sign of curvature, cannot be determined on *a priori* grounds. We may, however, examine the function $F(C)$ and determine how its form changes in the regions accessible to experiment, whether or not, for example, d^2K'/dC^2 increases or decreases as the concentration decreases. If it is found that the curvature increases with decreasing concentration down to 10^{-4} N, then, from our general notions as to the nature of dilute solutions, we should have reasonable grounds for assuming that the curvature continues to increase at lower concentrations. Certainly we should not be justified in assuming that the sign of curvature changes over a very short interval of concentration change.

Kraus and Bray examined practically all the available data on non-aqueous solutions, and found that the relation between conductance and concentration is expressed within the limits of experimental error by the equation

$$K' = \frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} = \frac{D(C\Lambda)^m}{\Lambda_0{}^m} + K, \tag{XIV}$$

where, as before, Λ_0 is the limiting value which the equivalent conductance approaches as the concentration diminishes without limit, while K is a limiting value which K' approaches under the same conditions. The constants D and m have no physical significance, but are both positive, while m has been found always less than 2. The above equation was found to fit the experimental values in the case of non-aqueous solutions within the limits of experimental error from the greatest dilutions to concentrations, in some instances, greater than normal. In the case of aqueous solutions there is some question as to the applicability of this function. Nevertheless, since this function reproduces the experimental values fairly closely from 3.0 to 0.001 N, we may assume that it holds approximately. In any case, it is a reasonable procedure to assume some function, which fits experimental values fairly closely over a considerable range of concentration, and then to investigate the changes which the constants undergo as we proceed along the curve.

Let us examine, then, the conductance function XIV. Applying Equations X and XI and using $C\Lambda$ as variable in place of C^1, we have

$$\frac{dK'}{d(C\Lambda)} = \frac{Dm(C\Lambda)^{m-1}}{\Lambda_0{}^m}, \qquad (XV)$$

and

$$\frac{d^2K'}{d(C\Lambda)^2} = \frac{Dm(m-1)(C\Lambda)^{m-2}}{\Lambda_0{}^m}, \qquad (XVI)$$

respectively.

Equation XV shows that the curve has a positive tangent, i. e., with increasing values of $C\Lambda$, K' increases. The curvature is determined by Equation XVI, which shows that this is determined by the value of the constant m. When we have $m < 1$, then

$$\frac{d^2K'}{d(C\Lambda)^2} < 0, \qquad (XVII)$$

while when $m > 1$

$$\frac{d^2K'}{d(C\Lambda)^2} > 0, \qquad (XVIII)$$

and when $m = 1$

$$\frac{d^2K'}{d(C\Lambda)^2} = 0. \qquad (XIX)$$

It follows therefore that, for values of $m < 1$, the curve of K' and $C\Lambda$ is concave toward the axis of $C\Lambda$, and, for $m > 1$, it is convex toward this axis. When $m = 1$, we have a limiting case, the curve has zero curvature, i. e., K' increases as a linear function of $C\Lambda$.

From Equation XV we see also that for $m < 1$

$$\lim_{C=0} \frac{dK'}{d(C\Lambda)} = \infty, \qquad (XX)$$

while for $m > 1$

$$\lim_{C=0} \frac{dK'}{d(C\Lambda)} = 0. \qquad (XXI)$$

That is, in the case of an electrolytic solution for which m is less than unity, the function K' approaches the limiting value K asymptotic to the axis of K', while for one in which $m > 1$, K' approaches the value K tangent to a line passing through K parallel to the $C\Lambda$-axis. In the limiting case $m = 1$, K' approaches K along the line whose tangent is $Dm/\Lambda_0{}^m$.

Whether m is greater or less than unity, the curvature increases as the

[1] In dilute solutions either C or $C\Lambda$ may be employed as desired. If we use Equation XIV, however, $C\Lambda$ is preferably used as variable, since in this case the result is not restricted to dilute solutions.

concentration decreases.[1] This is particularly apparent for values of m differing greatly from unity, as in the case of aqueous solutions. When m is nearly unity, the curve differs only a little from a straight line. The general form of the curves will be apparent from Fig. 1, where Curve I is calculated for the constants: $m = 0.52$, $D = 1.703$, $K = 0.001$ and $\Lambda_o = 129.9$. This curve corresponds to that of potassium chloride
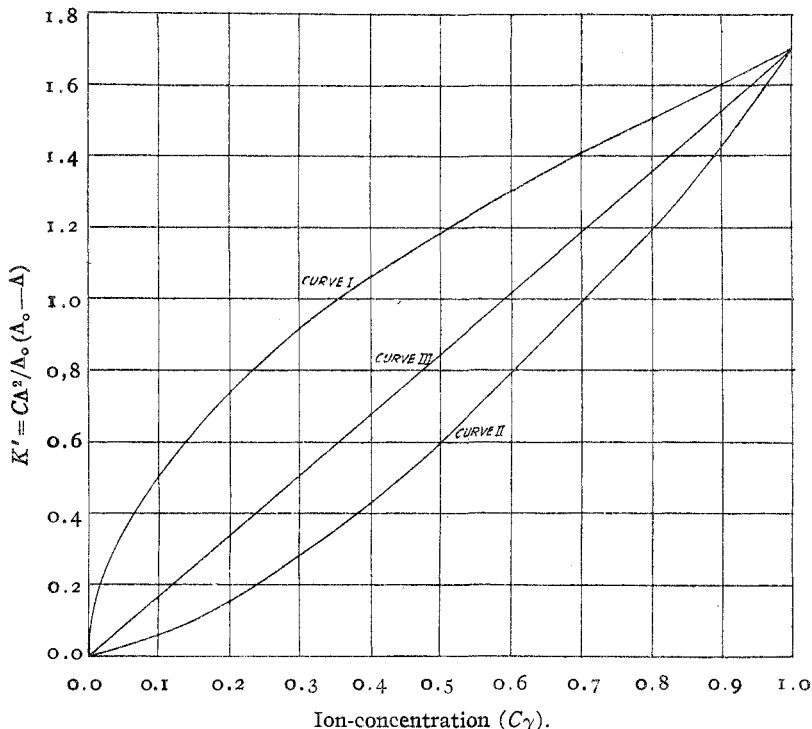

Fig. 1.—Showing typical K'-curves for different values of m.

[1] For the radius of curvature we have the expression

$$R = \frac{\left[1 + \dfrac{dK'}{d(C\Lambda)} \right]^{3/2}}{\dfrac{d^2K'}{d(C\Lambda)^2}}, \quad \text{or} \quad R^{2/3} = \frac{(C\Lambda)^{\frac{2(2-m)}{3}}}{[Dm(m-1)]^{2/3}} + \frac{m^{4/3}D^{4/3}(C\Lambda)^{\frac{2(2m-1)}{3}}}{(m-1)^{2/3}}.$$

The coefficient $2 - m$ of the exponent of the first term of the right-hand member of the equation is positive for all values of m less than 2. Since no case is known of an electrolytic for which m is greater than 2, we need consider only such cases for which $m < 2$. Under these conditions the radius of curvature increases with increasing values of $C\Lambda$ so far as the first term is concerned. For $m > 1$, the coefficient $2m - 1$ of the exponent of the second term is greater than unity and the radius of curvature increases with increasing values of $C\Lambda$. For $m < 1$, we always have $2 - m > 2m - 1$ so long as m is not negative. In this case, therefore, the first term overbalances the second and the radius of curvature increases with increasing values of $C\Lambda$. The curvature, therefore, decreases with increasing values of $C\Lambda$ for all values of m between 0 and 2.

in water. Curve II is calculated for the same values of the constants except that $m = 1.50$, while Curve III represents the case when $m = 1$. All these curves necessarily pass through the common points $K' = K$, at $C\Lambda = 0$, and $K' = D/\Lambda_0{}^m + K$, at $C\Lambda = 1$.

Having determined the geometrical properties of the two graphs with which we have to deal, let us examine Washburn's "New Graphical Method of Extrapolating." After discussing the various methods previously employed in determining Λ_0, Washburn introduces his method as follows: "In order to avoid the errors involved in what may be called the 'arbitrary function' methods of extrapolating, and also to avoid similar uncertainties involved in attempting a direct graphical extrapolation, the following method has been devised: It seems to the writer that no valid objection[1] can be urged against it. It rests only upon the following two assumptions: (1) That as C decreases, the value of the mass-action expression K_E[2] also decreases and will eventually gradually approach a constant, K_0, at extreme dilutions; and (2) that whatever be the true form of the curve connecting K_E with C, it must be one which does not show deviations from the mass-action law which *increase with dilution*, that is, in dilute solutions the curve must not exhibit any erratic behavior such as a sudden rise or a sudden fall with decreasing concentration." . . . "In other words, it is assumed that those influences which cause a strong electrolyte to deviate from the mass-action law at higher concentrations *gradually and steadily* become smaller and smaller and finally disappear at infinite dilution. No assumption is made as to the actual path over which the values of K_E shall approach the constant limiting value, nor in fact is any assumption whatever made as to the mathematical form of the function which connects the conductivity with the concentration *over any part of the concentration range* open to direct measurement."

The following footnote also appears as noted above: "Unless indeed the assumption that, $\lim_{C=0} dK_E/dC = 0$ is considered an objection."

In practice Washburn applies his method as follows: The measured values of Λ are plotted as ordinates against the measured values of C, or $C\Lambda$ as abscissas. Through these points a smooth curve is drawn and values of Λ are interpolated at round concentrations. With these interpolated values of Λ, values of $K' = C\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda)$ are calculated for different values of Λ_0. These values of K' are then plotted against values of C. Four types of curves result, depending on the value of Λ_0 employed in calculating K'. First, for the smaller values of Λ_0, a curve which at higher concentration is concave toward the axis of C but which,

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[1] Author's footnote quoted in text below.

[2] Washburn's function K_E corresponds to the function K' as employed in this paper, and his constant K_0 corresponds to the constant K.

between a concentration of 2×10^{-4} and $10^{-4}\,N$, passes through a point of inflexion, after which it is convex toward the axis of concentration, passing through a minimum, and thereafter rising very steeply as the concentration decreases. Second, for larger values of Λ_0, a curve which is initially concave toward the C-axis, and which passes through two inflexion points at concentrations below $2 \times 10^{-4}\,N$. Third, for an intermediate value of Λ_0, a curve concave toward the C-axis, at higher concentrations, which passes through an inflexion point between 2×10^{-4} and $10^{-4}\,N$, continuing to lower concentrations convex toward the C-axis, finally cutting the axis of K' tangent to a line parallel to the C-axis. Finally, for considerably larger values of Λ_0, a curve which is everywhere concave toward the C-axis. That value of Λ_0 which gives the third type of curve, Washburn assumes as the correct one.

On examination, it will be found that this method of extrapolation fails to conform to the second assumption made. An "erratic behavior" is to be judged not alone in discontinuities or sudden changes in the value of the primitive function, but also in any unusual changes in its derivatives. If we apply Condition XI with regard to the second differential coefficient, we find this remarkable behavior: At higher concentration, and down to approximately $2 \times 10^{-4}\,N$, the curve is concave
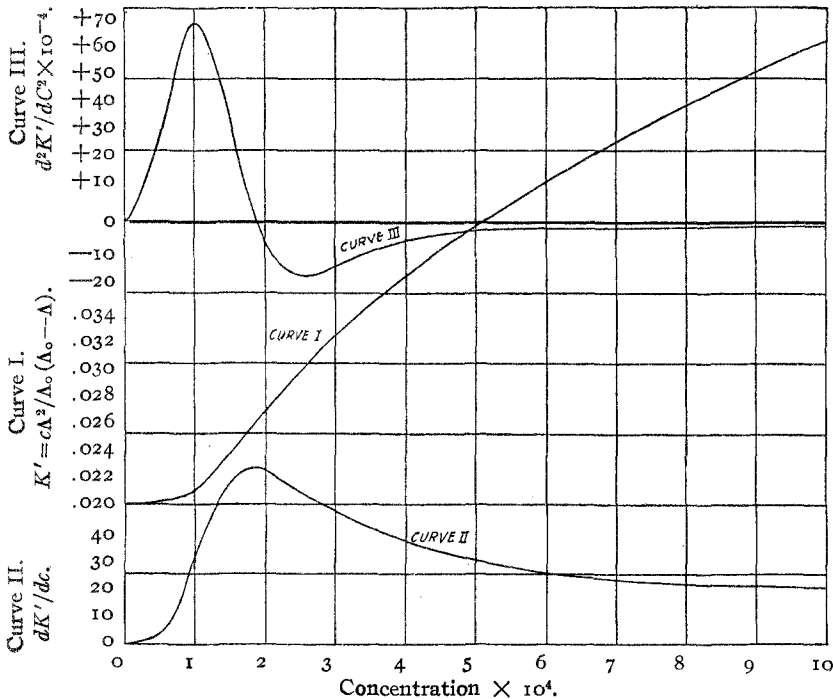

Fig. 2.—Showing derivatives of Washburn's function.

toward the axis of C, the curvature increasing as the concentration decreases. Then the curvature begins to decrease. When a concentration of approximately 10^{-4} has been reached, the curvature passes through zero and thereafter increases with extreme rapidity reaching a maximum a little below 10^{-4} N and thereafter again decreasing and approaching zero at zero concentration. In short, in dilute solutions, where we have least reason to expect an erratic behavior of the conductance function, Washburn assumes a function which exhibits extreme complexity. On the other hand, the curve which results from considerably larger values of Λ_0, is in every way a regular curve which retains, in dilute solution, the same form which it has in concentrated solution and whose curvature increases regularly, with decreasing concentration. The courses of the first and second derivatives of Washburn's function are shown in Fig. 2 as Curves II and III, respectively, while the primitive function is shown as Curve I. Curve I is the reciprocal of the derivative $d\Lambda/dC$ of the graph represented by the broken line in Fig. 5. If the primitive function at low concentrations possesses the same form as at higher concentrations, it has the form of Curve I in Fig. 3,[1] where Curves II and III represent the courses
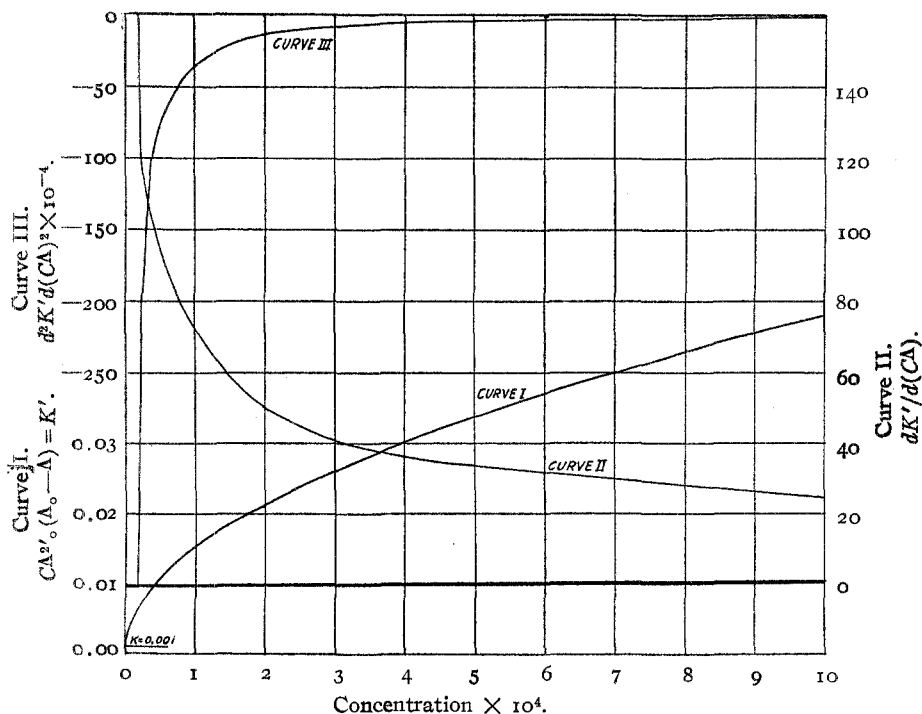

Fig. 3.—Showing derivatives of equation XIV.

[1] In this case $C\Lambda$ is employed as variable instead of C, in which case we are not restricted to the condition $\Lambda/\Lambda_0 = 1$. In any case, however, this ratio varies so little

of the first and second derivatives, respectively, of the primitive shown in Curve I.

Washburn's first assumption, also, is not fulfilled by his method of extrapolation for he imposes the condition $\lim_{C=0} dK'/dC = 0$. This condition, it is true, is compatible with the assumption in question, but it is not a necessary condition. The curve of K', so far as the assumption goes, might intersect the axis of K' not alone at the angle $0°$, with the $C\Lambda$-axis, but at any angle from $0°$ to $90°$.

In Fig. 4, the crosses represent experimentally determined values of Λ and of $C\Lambda$, values of Λ being plotted as ordinates and of $C\Lambda$ as abscissas. The points in question are those determined by Weiland in his first 3 series of measurements. The points are numbered in order except that the first point of the second series has been omitted. The point marked "K" is due to Kohlrausch and Maltby. Among the points a smooth curve has been drawn as represented by the continuous curve. From the point P, which is in the neighborhood of the last experimental points, let us draw a tangent to the curve and extend it until it cuts the axis of Λ at the value $\Lambda'_0 = 129.74$. If we calculate the value of K' for different points assuming for Λ_0 the value Λ'_0, we obtain for all points lying on the tangent the value K'_P corresponding to that of the point P. If, on the other hand, a point lies above the tangent, the value of K' calculated will be greater than K'_P, while if it lies below the tangent the corresponding value of K' will be less than K'_P, assuming the same value of Λ_0 to be used in all cases. If, then, assuming $\Lambda_0 = 129.74$, we calculate K' for points along the smooth curve, the value of K' will decrease with decreasing concentration approaching the value K'_P as a limit. In a graph of K' and C, the curve becomes tangent to a line parallel to the C-axis which intersects the K' axis at the value K_P. The concentration at which tangency occurs is C_P corresponding with that of the point P. If a value of Λ_0 is assumed, smaller than Λ'_0, such as $\Lambda_{01} = 129.64$, for example, the values of K' calculated on this assumption for points on the smooth curve will everywhere be greater than those calculated for a larger value of Λ_0. The K', C-curve in this case passes through a minimum corresponding to the point P_1, at which a line drawn from Λ_{01} to the smooth curve is tangent to that curve. At the point in question, the value of K' will be K'_{P_1}. For a value of Λ_0 greater than $\Lambda'_0 = 129.74$, the K', C-curve everywhere lies below that calculated on the basis of the latter value. This curve does not pass through a minimum but has two inflexion points. For sufficiently large values of Λ_0, however, the inflexion points disappear and the K', C-curve continues everywhere concave to the C-axis without any singularities until it be-

in comparison with C that the form of the curves is not affected materially. The constants of Curve I are those for potassium chloride whose values are given below.

comes tangent to the K' axis at some definite value K. In Fig. 4, the value $\Lambda_0 = 129.9$, at which the smooth curve, extended (shown by the broken line), cuts the Λ-axis, is such that the corresponding K', C-curve becomes tangent to the K' axis at the value $K = 0.001$. This value is equal to the cotangent of the angle, shown in the figure, at which the Λ, C-curve cuts the Λ-axis.

If, in drawing the smooth curve, the last points, 1, 6 and 10, had been neglected, the curve might have been halted at the point P_1, and extended to cut the Λ-axis at the value $\Lambda_{01} = 129.64$. In this case a K', C-curve would have been obtained which approached the limiting value K'_{P_1} as determined by the cotangent of the angle which the tangent $\Lambda_{01}P_1$ makes with the Λ-axis. If the points at lower concentrations were lacking up to P_3, for example, a value $\Lambda_{03} = 129.44$ could be extrapolated, and the values of K' calculated on the basis of this value of Λ_0 would approach a limiting value K'_{P_3} determined by the cotangent of the angle as shown in the figure.
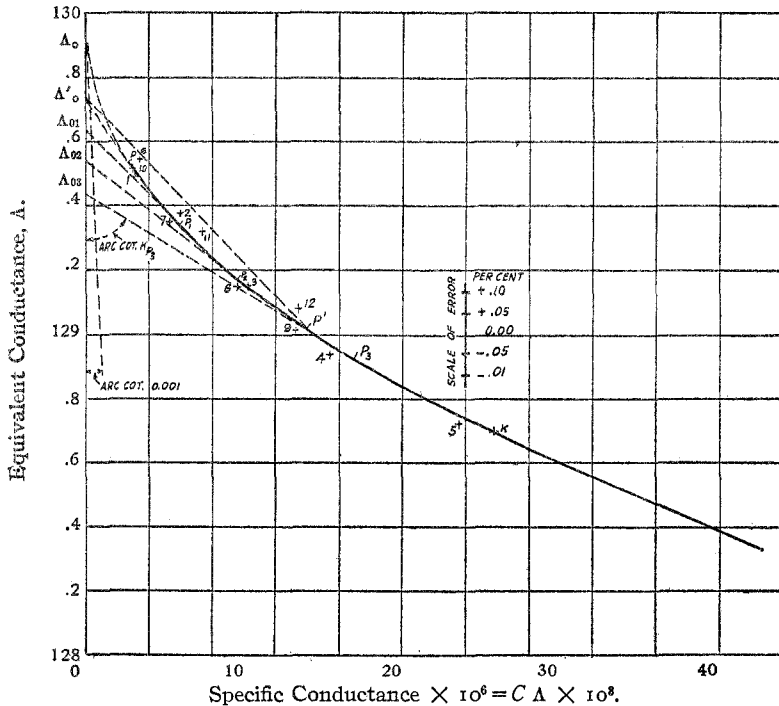

Fig. 4.—Illustrating method of extrapolating for Λ_0.

So long as the points at the lower concentrations are available, it is clear that the tangents drawn to P_3 and P_2 are out of the question. On the other hand, the tangent to P_1 lies within the limits of experimental error of two of the three points near P. The tangents drawn to P and

to P_1 differ by less than 0.02% at the lowest concentration at which measurements have been made. The values of Λ_0 based on these two tangents are 129.74 and 129.64 respectively. If we grant for the moment that the method of extrapolation here in question is correct, it is evident that the values obtained for Λ_0 and K admit of considerable variation within the limits of experimental error. But there is no reason for believing that this method of extrapolation is justified. In fact, as we have seen, this method of extrapolation imposes on the conductance function a degree of complexity which appears altogether improbable. If we assume that the conductance function in dilute solutions follows the same general trend as it does in concentrated solutions,[1] no singularities arise either in the function itself or in its first and second derivatives. The extrapolation of this function is indicated in Fig. 4 by the continuation of the curve as a broken line until it intersects the Λ-axis at the value 129.9. From the equation of the curve, which is given below, it follows that the limiting angle at which the curve approaches the axis is arc cot $K = 0.001$. Here again we have another value of Λ_0 consistent with the experimental points well within the limits of error. An examination of Fig. 4 will make it clear that the values of Λ_0 and of K are not to be determined with any degree of precision from measurements in dilute solutions alone. Even higher values than 129.9 would be in agreement with the experimental points within the limits of error. To extrapolate the function we must take into account the experimental values at higher concentrations.

The foregoing analysis shows that Washburn's method of extrapolation by means of the K', C-plot must give identical values of Λ_0 with those obtained from the Λ, C-plot if, from the last point on the experimental curve, a straight line is drawn tangent to this curve until it intersects the Λ-axis. The statement, "No assumption is made as to the actual path over which values of K_E shall approach the constant limiting value . . . ." is not correct. This method of extrapolation is based on the assumption that K' approaches its limiting value horizontally.

Let us now examine the conclusions which Weiland draws from his experiments. He made 5 series of determinations between approximately 10^{-4} and 2×10^{-5} N; two of the series comprize 4 points, two others 3 points, and the fifth comprizes 4 points up to 1.5×10^{-4} N. Weiland states that in the most dilute solutions the error may reach 0.05%, due to error in weighing out the salt. If this is true, some of the more concentrated solutions may be in error to this extent, since they were made up by weighing out successive amounts of salt of this order of magnitude.

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[1] It may safely be assumed that the C, Λ-curve is not concave toward the C-axis at any point for, otherwise, the value of K' would diminish with increasing concentration. There is no experimental evidence which indicates such a course.

Weiland ascribes the failure of the points of different series to lie on the same smooth curve to variations in the cell constant. In 3 runs, however, he measured solutions whose concentration lay near 10^{-3} N. As may be seen from Curve A of Weiland's Fig. 10, these determinations check with one another and with those of Kohlrausch within the limits of the electrical measurements. It must be assumed, therefore, that the cell constant did not vary and that any variation of the points from a smooth curve is due to other sources of error. The procedure which Weiland adopts, of treating each series by itself on the assumption that the variations between series are due to changes of the cell constant, does not appear justified, although the rejection of the last series may be allowable on the grounds that some consistent unknown source of error affects it.

Weiland plots the values of Λ as ordinates against those of C as abscissas and draws curves among the points of each series individually. Between 10^{-4} and 2×10^{-5} N these curves approximate closely to straight lines, particularly in the more dilute solutions. These curves probably lie within the limits of experimental error. Nevertheless, in drawing the curves so as to approximate straight lines, a tacit assumption is made as to the manner in which the curves should proceed, and since Weiland's conclusions rest entirely upon the form of the curve in these dilute solutions, his conclusions are a result of this assumption. On the smooth curves, Weiland interpolates values at 10^{-4}, 7.5×10^{-5}, 5×10^{-5} and 2×10^{-5} N. With these interpolated values he then calculates the values of K' for different assumed values of Λ_0 and plots them against the concentration. That value of Λ_0, which causes the curve to approach the axis of K' parallel to the axis of C, he assumes as the correct one,[1] and the intercept on the K'-axis he assumes as the value of the mass-action constant K.

As was shown above, any curve in the C, Λ-plot which is extrapolated as a straight line will give a value of Λ_0 yielding a corresponding K', C-graph which approaches the K'-axis parallel to the C-axis and which intersects the K'-axis giving a value of the mass-action constant in harmony with this value of Λ_0. The fact that a certain value of Λ_0 renders the K', C-curve horizontal and yields a corresponding intercept on the

[1] Washburn (*Loc. cit.*, p. 130) believes that, since a change of 0.01 unit in the value of Λ_0 causes the K', C-curve to rise or fall rapidly, the value of Λ_0 is determined with approximately this precision and that this precision is greater than it would have been for a direct extrapolation on the C,Λ-plot. It is obvious that if the ends of the curves in the C,Λ-plots had been extrapolated to the concentration zero, the value of Λ_0 would have been determined with the same precision as in the K', C-plot. In both cases the precision is not one of experimental measurements, but of reading off and extrapolating graphs, which is solely a function of the scale used in plotting.

K'-axis, in no wise proves that this is the correct value of Λ_0, nor that the value of K is the true one, nor, indeed that the mass-action law is obeyed at all, unless the curve drawn in the C, Λ-plot is the only curve which can be drawn through the experimental points which lies within the limits of experimental error and unless this curve is a straight line in the regions where the conductance has been experimentally determined. So long as the points as actually measured lie on a curve in the C, Λ-plot, the mass-action law can not be obeyed and the extrapolation of the curve to zero concentration remains uncertain. In fact, an extrapolation to zero concentration by Washburn's method cannot give a correct result unless the curve in the experimental region is a straight line in the C, Λ-plot.

An inspection of Weiland's Fig. 10, or Figs. 4 and 5, of this paper, makes it clear that the limits of error between 10^{-4} and 2×10^{-5} N are sufficiently large to make it possible to pass a great many curves among these points, all lying well within the limits of experimental error. Indeed, it will be observed from Weiland's Fig. 10 that 3 series of measurements give points which lie on curves decidedly convex toward the axis of C, while 4 out of 5 points of another series lie on a curve convex in the same direction. Only in the case of one curve, comprizing 3 measurements, do the points lie on a straight line. On the other hand, in not a single case do the points lie on a curve concave toward the C-axis. In the light of these facts, it is difficult to avoid the conclusion that the true form followed by the curve in the C, Λ-plot is one convex toward the C-axis and not a straight line as Weiland and Washburn tacitly assume.

Because of the small value of the non-ionized fraction of the salt in these solutions, and the consequent great variation in the function K' due to a small error in the determination of Λ, the true variation of this function with concentration is entirely masked. There is little hope that measurements may be carried out at these high dilutions with sufficient precision to enable us to determine what is the true form of the function. To get a notion of this, we must fall back on other considerations, such as an examination of the variation of the function at higher concentrations and the behavior of other solutions. Kraus and Bray have shown that Equation XIV represents the conductance function within the limits of error in the case of a large number of electrolytes dissolved in several different solvents over a large range of concentration, and for others in more concentrated solutions, no data being available at low concentrations. They showed, also that this equation applies very nearly to aqueous solutions from a concentration of $3 N$ to $10^{-3} N$. To apply the equation over this range in aqueous solutions, however, it was necessary to assume a value of Λ_0 not in harmony with the measurements of Kohl-

rausch and Maltby[1] between 10^{-3} and 10^{-4} N. Since the measurements of Weiland confirm those of Kohlrausch, it is evident that this assumption is not allowable. However, it is clear that, in any case, the function applies very nearly, and it is possible that at lower concentrations it will apply more exactly. Even though this equation should not apply exactly, it is of interest to examine what variation the constants undergo as the concentration decreases, and it will be reasonably safe to assume that the direction in which the constants change as the concentration decreases will not undergo a reversal of sign at low concentrations and, in particular, that any such change will not take place in a small interval of concentration.

Employing the measured values of Kohlrausch and Maltby and of Weiland, the constants of Equation XIV were calculated from 10^{-2} N to the lowest concentrations measured. The following values were obtained: $m = 0.52$. $D = 1.703$, $\Lambda_0 = 129.9$ and $K = 0.001$.[2] The curve
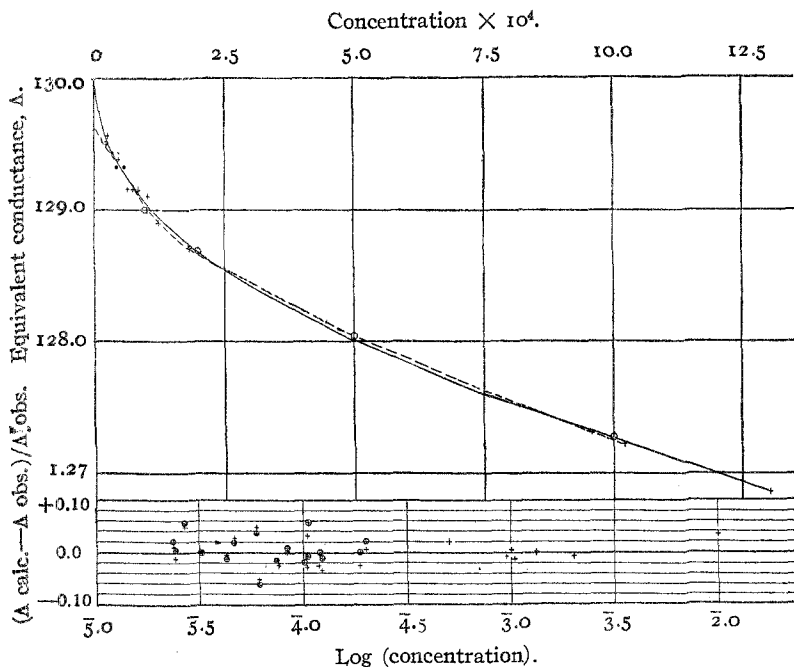

Fig. 5.—Showing deviation of calculated curve from experimental values.

[1] *Wiss. Abh. phys.-tech. Reichsanstalt*, 3, 210 (1900).

[2] Between 3 N and 10^{-3} N Kraus and Bray found the values: $m = 0.763$, $D = 2.707$, $\Lambda_0 = 128.3$ and $K = 0.080$. On comparison it is evident that D decreases slightly at lower concentrations. The constant K is much smaller than that of Kraus and Bray. Correspondingly the value of Λ_0 is larger. Most significant is the fact that the exponent m is markedly smaller, a result which does not harmonize with the function which Washburn assumes.

of this equation, together with the experimental values,[1] are shown in Fig. 5 up to 10^{-3} N, values of Λ being plotted as ordinates and those of C as abscissas. At the bottom of the figure are shown the deviations of the experimental values from the calculated curve, up to 10^{-2} N, the logarithms of the concentrations being plotted as abscissas and the values of the percentage deviations $(\Lambda_{calc.} - \Lambda_{obs.})/\Lambda_{obs.}$ as ordinates. These values are represented by the crosses. The values of Kohlrausch and Maltby are included up to 0.01 N. The greatest deviation of any point is 0.055% for Weiland's measurement at 6.1994 $\times$ 10^{-5} N. The curve agrees almost exactly with the mean values of Kohlrausch except at 10^{-2} N, where the deviation is +0.032% and at 10^{-4} N where the deviation is —0.04%. At higher concentrations than 10^{-2} N, the equation yields values considerably higher than those measured, and the deviation of +0.032% at 10^{-2} N is the result of this trend. There can be no question that the function represents the experimental values within the limits of error, up to 10^{-2} N. The deviation of Weiland's measured values from his best, smooth curves are represented on the same plot by circles.[2] It will be seen that, even though he had only the dilute solutions to consider, his curve fits the results little if any better than does the calculated curve. The maximum variations from Weiland's smooth curve are slightly greater than those from the equation. Only in the case of the points very near to 10^{-4} N does Weiland's curve agree better than that calculated. On the other hand, in the most dilute solutions the experimental values lie slightly more favorable in the case of the calculated curve. At no point, however, is there a consistant deviation of the experimental values away from the calculated curve. Wherever the deviations are large, experimental values will be found lying on both sides of the curve. Leaving aside all other considerations, the fact that the experimental values may be so exactly reproduced by means of a function which is so radically different from that which Washburn deduces from the measurements of Weiland in dilute solutions, shows conclusively that Washburn's conclusion as to the mass-action law and the value of Λ_0 are not binding.

When we examine Washburn's conclusion from other points of view it becomes even less probable. Should we grant these conclusions, then, in the light of the geometrical properties of the curve which he obtains,

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[1] In this, Weiland's fifth series, which he has himself rejected, is not included.

[2] Weiland's smooth curve is shown in Fig. 5 as a broken line. It will be observed that it differs from the calculated curve only within the limits of error. It will also be observed that Weiland's curve consists of two parts, one in dilute solutions which approximates a straight line, another in more concentrated solutions which exhibits a slight curvature. The two parts are joined by a short length between 0.9 $\times$ 10^{-4} and 2.5 $\times$ 10^{-4} N of very pronounced curvature. The eccentricities of the curve in this region are shown more clearly by the curves in Fig. 2, of which this is the primitive.

the function K' must pass through a series of very rapid changes between 2×10^{-5} and 10^{-4} N. The value of d^2K'/dC^2 must change sign and the curvature of the K', C-curve, which is increasing in a regular manner with decreasing concentration up to 2.5×10^{-4} N, suddenly begins to decrease, passes through zero, reverses, increases very rapidly, and then decreases to zero. Now all these changes take place between 2.5×10^{-4} N and 2.0×10^{-5} N in the case of a function which has been following a regular and simple course up to this point.[1] In view of the fact that the experimental values throughout the region from 2×10^{-5} to 2×10^{-4} N may be reproduced well within the limits of experimental error by the same function which is known to apply at higher concentrations in the case of a very large number of electrolytes, it is evident that the complex function found by Washburn is fictitious and that it is founded on the arbitrary assumption that $\lim_{C=0} dK'/dC = 0$, or, in other words, that the K', C-curve must approach a limiting value asymptotic to a line parallel to the C-axis.

If the K', C-curve has the form ascribed to it by Washburn, we should expect to find it reproduced in other cases such, for example, as that of the weak acids, which at moderate concentration obey the mass-action law within the limits of experimental error. It develops, however, from the work of Kendall[2] that this is not the case. If the K', C-curves are constructed for the acids, they are found to be concave toward the axis of concentration. In terms of Equation XIV, this means that m is less than unity for the acids as it is for strong electrolytes. Kraus and Bray have shown that in non-aqueous solutions m is constant for a given electrolyte in a given solvent over a large range of concentrations. It follows also from their results that there are cases in which the K', C-curve approaches the K'-axis asymptotic to a line parallel to the C-axis. In all such cases, however, the curve has a constant direction of curvature and this curvature increases as the concentration decreases up to the lowest concentrations. Washburn's function, however, does not do this. In the case of this function the curvature is zero at the lowest concentrations and changes sign at higher concentrations. The conductance function in the case of different electrolytes in different solvents is remarkably regular. No case is so far on record where the K', C-curve exhibits an inflexion point if we exclude that which Washburn believes to have discovered.

[1] Inspection of Fig. 2, already described, will make clear the extremely complex character of Washburn's function, while Fig. 3 shows equally clearly the regular trend of the function based on the constants given above for Equation XIV. It is to be borne in mind that, at higher concentrations, Washburn's function corresponds to this equation within the limits of experimental error up to 0.01 N.

[2] *Medd. K. Vetenskapsakad Nobelinst.*, **2**, 38 (1913).

As regards the mass-action law, it cannot be said that this law has been shown to be a limiting form of the conductance function in the case of aqueous solutions of strong electrolytes. It is possible that the conductance curve for potassium chloride might be fitted within the limits of error with a value $K = 0$, by slightly reducing the value of m. However, it is equally possible that values of K greater than 0.001 might be employed. In fact, they may be so employed, although they will not reproduce the experimental results quite as closely as the constants given above. Nevertheless, the curves fall within the limit of experimental error. A change of less than 0.05% in a few experimental points might admit a value of K as high as 0.01 or even 0.015. With present experimental material, however, it would be profitless to attempt a solution of this problem.

Finally, it should be borne in mind that the mass-action law is a limiting expression which is approached more or less closely, but which is never fulfilled exactly. As our experiments become more precise, the limits within which it holds constantly recede. The manner in which the limiting form is approached under given conditions depends upon the nature of the solvent and that of the electrolyte while, for a given combination of solvent and electrolyte, it depends upon the temperature. In the case of solutions which exhibit a K', C-curve concave toward the C-axis, the limiting value is approached asymptotic to the K'-axis.

WORCESTER. MASS.

A STUDY OF THE HEATS OF DILUTION OF CERTAIN AQUEOUS SALT SOLUTIONS.[1]

BY ALLEN EDWIN STEARN AND G. McP. SMITH.

A. Introduction.

1. **Purpose of the Investigation.**—A series of investigations[2] undertaken in this laboratory with the object of studying ionic relationships in aqueous solutions of mixed strong electrolytes has indicated the formation of higher order compounds in the ionization process, in harmony with Werner's ideas in regard to its mechanism.

The method of investigation in the papers referred to has been to study the equilibria between aqueous and metallic solutions, using mixed salt

[1] From a thesis submitted to the Graduate School of the University of Illinois by Allen Edwin Stearn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] G. McP. Smith, *Am. Chem. J.*, **37**, 506 (1907); THIS JOURNAL, **32**, 502 (1910); **35**, 39 (1913); Smith and Ball, *Ibid.*, **39**, 179 (1917); Smith and Braley, *Ibid.*, **39**, 1545 (1917); **40**, 197 (1918); Smith and Rees, *Ibid.*, **40**, 1802 (1918).