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THE EXTRAPOLATION OF CONDUCTIVITY DATA TO ZERO CONCENTRATION. II.

BY EDWARD W. WASHBURN.

Received January 19, 1920.

The recent series of papers by the writer and H. J. Weiland,[1] dealing with the equivalent conductance of electrolytes in dilute aqueous solution, has recently been made the subject of adverse criticism by Kendall[2] and by Kraus.[3]

Kendall's criticism is to the effect that the method described by the writer for evaluating Λ_0 is "identical with, and founded on precisely the same assumption" as a method which Kendall employed in 1912, and is, therefore, not a new contribution, while Kraus's criticism is in substance to the general effect that the method in question is illogical, incorrect and quite unjustifiable either mathematically, physically, or chemically. As the points at issue deal with questions of fundamental importance to our interpretation of the behavior of strong electrolytes in dilute solution, it seems to the writer justifiable to discuss here in some further detail the method which he employed in evaluating Λ_0, especially with respect to those features of it which have been adversely criticised.

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[1] THIS JOURNAL, **40**, 106–158 (1918).

[2] *Ibid.*, **40**, 622 (1918).

[3] *Ibid.*, **42**, 1 (1920).

Kendall's Criticism.

Kendall's criticism, aside from its implication of carelessness on the part of the writer in failing to give him due credit for originating the method, would also imply that the agreement of potassium chloride with the mass-action law at high dilutions, as shown by Weiland's investigation, was due to the fact that the method of selecting Λ_0 was based upon the *a priori* assumption that within the range covered by the lowest concentrations measured, the mass-action law must be obeyed. Kendall applied his method only to acids, using it as a method for determining the conductivity of the hydrogen ion. He describes his method in the following words:[1] "The value of K_0 is found from the conductivity results of a series of dilutions by use of that particular value for the velocity of the hydrogen ion that gives values for $\frac{\alpha^2 C}{1 - \alpha}$ $(= K_E)$, slowly falling as dilution increases and ultimately approaching (so far as can be perceived within the experimental error) a limiting value."

His method thus involves the assumption that within the range covered by the data there shall be a series of (*i. e.*, more than 2) values of K_E which are constant within the experimental error. Such constant values do in fact appear in all of the tables (14 to 16, inclusive) which he uses to illustrate the application of his method. There is no suggestion in his paper that he considered his method to be a special case of a more general one which would be applicable also to cases where the observed values of K_E could not be made to become even approximately constant with any value of Λ_0 which might be selected. This is further borne out by the fact that when he has to deal with strong electrolytes, Kendall entirely abandons his method and employs a method which implicitly assumes that such electrolytes will not obey the mass-action law over any finite concentration range whatever. Further, in speaking of the behavior of hydrochloric acid, he states that "the values of $\frac{\alpha^2 C}{1 - \alpha}$ certainly do fall away as dilution increases to a limiting value K_0, but that limiting value is zero," thus apparently implying that he did not regard the value zero as necessarily inconsistent with the assumptions upon which his method was based.

Now a limiting value of zero[2] for K_E or an asymtotic (*i. e.*, asymtotic to the K_E axis) approach to some finite limiting value are both directly contradictory to the assumptions upon which the writer's method is based. Furthermore, his method is entirely applicable to the conduc-

[1] *J. Chem. Soc.*, 101, 1291 (1912).

[2] To state that the ionization constant of an electrolyte is zero is equivalent to stating that its free energy of ionization is infinite, in other words, that it is a "non-electrolyte."

tivity data for a strong electrolyte in regions where there is not the slightest evidence of obedience to the mass-action law with any value of Λ_0 which can be chosen. In these 2 fundamental respects the writer's method differs from that of Kendall, although the 2 methods will obviously outwardly resemble each other whenever the electrolyte to which they are applied actually does obey the mass-action law over a portion of the range covered by the experimental data.

To Kendall is due full credit for developing what seems to the writer the only logical method for determining Λ_0 in the case of electrolytes which obey the mass-action law within a portion of the concentration range covered by the measurements, and if the writer erred in failing to indicate the points of resemblance of his method to that of Kendall for such cases, he is glad of this opportunity to extend his apologies. The fact that Weiland's success in extending the data on potassium chloride below 0.0001 *N* yielded conductivity values which vary with the concentration in accordance with the mass-action law makes the writer's method, when applied to these data, resemble, apparently quite closely, the method of Kendall, since his method applied to such data will yield the same Λ_0 value.

A very important difference, between the 2 methods, however, lies in the fact that, if the conductivity values had not been found to vary with the concentration in accordance with the mass-action law, the writer's method of determining Λ_0 would still have been entirely applicable to the data, while Kendall's method would not. This can best be illustrated by applying the method to Kohlrausch's data for potassium chloride which extend only down to 0.0001 *N*.[1]

Before doing this, however, it may be well to restate the assumptions upon which the method is based. They are as follows: (1) Potassium chloride will obey the law of mass action over some *finite* range of concentration, but this range might, of course, be far below any limit which could be reached experimentally.

(2) In the neighborhood of a few ten-thousandths *N* and below, the behavior of potassium chloride with respect to the mass-action law must be such that whatever the magnitude of its deviation from that law may be, this magnitude will not increase (or change its sign) with further dilution, that is, the percentage change of K_E with C will not increase as C decreases, after C has become as small as 0.0001 or 0.0002 *N*. There is evidently no implication in either of these assumptions that the value of Λ_0 selected must be one which causes the deviations from the mass-action

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[1] In the writer's previous paper (p. 130) it was stated that the method could be employed to determine Λ_0 with an accuracy of about 0.2% in the case of conductance data which did not extend below 0.0001 *N*, but this statement was not further elaborated because it seemed to the writer that the applicability of the method to such data was sufficiently evident from the curves in Fig. 5 of that paper.

law to disappear gradually in the lower portion of the concentration range covered by the data, in fact as we shall show in a moment, values which might conceivably be assumed to produce this behavior are rejected by the method.

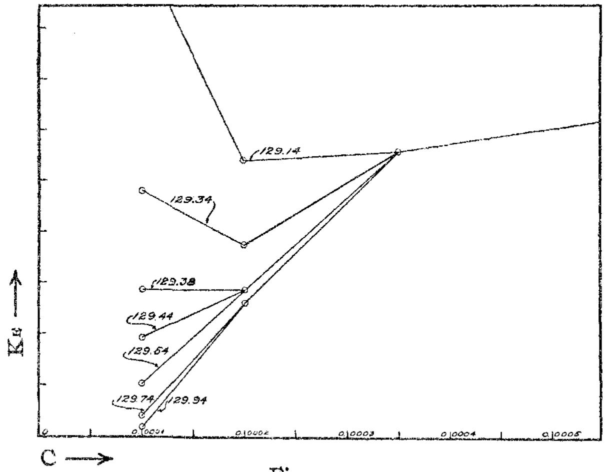

Fig. 1.

In order to illustrate this, a portion of Fig. 5 of the preceding paper (Fig. 2 of the present paper) lying between the concentrations 0.0001 and 0.00035 *N* will be magnified and instead of attempting to draw smooth curves between points, straight lines will be used. The figure thus obtained is shown herewith (Fig. 1). In constructing this figure the values of the ordinates of the different curves have been displaced so as to cause the curves to intersect at $C = 0.00035\ N$.

Applying the above 2 assumptions to this figure it is evident that the value $\Lambda_0 = 129.34$ is to be rejected and that similarly the value 129.7 (or thereabouts) is similarly to be rejected, as are all of the values which lie outside of the limits set by these two. It is evident from this figure that no value can be selected for Λ_0 which gives a behavior even approximately in accordance with the mass-action law, unless indeed the value 129.14 should be so selected on the assumption that the datum for 0.0001 *N* is inaccurate. Down to 0.0002 *N* the value 129.14 evidently gives a curve which does nor deviate very markedly from the requirements of the mass-action law and if the point at 0.0001 *N* were rejected (and such rejection might indeed have been justified previous to Weiland's work, on the grounds that at this low concentration small errors in the conductivity or in the method of applying the water correction would have a very large influence on the computed value of K_E), the application of Kendall's method to the data for potassium chloride might point to 129.14 as the most probable value for Λ_0. This value would, however, of course be rejected by the writer's method, which method does indeed not directly determine the value of Λ_0 at all, but merely places an upper and lower limit on it. The method is thus not a method of selection but rather a criterion for rejection.[1]

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[1] (Note by James Kendall).—"I am entirely in agreement with the differentiation

Kraus's Criticisms.

The first part of Kraus's paper is devoted to a mathematical analysis of the $K_E - C$ curve and this analysis is, in the main, accurate for the assumptions which he makes. In the interests of exactness the following points may be noted, however. The 2 sentences immediately following his Equation XI are exact statements only if the values assumed for Λ_0 are greater than approximately 129.65 in the first statement, and 129.5 in the second. The statement immediately following his inequality No. XII is obviously true, but in the writer's opinion the most important part of the statement is the conditional clause which introduces it. One of the fundamental differences in the view points of Kraus and the writer is brought out in the paragraph immediately following his inequality No. XIII. The writer is unable to see any force whatever in the arguments which he there advances.

In the previous paper by Kraus and Bray, these authors fitted to the conductance curve for potassium chloride the following empirical equation:

$$\frac{\Lambda^2 C}{a(a - \Lambda)} = b + c\left(C\,\frac{\Lambda}{a}\right)^d,$$

in which a, b, c and d are parameters to be evaluated from the data. They were able to fit the equation to the data, with satisfactory agreement, from the concentration $C = 3\ N$ down to $C = 0.001\ N$, but below the latter concentration the equation did not agree with the experimental data of Kohlrausch. Because of this, they argued that Kohlrausch's data below 0.001 N were incorrect, stating that it would be "an unjustifiable procedure to assume, after showing that a certain dilution law holds from 3 N to 0.001 N within the limits of experimental error, that the law suddenly undergoes an enormous change after reaching a dilution where there is good reason from a theoretical standpoint for believing that the law must hold."

This line of reasoning has already been discussed by the writer in his previous paper and the discussion need not be repeated here. Since the measurements by Weiland have confirmed those of Kohlrausch, Kraus in his last paper (p. 15) rejects the above conclusion of Kraus and Bray, but seeks, nevertheless, to retain intact the argument which lead to that conclusion, that is, since his equation cannot be fitted to the whole conductance curve from 3 N down, he proceeds, so to speak, to pull the equation down the curve so as to start it at about 0.02 N instead of 3 N. Then by re-evaluating the 4 parameters (and incidentally obtaining quite different values for them) he finds, not unnaturally, that the equation can be fitted satisfactorily to all of the lower end of the curve.

here drawn by Prof. Washburn between our respective methods for the determination of Λ_0, and extend my apologies in return to Prof. Washburn if I have erred in directing attention too strongly to the striking points of similarity which they exhibit."

Now the extrapolation of such purely empirical functions will naturally give as many different results for Λ_0 and K_0 as there are different kinds of empirical functions which can be fitted to the experimental data within the range open to measurement, and in this respect there is no particular virtue in the Kraus empirical function over others (for example, the Bates function), which might be equally satisfactorily fitted to the experimental portion of the curve. In fact we can never hope to determine Λ_0 and K_0 with any feeling of confidence unless the determination can be based upon some guiding principle other than the mere extrapolation of some one of the various empirical functions which might be fitted to the experimental data. The method employed by the writer is based upon such a guiding principle and if the principle in question is admitted to be reasonable (which Kraus does not admit), the method of employing it is mathematically sound. Before going into further detail concerning the reasons for making the assumptions upon which the method is based, we will first consider in sequence some of the specific criticisms which Kraus makes of the method and of the manner in which it is applied.

(1) On page 8 of his paper Kraus advances the opinion that an "erratic behavior" of a curve is to be judged not alone by the form of the primitive function but also by any unusual changes in its derivatives. He then proceeds to show that the first and second derivatives of the $K_E - C$ graph obtained by the writer's method are rather complex in their behavior. The argument that a given type of regular and smooth curve is to be condemned on the ground that its higher derivatives go through some rather rapid changes in certain regions, is at least a novel one. If potassium chloride is to obey the mass-action law over any finite range of concentration whatever, the $K_E - C$ curve *must* evidently be of exactly the type which the writer's method of extrapolation gives and its higher derivatives *must* exhibit the behavior which Kraus indicates. His condemnation of the method on the grounds of this behavior is, therefore, only a reiteration in other terms of his own view that it is unreasonable to assume that such electrolytes will obey the mass-action law within any finite concentration range whatever. Incidentally it may be noted that the atomic-heat curves of all the solid elements and the Debye and the Nernst-Lindemann equations which express them, have the same general form as the $K_E - C$ curve which Kraus condemns and their higher derivatives will exhibit the same "remarkable behavior," upon which he bases this condemnation. The reason why Kraus's own function can never exhibit such a behavior is, of course, merely because of its exponential form. There are plenty of other types of empirical functions which could be fitted just as satisfactorily to the data but whose derivatives would, of course, not behave like those of his exponential function.

(2) On p. 10 Kraus states that the writer's first assumption, namely,

that the values of K_E will eventually gradually approach a constant at extreme dilutions, is not fulfilled by the method of extrapolation. This statement is perhaps due to a misunderstanding. The expression "gradual approach to a constant limiting value," was intended to mean simply an *eventual* perpendicular approach to the E_E axis attained by a gradual and smooth decrease in K_E with decreasing C, and this assumption is certainly entirely consistent with the method of extrapolation employed.[1]

(3) Kraus further concludes (p. 12) that the writer's statement, "that no assumption is made as to the actual path over which values of K_E will approach the constant limiting value * * * * " is not correct, on the ground that this method of extrapolation is based on the assumption that K_E approaches its limiting value horizontally. Of course it is based upon this assumption, this being, as stated above, the first of the 2 assumptions which constitute the principle of the method, but nevertheless no assumption is made as to a particular mathematical equation with numerical parameters determined by the measured portion of the curve, which rigidly fixes the path of the curve below the lowest measured point. In this essential respect it differs from all of the "empirical function" methods of extrapolating.

(4) Kraus then criticises (p. 13) adversely Weiland's procedure by which he first treats individually each of his 4 series of measurements, subsequently averaging the results thus obtained. If there had existed only one set of measurements certainly no objections could have been made to treating this set by itself. It is difficult to see how the fact that more than one series of measurements was made should be considered an objection to the initial treatment of each series by itself, even without the suggestion of any possible cause for the slight differences among the different series. Kraus also objects to Weiland's suggestion that the cause of the slight differences among the different series might be small variations in the cell constant. He bases this objection upon the fact that in the cases of 2 of the 4 series finally employed (and a third one which was rejected), the concentrations were extended sufficiently high to enable the cell constant to be determined by comparison with Kohlrausch's data and that in these cases the cell constants were found to be identical within the experimental error. Whether or not the apparent deviations are to be ascribed to slight variations in the cell constant this seems hardly adequate grounds for objecting to the initial treatment of each series as consistent within itself. Moreover, it should be noted that a variation

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[1] It is true that the method could still be formally applied if the first assumption were dropped and only the second one used, but without the first assumption the second one would appear to be entirely arbitrary, because there would then be no particular reason why it should be valid. The 2 assumptions are complementary and together constitute a logical and reasonable principle upon which to base the determination of Λ_0.

in the cell constant, too small to be detected by comparison of the conductances of a 0.0001 N solution at the end of 2 different runs, might still be large enough to produce very appreciable differences in the K_E values calculated from measurements below 0.00005 N. Since with the data obtained in a single run, the cell constant cancels out of the mass-action expression, the procedure of initially treating each series by itself in order to eliminate any possibility of error due to a slight change in the cell constant is certainly not an illogical one.

(5) Kraus then advances the criticism (p. 13) that since the interpolation curves drawn by Weiland through his experimental points approximate straight lines, a tacit assumption, namely, that of linearity, is made, as to the manner in which the curves should proceed. It is difficult to understand how Kraus can offer this as an objection since in the preceding sentence he admits that Weiland's curves lie within the limits of the experimental errors. It is certainly a sound procedure for interpolation purposes to put a straight line, rather than some more complicated curve, through a series of experimental points, if the straight line fits the data within the experimental error. Such a procedure, of course, does not assume that some other type of curve might not also be drawn through the points and reproduce the data equally well.

If, however, as in this case, the data *require* a straight line or a curve approximating to it, it is hard to see why drawing such a curve can contain "a tacit assumption as to the manner in which the curves should proceed." The manner in which the curves should proceed is, within the experimental error of the data, determined by the loci of the observed points and not by any kind of assumption which it is possible to make, unless indeed one wished to admit the reasonableness of putting an *oscillating* curve through the points.

(6) On p. 14 Kraus makes a series of statements which he sums up in the following sentence: "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," and he goes on further to point out the obvious fact that it is possible to pass a great many curves through Weiland's observed points, all lying within the limits of experimental error. He then finally concludes that the "true form * * * * * is one convex toward the C-axis and not a straight line as Weiland and Washburn tacitly assume."

To these criticisms the writer must most emphatically demur. The result obtained by the writer's method of extrapolation is *not dependent* upon the passing of a straight line through the observed points. The *method* is entirely applicable, as already explained in the first part of this paper, *even though the points do not lie on a straight line or on anything resembling a straight line.* Furthermore, *any* empirical function which will express Weiland's data within the limits of experimental error, provided, of course, that some oscillating function like a sinusoidal curve is not employed, may be used (instead of the objectionable "straight line") for interpolating the values which are employed in constructing the family of $K_E - C$ curves shown in Fig. 2. This can be illustrated, for example, *by taking Kraus's own function* which he has fitted to these data and which, according to his own arguments, possesses all the desirable qualities which such a function should have, and employing *it* for the purpose of interpolating the necessary values for constructing the family of curves. If this is done a family of curves identical with that shown in Fig. 2 will be obtained, except that the central curve from which the others branch off will have the value of 129.65 instead of 129.64. In fact the only result of using different interpolation curves through the experimental points is to change slightly the Λ_0 value of this central curve of the family, a behavior which is in fact clearly illustrated by Weiland's own treatment of his 4 curves.[1]

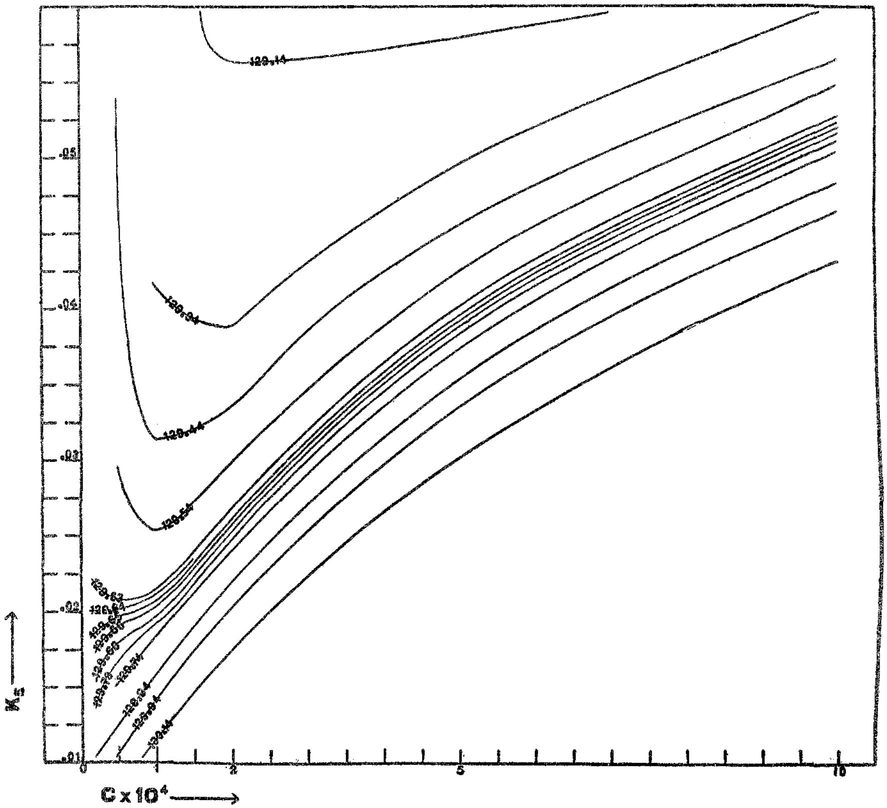

Fig. 2,

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[1] See Fig. 12, p. 143 of his paper.

The different curves in Fig. 2 are due to the selection of different assumed values for Λ_0. Among these various curves the criterion which the writer employs says that the true value of Λ_0 belongs to a curve lying between the 2 limits determined by the curves marked 129.63 and 129.65, while Kraus claims that the correct curve is the one marked 129.9. From studying this figure, it is difficult to see any reason whatever for selecting from the various curves there shown, the one marked 129.9 and claiming that it is the correct one. Certainly the selection of this curve must apparently be made without any adequate guiding principle. The curves marked 129.7 to 130.1 in the lower part of the figure appear to have no distinguishing characteristics which offer a basis for selecting one of them in preference to the others. The rejection of curve 129.63 and those above it and of curve 129.65 and those below it, however, is based upon the thoroughly reasonable assumption that immediately below the concentration 0.00005 *N* the mass-action expression for potassium chloride is not going to change with the concentration at a more rapid rate than it does at concentrations immediately higher, nor is the rate of change going to alter in sign.

The reasons for the 2 fundamental assumptions employed by the writer are the following. (1) The mass-action law is a direct deduction from the Second Law of Thermodynamics for any chemical equilibrium in a solution within which the thermodynamic environment of the reacting species remains constant. This will be the case whenever the solution is so dilute that the nature of the environment of each reacting species is determined entirely by the properties of the water molecules which surround it, the other ions and molecules being too far away to exert an appreciable influence upon its environment. In the nature of the case this condition will be attained after sufficient dilution but the degree of dilution required cannot, of course, be predicted in advance.

(2) The second assumption, namely, that, after a dilution of 5,- or 10,000 liters has been reached, the deviation from the mass-action law $\left(i.\ e., \frac{1}{K_E}\frac{\mathrm{d}K_E}{\mathrm{d}C}\right)$ will thereafter not at any rate increase with further dilution or change in sign, is perhaps more difficult to justify by formal reasoning. The selection of the particular dilution limits named is admittedly based largely upon "physico-chemical instinct" arising out of the whole body of knowledge which we have concerning the behavior of dilute solutions. In a 0.0001 *N* solution of potassium chloride the solute particles are on the average separated from one another by a distance of 60 water molecules and it seems not unreasonable to suppose that further separation will not at all events *accelerate* the rate at which the molal fugacity of any of the species is changing with the concentration.

The method employed by Kraus for evaluating Λ_0 is based upon, or 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-

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