

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 $2 \times 10^{-5} N$.

WORCESTER, MASS.

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

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).

tion curve being incorrect and unjustified according to Kraus' point of view.

Now obviously one way of avoiding all question on this point is to abandon entirely the use of any interpolation curve and to apply the extrapolation method directly to the observed points. By such a method of procedure one, of course, loses the very desirable advantage of smoothing out the irregularities of the observations, these irregularities naturally appearing in a very highly magnified form in the $K_c - C$ diagram, but at all events no allegation of personal bias as to the proper locus and course of the $C - \lambda$ curve can be brought against the method.

Of the several series of measurements made by Weiland, one, that of January 24, contains 5 measured points ranging from 2 to 180 micro-equivalents per liter. Moreover, as evident from Fig. 10 of Weiland's paper, the points of this series are not only more numerous and regular than those of any other series, but by their location they evidently represent more nearly the average of all the measurements than do those of any other series. We shall, therefore, employ directly this series of points for extrapolation.

In this way the graphs shown in the accompanying figure are obtained, all attempts at smoothing being also avoided here. From these graphs the writer's method of extrapolation evidently places the true λ_0 value between 129.60 and 129.70, the most probable value being about 129.64 or 129.65, and this value is selected not at all for the reason that it gives results in agreement with the mass-action law, but for reasons which have been sufficiently explained above.

The above conclusion is, of course, wholly dependent upon the assumption that the data employed are correct and is valid only insofar as they are correct. Anyone is, of course, at liberty to claim that Weiland's data do not have the accuracy which their consistency with one another would seem to indicate and such a claim may indeed be true. Certainly the writer would not go so far as to assert the contrary, but until experimental proof of their inaccuracy is brought forward they are entitled to acceptance, at least tentatively, at their face value. To do otherwise would resemble too much Kraus' former proposal to reject Kohlrausch's data below 0.001 N because they did not harmonize with the empirical function which he had succeeded in fitting to the data above that point.

