at all events involves, the assumption that the magnitude of the deviation of potassium chloride from the mass-action law $\left(i.\ e.,\ \frac{1}{K_E}\ \frac{dK_E}{dC}\right)$ increases with dilution at a constantly accelerated rate until it finally reaches an infinite value at $C = 0$. His assumption is thus the exact opposite of the one employed by the writer, or mathematically expressed:

$$\lim_{c=0} \frac{1}{K_E}\ \frac{dK_E}{dC} = 0 \quad \text{(Washburn)}$$

$$\lim_{c=0} \frac{1}{K_E}\ \frac{dK_E}{dC} = -\infty \quad \text{(Kraus).}$$

URBANA, ILLINOIS.

THE EXTRAPOLATION OF CONDUCTIVITY DATA TO ZERO CONCENTRATION. A REPLY.

BY CHARLES A. KRAUS.

Received February 27, 1920.

Through the kindness of the Editor of THIS JOURNAL, the foregoing article by Dr. Washburn was submitted to the writer in manuscript form for reply. The various points of difference have for the most part been treated sufficiently in the preceding papers and need not be discussed further here. However, Dr. Washburn has made his position somewhat clearer in certain respects and has raised one or two new points which may be considered further.

In the first place, Dr. Washburn now states that the mass-action law is assumed to hold at finite concentrations.[1] Without entering into a discussion of the probability of the correctness of this assumption from a physical point of view, it is at once clear that this is, indeed, the fundamental element underlying Dr. Washburn's position. In his method of extrapolation he assumes the mass-action law to hold. The graphical means employed to carry out the extrapolation naturally conform to this assumption and the extrapolated values are necessarily in harmony with it. The fallacy lies in that the agreement of the extrapolated values with the mass-action law are looked upon as a proof that this law holds, whereas, in fact, such agreement is merely a consequence of the assumption made. Naturally, somewhat the same condition prevails in the case of any extrapolation. The extrapolated values necessarily agree with the functional relation assumed in carrying out the extrapolation. There is this difference, however, in the 2 cases: Dr. Washburn's extrapolation function holds only for the last point of the experimentally determined curve, while other methods employ a function which holds over a considerable range of concentration. The greater the range of experimentally deter-

[1] Washburn, THIS JOURNAL, 42, 1079 (1920).

mined values that can be accounted for by means of the function in question, the greater the probability that the extrapolated values lie within a given limit of precision.

As Dr. Washburn himself points out, his method of extrapolation may be applied to a solution at any concentration and for any form of conductance curve. This is obviously the case, since he assumes his function to hold only for the last experimentally determined point; in other words, the function does not hold over an appreciable range of concentration in the regions where measurements exist and it may, therefore, always be applied. It follows, further, that the agreement of his extrapolated values with the measured values will always be equally good, *i. e.*, they will hold exactly at the last point.

This is illustrated in the following table, in which are given values of K and Λ_0 as determined by extrapolation by Dr. Washburn's method, for the intervals 10^{-3} to $10^{-4}\,N$ and 10^{-2} to $10^{-3}\,N$, together with the values of $K'(K_E)$, at different concentrations. The values relate to potassium chloride in water at 18° and the data are taken from the work of Kohlrausch and Maltby:

Table I.—Values of K′ and Λ_0 over Different Concentration Intervals According to Washburn's Method.

$C.$	10^{-4}.	1.5×10^{-4}.	2×10^{-4}.	3×10^{-4}.	5×10^{-4}.	7×10^{-4}.	10^{-3}.
K'........	0.03605	0.03612	0.03626	0.03878	0.04634	0.05282	0.05860

$K = 0.03605$, $\Lambda_0 = 129.408$.

$C.$	10^{-3}.	1.5×10^{-3}.	2×10^{-3}.	3×10^{-3}.	5×10^{-3}.	7×10^{-3}.	10^{-2}.
K'........	0.1147	0.1151	0.1165	0.1267	0.1594	0.1686	0.1941

$K = 0.1147$, $\Lambda_0 = 128.372$

It will be seen that in both intervals K' decreases and gradually approaches a limiting value. For the interval 10^{-3} to $10^{-4}\,N$ we obtain the limiting values $K = 0.03605$ and $\Lambda_0 = 129.408$, while for the interval 10^{-2} to $10^{-3}\,N$ we obtain the values $K = 0.1147$ and $\Lambda_0 = 128.372$. It is evident that Dr. Washburn's method may be applied to any concentration interval and it will in every case be found that the extrapolated values conform to the mass-action law at the end of this interval. But the values of Λ_0 and K determined in this way will be different for different intervals. If, therefore, the method is applied to the last points at which experimental data are available, it will appear that the point has just been reached where the mass-action law applies. But this condition was assumed in the first place, and the apparent agreement is without weight in determining whether or not the mass-action law really holds.

In principle, Dr. Washburn's method is not new. The same method was employed by Wegscheider,[1] the only essential difference being that Wegscheider did not employ graphical means in carrying out the extrapolation. He showed, however, that a value of Λ_0 may be assumed such

[1] Wegscheider, *Z. physik. Chem.*, 69, 603 (1909).

that the points for a limited concentration interval conform to the mass-action law within the limits of experimental error. Obviously, such a result may be obtained at any point of the conductance concentration curve and, if the point chosen be the last point for which experimental data are available, then it will appear that the mass-action law is approached in the manner which Dr. Washburn has found in the case of Weiland's measurements. Other investigators have likewise employed this method of extrapolation, notably Dutoit in dilute non-aqueous solutions.[1]

In the treatment of his results Weiland has drawn his individual curves as well as his average curve in such a manner as to conform approximately to the mass-action law between the last 2 interpolated points. Dr. Washburn defends Weiland's method of treating his results as individual series and the manner of drawing his curves. If the relative precision in a given series of measurements is sufficiently high with respect to the precision obtained in different series, then this method of treatment may be justified. There is, however, much doubt as to whether Weiland actually attained a sufficient precision to justify such a procedure. In any case, if the different series have sufficient precision so that they may be treated individually, then the curve which is drawn through the points in any series should as nearly as possible pass through all the points. Of course, in drawing a curve in the case of the C, Λ-plot, it would hardly be permissible to assume a high degree of complexity, since at higher concentration it is known that the curve is of comparatively simple form and it is improbable that the curve becomes more complex at lower concentrations. In any case, if it is possible to pass a simple form of curve through a given series of points, the curve should unquestionably be so drawn. But this has not been done in Weiland's treatment of his result. Weiland's data not only do not *require* that a straight line should be drawn through them, as Washburn states,[2] but they *do* require that a *curve* should be drawn through them and this curve is in general convex toward the C-axis but in no case concave. Neither the points of individual series nor the points of the average curve actually conform to the curves as Weiland has drawn them. As stated in the writer's previous article, the curves for the individual series are for the most part convex toward the axis of concentrations, particularly in the more dilute solutions, while none of them are concave toward this axis, which result might reasonably be expected if the true form of the curve were a straight line, *i. e.*, if the mass-action law applied. So, too, if the value of all the determinations are averaged, they yield a curve distinctly convex toward

[1] Dutoit and Duperthuis, *J. chim. phys.*, 6, 705 (1908); Dutoit and Gyr, *ibid.*, 7, 198 (1909).

[2] Washburn, *loc. cit.*, p. 1084.

the axis of concentration, thus precluding the conclusion that the mass-action law applies within the range of concentrations actually measured.

In his last paper, Dr. Washburn claims that his method of extrapolation is independent of the nature of the interpolation function employed in obtaining values on a smooth curve at round concentrations.[1] He claims, in fact, that the values interpolated by means of the writer's function yield, when treated according to his (Dr. Washburn's) method, the value $\Lambda_0 = 129.65$, a value practically identical with that deduced by Weiland. This is not correct. If the writer's interpolated values are treated in this way, the value $\Lambda_0 = 129.74$ will be obtained corresponding to the tangent $\Lambda_0' - P$ as shown in Fig. 4 of the writer's previous article.[2] The value $\Lambda_0 = 129.65$ corresponds approximately to the tangent $\Lambda_{01} - P'$ of the same figure. In this case the value assumed for the conductance at the concentration corresponding to the point P does not represent a value interpolated by means of the writer's function.

As was pointed out above, Washburn's method may indeed be applied to any form of curve and at any concentration, but the value of Λ_0 will be different for the different concentrations and for the different forms of curves, save in the exceptional case that Λ is a linear function of the concentration, in which case the mass-action law is actually obeyed.

It is evident that, in order to demonstrate that the mass-action law applies, it must be shown that the points in the Λ, C-plot lie on a straight line; that is, that a straight line will represent the results within a smaller limit of error than any other simple type of curve. This Weiland's measurements do not do. The average values of his measurements yield a curve distinctly convex toward the C-axis. Weiland's results, therefore, indicate that the mass-action law does not hold up to 2×10^{-5} N.

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THE EXTRAPOLATION OF CONDUCTIVITY DATA TO ZERO CONCENTRATION. FINAL REJOINDER.

BY EDWARD W. WASHBURN.

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From Kraus' latest contribution to the discussion of the above topic it is evident that the writer has failed entirely to make clear the nature of his method of extrapolation and its essential differences from previous methods. Despairing of his ability to improve the lucidity of his previous attempts, the writer desires only to add one more illustration in further refutation of Kraus' reiterated claim, that the character of the results obtained arise from the asserted "linear" nature of the interpolation curve which Weiland passed through his observed points, this interpola-

[1] Washburn, *loc. cit.*, p. 1084.

[2] THIS JOURNAL, 42, 11 (1920).