The last objection is not needed in the condemnation of the method, however, since it is very plain that there is no relation between the sign of the electrical charge of a colloid and its capillarity ascent of a strip of filter paper which may be immersed in it.

The height of ascent is dependent upon the dilution of the sol, the presence of electrolyte, the external conditions such as surrounding atmosphere, and the nature of the filter paper used.

We believe that the method was innocently proposed due to the result of the peculiar circumstance that the positive colloids which the originators of the methods used were concentrated while their negative colloids were dilute. In fact it is very difficult to obtain the negative colloids in a concentrated state in the absence of a protective colloid. It is impossible to get the colloidal noble metals concentrated, we succeeded only with the sulfides.

New York City.

THE EQUIVALENT CONDUCTANCE OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION.

I. THE WATER CORRECTION.

By Edward W. Washburn.

Contents.—1. Introduction to the Series. 2. The Magnitude and Nature of the Water Correction. 3. The Stability of Conductivity Water in Contact with the Atmosphere. 4. The Carbonic Acid Concentration and the Acidity of Conductivity Water. 5. The Relation between Specific Conductance and Degree of Ionization. 6. Calculation of the Carbonic Acid Metathesis Correction. 7. Salts of Strong Acids and Bases. 8. Influence of Saline Impurities upon the Metathesis Correction. 9. Salts of Weak Acids and Bases. 10. Salts of Higher Valence Types. 11. Acids and Alkalies.

1. **Introduction to the Series.**—Any theoretical interpretation, in terms of the Ionic Theory, of the properties and behavior of solutions containing electrolytes involves as one of its essential factors a knowledge of the degrees of ionization of the electrolytes present in the solution. The most reliable method of determining the degree of ionization, α, of a uni-univalent electrolyte at the concentration C is by means of the relationship $\alpha = \Lambda_c/\Lambda_o$ where Λ_c is the *true equivalent conductance* of the electrolyte at the concentration C (corrected, if necessary, for viscosity influences) and Λ_o is its *true equivalent conductance* at zero concentration.

By *true equivalent conductance* is meant the equivalent conductance of the electrolyte at the concentration in question, when the solution contains no ions other than those resulting from the direct ionization of the elec-

trolyte itself.   The *measured equivalent conductance* differs in general from the true equivalent conductance not only directly, because of the presence of other ions (H^+ ion and OH^- ion from the water and other ions from impurities dissolved in the water), but also indirectly due to metathesis which occurs between the electrolyte and the water (hydrolysis) and between the electrolyte and the impurities present in the water.

The value of Λ_0 is usually obtained by extrapolating, to $C = 0$, some empirical function which is found to represent more or less satisfactorily the observed relation between Λ_c and C over at least the lower portions of the concentration range.   The lowest concentration to which any observer has hitherto found it practicable to push conductivity measurements is $C = 0.0001\ N$.   This limitation of the concentration range open to measurement is due to the magnitude of the "water correction" in the very dilute solutions and the uncertainty involved in applying it.

Conductivity   water   which   is   approximately   stable   in   contact with the atmosphere ("equilibrium water") has a specific conductance of the order of magnitude of 1×10^{-6} reciprocal ohms, due to the impurities (chiefly carbon dioxide) which it dissolves from the air.   The direct "water correction" which must therefore be made to the measured value of the conductivity of a dilute salt solution may amount at $C = 0.0001\ N$ to as much as *10 %*, at $C = 0.00001\ N$ to as much as *100 %*, and at $C = 0.000001\ N$ to as much as *1000 %* of the conductivity of the salt itself, and aside from the magnitude of the correction the proper method of applying it is rendered uncertain in many cases owing to our lack of knowledge as to the exact natures and amounts of the impurities present in the conductivity water, as well as to lack of sufficient constancy in the conductivity of the water during the time which is required to prepare and measure the conductivity of the salt solutions.

The Λ_0 values in use at present have, consequently, been obtained by extrapolation from conductivity data which in the most favorable cases do not extend below $C = 0.0001\ N$ and which in many cases stop at about $C = 0.001\ N$.   The values of Λ_0 deduced by different observers from the same conductivity data are, therefore, almost as numerous as the different functions which have been proposed for representing the data over the range open to measurement; ranging, for example, in the case of KCl at $18°$ from $\Lambda_0 = 127.9$ (Muller and Romann[1]), $\Lambda_0 = 128.3$, (Kraus and Bray) and $\Lambda_0 = 128.5$, (Wegscheider[2]), to $\Lambda_0 = 130.0$ (Kohlrausch, Noyes and Falk).   Now unless the Λ_0 value for a salt can be determined with a certainty of at least 0.01 to 0.02% we cannot hope to obtain any information concerning questions which involve a knowledge of the concentration of the un-ionized molecules of strong electrolytes in dilute solu-

[1] Muller and Romann, *Compt. rend.*, **157**, 400 (1913).
[2] *Z. physik. Chem.*, **69**, 624 (1909).

tions, such questions, for example, as the behavior of strong electrolytes with respect to the requirements of the Mass Action law.

About eight years ago the writer became convinced that the *only possible way* of securing an unequivocal answer to these much discussed questions was to obtain accurate conductivity data in the region of concentration below 0.0001 N and that in spite of the great difficulties which such an investigation presented, the questions at stake were of sufficient importance to make the attempt worth while. Accordingly, with the aid of a grant from the Bache Fund of the National Academy of Sciences, the investigation was begun in 1911.

The first part of the problem consisted in so developing and perfecting the Kohlrausch method for measuring electrolytic conductance that an accuracy of better than 0.01% could be obtained in measuring the conductance of very pure water and of these very dilute solutions. With the valued assistance of J. E. Bell and Karr Parker this part of the problem was so successfully solved that the resistance measurement itself can be made with practically no error whatever. This part of the work has already been partly published.[1]

The second part of the problem resolved itself into the preparation, in large quantities, of conductivity water which should be almost chemically pure and the preservation of the purity of this water during the operations of preparing and measuring the conductivity of the solutions. The methods by which this was successfully accomplished are described in the third paper of this series.

The problem of the correct method of extrapolating in order to obtain a reliable Λ_0 value is discussed in the second paper, while the fourth paper describes some new laws which have been established as a result of the investigation and presents a revised table of Λ_0 values computed by means of a new rule with the aid of which it is possible to calculate Λ_0 values from a single Λ_c value, for a sufficiently dilute solution.

2. **The Magnitude and Nature of the "Water Correction."**—The subject of the amount and nature of the impurities in conductivity water and the method of applying the "water correction" has been discussed by many investigators. A comprehensive review of previous work in this field and a new discussion of the problem has been given within the last year in a series of papers by James Kendall.[2] The recent publication of Kendall's papers renders it unnecessary to include here a review of the previous work on this topic and in fact all further discussion of the question would be omitted here were it not for the fact that the writer's conclusions are, in several important respects, at variance with those reached by Ken-

[1] THIS JOURNAL, **35**, 177 (1913); **38**, 2431 (1916); **39**, 235 (1917); and one additional paper by Washburn and Parker, yet to be prepared for publication.

[2] THIS JOURNAL, **38**, 1480 and 2460 (1916); **39**, 9 (1917).

dall. A sufficient discussion of the subject will therefore be presented to make clear the writer's views on the disputed points and the reasons therefor, as well as to present certain derivations and equations which will be employed in the subsequent papers of this series.

TABLE I.

Illustrating the Relative Magnitudes of the "Water Correction" in the Case of Conductivity Water of Different Degrees of Purity.

Concentration of KCl. Mol per liter.	Specific conductance of the salt $\times 10^6$.	Magnitude of the water correction expressed in per cent. of the conductance of the salt; for water having the specific conductance.		
$C.$	$L_E \times 10^6.$	$1 \times 10^6.$ [1]	$0.06 \times 10^6.$ [2]	$0.04 \times 10^6.$ [3]
0.000001	0.129	886.0	31.0	24.0
0.00001	1.296	44.0	4.4	3.0
0.0001	12.90	7.7	0.46	0.31
0.001	127.3	0.78	0.047	0.031
0.01	1224.0	0.082	0.0049	0.003
0.1	11200.0	0.009	0.00054	0.00036

The data in Table I illustrate the relative magnitudes of the "water correction" for different grades of conductivity water in the case of potassium chloride. The figures in the third column show clearly why it is impracticable to extend conductivity measurements below 0.0001 N when measurements are carried out in contact with the atmosphere, as long as the slightest uncertainty exists as to the exact value of the "water correction." The figures in Col. 5 illustrate the magnitude of the "water correction" for practically chemically pure water. A comparison between the values in Cols. 4 and 5 brings out the interesting fact that as far as salts of strong acids and bases are concerned there is practically no advantage to be gained in working with water which has a specific conductance lower than 0.06×10^{-6} since the magnitude of the "water correction" with this water is substantially the same as that for chemically pure water. Water for which this statement is true will hereafter be referred to as "ultra-pure conductivity water," a term suggested by Kendall.

Kendall in his discussion of this point makes the statement[4] that if it were possible to employ chemically pure water in conductivity work, "then it is obvious that we should never need to apply to our results any

[1] "Equilibrium water," *i. e.*, water saturated with carbon dioxide under atmospheric conditions. This is the grade of water employed in obtaining the most reliable conductivity data at present available.

[2] Water which can be prepared and kept in an atmosphere of purified air.

[3] Water obtained in small quantities by Kohlrausch and Heydweiller; practically chemically pure.

[4] THIS JOURNAL, 38, 2460 (1916); 39, 9 (1917).

'water correction' at all." This statement is somewhat inaccurate since with such water the correction at 0.0001 N would still amount to about 0.3% and that at 0.00001 N to about 3%. The advantage to be gained in working with the ultra-pure water is not the entire elimination of a "water correction" but rather the elimination of all uncertainty as to the correct method of applying such a correction.

There are two conceivable methods of obtaining reliable conductance data in very dilute solutions: one of these is to employ, for the conductivity measurements, water of a very high degree of purity under such conditions that no contamination can take place during the work; the other is to determine the amounts and nature of the impurities present in conductivity water in equilibrium with the atmosphere and then to calculate with the aid of the Mass Action law the corresponding metathesis corrections. Kendall considers the first method impracticable stating[1] that

"In order to do this, however, it would be essential to carry out all manipulations, preparation of solutions and measurements of conductivities in evacuated vessels. This is a feat which has been frequently attempted, but owing to the extraordinary experimental difficulties involved, not yet been successfully concluded."

The great difficulties associated with preparing and working with the ultra-pure water were thoroughly appreciated by the writer before the present investigation was started and this appreciation did not materially diminish during the first five years of the work. In spite, however, of the obvious difficulties of applying this method to the solution of the problem the writer is convinced that it is *the only one* of the two which is capable of yielding reliable results.

The second method—the one preferred by Kendall—does not seem to the writer capable of solving the problem at all, for the following reasons: first, because although undoubtedly most of the conductance of conductivity water in contact with the atmosphere is caused by carbon dioxide, the evidence brought together by Kendall does not demonstrate by any means that all of the conductance is due to this substance. In fact some of his evidence, as will be pointed out below (Sec. 11), shows, it seems to the writer very definitely that the conductance cannot all be due to carbon dioxide; second, because, as will be shown below, it is essential that the conductance of such water shall be maintained constant to 0.01% during the operations of preparing and measuring the conductivity of the solutions, a feat which would be quite as difficult as that of preparing and working with ultra-pure water.

3. **The Stability of Conductivity Water in Contact with the Atmosphere.**—If conductivity water in equilibrium with the atmosphere is employed, the "water correction" for a 0.00001 N solution amounts to about 40 % in case of potassium chloride and to about 100 % in case of

[1] THIS JOURNAL, **39**, 9 (1917); **38**, 2460 (1916).

LiCl.   In order, therefore, to avoid introducing an error of more than 0.01% when applying the "water correction" at this concentration, it would in general be necessary to maintain the conductivity of the water itself, constant, to within about 0.01% of its initial value.   Now, it is true that when very pure water is allowed to stand in contact with the atmosphere it absorbs carbon dioxide and its conductivity rises at first rapidly and then more slowly until it reaches a maximum value somewhere between 0.8 and 1.0×10^{-6} depending upon the atmospheric conditions of the locality.   This conductivity corresponds *approximately* to a saturated solution of carbon dioxide under atmospheric conditions[1] and such conductivity water is referred to in this paper as "equilibrium water."

If solutions are to be made up and handled in contact with the atmosphere, the logical procedure is, as repeatedly pointed out by Kohlrausch, to employ water whose conductivity does not change in contact with the atmosphere, rather than to employ a purer water than this.   It by no means follows, however, that the conductances of solutions below $0.0001\ N$ could be accurately determined by employing such water even though the only impurity in it were carbon dioxide and the method of applying the "water correction" not open to any question.   Before such a conclusion could be justified it would first be necessary to demonstrate that the conductivity of the "equilibrium water" is itself constant to the required degree of precision under working conditions.

Now the variability of the conductivity of "equilibrium water" will of course depend upon local conditions and experimental methods, so that a general exact quantitative answer to this question cannot be given.   The best that can be done is to present some data showing what the magnitude of the variation has amounted to in some specific instances.

This question was definitely investigated by Kohlrausch.   His investigations[2] extended over a whole week and show very clearly that there is considerable variability in the conductivity of such water even when air from outdoors is bubbled through it on different days.   Moreover, he states that if a current of air freed from carbon dioxide is drawn through equilibrium water so as to reduce its conductivity from 1.0 to 0.6 it does not again attain its original value on contact with the atmosphere.   Furthermore, he points out that air taken from the room exhibits a great and erratic variability.   The presence of a man or of a gas burner in the room can be easily detected from its influence upon the conductance of the water.

Kohlrausch's results are in accordance with the experience of the writer.

[1] Kohlrausch, *Gesammelte Abhandl.*, **2**, 871; Kendall, THIS JOURNAL, **38**, 2464 (1916).

[2] *Gesammelte Abhandl.*, **2**, 996.

In this connection the following experiment, carried out in the writer's laboratory, may be cited:

Conductivity water was collected hot in a three-liter quartz flask fitted with electrodes and with means for passing air through the water without permitting the water to come in contact with anything but quartz or platinum. Some of the same water was also placed in a bottle which was connected to the quartz flask in such a way that all the air which entered the quartz flask first bubbled through the water in the bottle. Air from the laboratory[1] was first drawn through the water in the quartz flask which was maintained at a temperature of $18°$ in an oil thermostat.

After about 24 hours of this treatment the water had a specific conductance of 0.836×10^{-6} reciprocal ohms, but did not exhibit any tendency to become constant to a very high degree or precision. It was therefore decided to draw the air from out of doors. The experiment was therefore continued with filtered outdoor air passing through the system. The following series of results was obtained, the air being shut off temporarily each time while the conductance measurement was made:

Time.	$L \times 10^6$.	Time.	$L \times 10^6$.
3.20 P.M.	0.836	8.20 A.M.	0.846
3.22 P.M.	Out of door air introduced	8.22 A.M.	Air supply shut off
3.50 P.M.	0.816	8.26 A.M.	0.848
4.10 P.M.	0.813	9.10 A M.	0.855
4.40 P.M.	0.810	9.11 A.M.	Flask shaken
6.35 P.M.	0.797	9.15 A.M.	0.860
7.10 A.M.	0.840	9.16 A.M.	Flask shaken again
7.35 A.M.	0.846	9.17 A.M.	0.8608
8.00 A.M.	0.850	9.26 A.M.	0.8648

It is evident from the above data that there is no tendency for the water to reach a sufficiently constant conductance with the air passing through it, even when, as in this experiment, the air is subjected to a preliminary washing with conductivity water.

The writer is unable, therefore, to accept the conclusion that in attacking the problem of the conductivity of very dilute solutions the most logical procedure is to employ "equilibrium water" and to compute an exact water correction on the assumption that the conductivity is due solely to carbon dioxide. It seems to the writer that one of the chief errors in any such conclusion arizes from the tacit assumption that it is more difficult to maintain, to the necessary degree of precision, the purity of "ultrapure conductivity water" than it is to maintain that of "equilibrium water." The entrance of a given amount of carbon dioxide into the con-

[1] The room in which the experiment was conducted was a laboratory especially located and designed to insure a minimum contamination of the air. No gas flames were in the neighborhood and no person was in the room except for the brief periods necessary for making the measurements, during which the observer was shut up in a telephone booth.

ductivity water produces, it is true, an enormously greater *relative* change in the conductivity of the "ultra-pure water" as compared with that produced in the conductivity of the "equilibrium water," but the *absolute* change in conductivity will be of approximately the same order of magnitude in both cases[1] and it is the *absolute change only, which is here involved.*   It should not, therefore, be much if any, more difficult to protect the ultra-pure water from contamination than it would be similarly to protect the equilibrium water from an equally harmful variation in its conductance.

4. The Carbonic Acid Concentration and the Acidity of Conductivity Water.—If the only impurity present in conductivity water is carbon dioxide, the total concentration, C_{CO_2}, of this substance can be calculated from the relation

$$C_{CO_2} = \frac{[H^+]^2_W}{K_I} + [H^+]_W - \frac{K_W}{K_I} - \frac{K_W}{[H^+]_W} \qquad (1)$$

where K_I and K_W are defined by the Equations 17 and 19.   The hydrogen-ion concentration, $[H^+]_W$, will be given by the expression

$$[H^+]_W = \frac{L_W \times 10^3}{2\Lambda_{H_2CO_3}}\left[1 + \sqrt{1 - \frac{4\Lambda_{H_2CO_3}(\Lambda_{OH} - \Lambda_{HCO_3})}{\Lambda^2_{H_2O}}\left(\frac{L_P}{L_W}\right)^2}\right] \qquad (2)$$

where L_W is the specific conductance of the conductivity water and L_P is the specific conductance of chemically pure water at the same temperature. For conductivity water in contact with the atmosphere Equation 2 reduces to the simple form

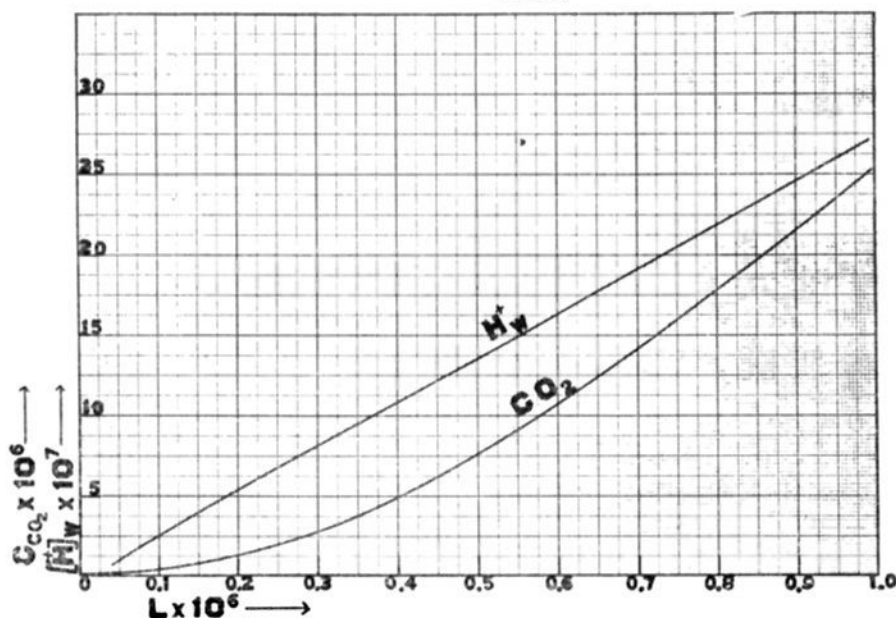$$[H^+]_W = \frac{L_W \times 10^3}{\Lambda_{H_2CO_3}}. \qquad (3)$$

Fig. 1.—Illustrating the relation between the conductance of conductivity water and (a) the carbon dioxide concentration, (b) the hydrogen-ion concentration.

[1] Cf. curve $[H^+]_w$ in Fig. 1.

Graphs showing the variation of C_{CO_2} and of $[H^+]_W$ with L_W at $18°$ are shown in Fig. 1.

5. The Relation between Specific Conductance and Degree of Ionization.—If a solution containing C equivalents of a salt BA per liter could be prepared with water possessing zero conductance, then the specific conductance L_E of this solution would be

$$1000\,L_E = \alpha C\,(\Lambda_B + \Lambda_A) \tag{4}$$

where α is the degree of ionization of the salt and Λ_B and Λ_A are the equivalent conductances of its two ions in the solution in question. In order, therefore, to calculate the degree of ionization of a salt from conductance data, it is the quantity L_E, that is, the *true specific conductance* of the salt, which must be determined.

Now in practice it is, of course, not possible to employ water possessing zero conductance. Consequently, the measured specific conductance of the salt solution will not be its true specific conductance. If the specific conductance of the conductivity water is L_W, then the measured specific conductance L_S of the resulting salt solution will be

$$L_S = L_W + L_E - \Delta L \tag{5}$$

where ΔL represents the total amount by which the *two conductances L_W and L_S* are decreased as a result of the metathetical processes which occur when the salt is dissolved in the water. These metathetical processes bring about a *decrease* in the total conductance owing to the formation of the un-ionized molecules BOH, HA, and $BHCO_3$, provided that carbon dioxide is the only impurity in the conductivity water which needs to be reckoned with. The purer the conductivity water and the higher the concentration of the salt, the smaller will be the percentage correction involved in the quantity ΔL. Even in the case of absolutely pure water, however, this metathesis correction would be very large in the case of salts of weak acids and bases.

6. Calculation of the Carbonic Acid Metathesis Correction.—*The General Equations.*—From Equation 5 we have

$$\Delta L = L_W + L_E - L_S \tag{6}$$

or substituting

$$1000\,\Delta L = (\Lambda_H[H^+]_W + \Lambda_{OH}[OH^-]_W + \Lambda_{HCO_3}[HCO_3^-]) + (\Lambda_B \alpha C + \Lambda_A \alpha C)$$
$$- (\Lambda_H[H^+]_S + \Lambda_{OH}[OH^-]_S + \Lambda_{HCO_3}[HCO_3^-]_S) +$$
$$\Lambda_B[B^+]_S + \Lambda_A[A^-]_S \tag{7}$$
$$= \Lambda_H \Delta_H + \Lambda_{OH} \Delta_{OH} + \Lambda_{HCO_3} \Delta_{HCO_3} + \Lambda_B \Delta_B + \Lambda_A \Delta_A \tag{8}$$

where

$$\Delta_H = [H^+]_W - [H^+]_S, \tag{9}$$
$$\Delta_B = \alpha C - [B^+]_S, \text{ etc.} \tag{10}$$

In the above expressions a bracketed symbol indicates the equivalent

concentration of the bracketed quantity and the subscript following the bracket indicates whether it is the concentration in the conductivity water (w) or in the salt solution (s) which is intended. The Δ's for the separate ions evidently indicate the decreases in the concentrations of the ions in question which result from the metatheses. The values of these individual ion Δ's and hence also the value of ΔL, the total metathesis correction, can be computed for all possible cases from the simultaneous solution of the following set of equations:

$$\frac{[B^+][A^-]}{[BA]} = K_S \qquad (11) \qquad\qquad [BA] = \frac{[B^+][A^-]}{K_S} \quad (12)$$

$$\frac{[H^+][A^-]}{[HA]} = K_A \qquad (13) \qquad [HA] = \frac{[H^+][A^-]}{K_A} = [H^+]\frac{\alpha C}{K_A} \quad (14)$$

$$\frac{[B^+][HCO_3^-]}{[BHCO_3]} = K_C \quad (15) \quad [BHCO_3] = \frac{[B^+][HCO_3^-]}{K_C} = [HCO_3^-]\frac{\alpha C}{K_C} \quad (16)$$

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_I \quad (17) \qquad\qquad [HCO_3^-] = \frac{K_I[H_2CO_3]}{[H^+]} \quad (18)$$

$$[H^+][OH^-] = K_W \quad (19) \qquad\qquad [BOH] = \frac{K_W \alpha C}{[H^+]K_B} \quad (20)$$

$$[H_2CO_3] + [HCO_3^-] + [BHCO_3] = C_{CO_2} \tag{21}$$

$$[H_2CO_3] + \frac{K_I[H_2CO_3]}{[H^+]} + \frac{K_I[H_2CO_3]\alpha C}{[H^+]K_C} = C_{CO_2} \tag{22}$$

$$[H_2CO_3] = C_{CO_2} \div \left(1 + \frac{K_I}{[H^+]}\left(1 + \frac{\alpha C}{K_C}\right)\right) \tag{23}$$

$$[HCO_3^-] = K_I C_{CO_2} \div \left([H^+] + K_I\left(1 + \frac{\alpha C}{K_C}\right)\right) \tag{24}$$

$$[BHCO_3] = K_I C_{CO_2}\alpha C \div K_C\left([H^+] + K_I\left(1 + \frac{\alpha C}{K_C}\right)\right) \tag{25}$$

$$[B^+] + [BA] + [BHCO_3] + [BOH] = C \tag{26}$$
$$[A^-] + [BA] + [HA] = C \tag{27}$$
$$[H^+] + [B^+] = [HCO_3^-] + [A^-] + [OH^-] \tag{28}$$

The general solution of this set of equations will not be discussed here as only the special case of a salt of a strong acid and base will be required in what follows. For this case the solution of the equations can be considerably simplified as the metathesis correction will obviously be very small.

7. The Carbonic Acid Metathesis Correction for Salts of Strong Acids and Bases.—For this case we can write

$$K_A = K_C = K_S = \frac{\alpha^2 C}{1 - \alpha}. \tag{29}$$

Making this substitution and solving the above set of equations we find the following sufficiently exact expressions:

$$\Delta_H = [H^+]_W - [H^+]_S =$$

$$\frac{\left[1 - \alpha - \dfrac{\{[H^+]_W(1 - \alpha) + \alpha\Delta_H\}\alpha}{K_I + \alpha([H^+]_W - \Delta_H)}\right]\left([H^+]_W - \dfrac{K_W}{[H^+]_W}\right)}{2 + \left[\alpha + \dfrac{\{[H^+]_W(1 - \alpha) + \alpha\Delta_H\}\alpha}{K_I + \alpha([H^+]_W - \Delta_H)}\right]\left(\dfrac{K_W}{[H^+]^2_W} - 1\right) - \dfrac{\Delta_H}{[H^+]_W}} \quad (30)$$

from which Δ_H can be obtained by a series (three) of approximations, $[H^+]_W$ being given by Equation 3 and α being obtainable from Table VII;

$$\Delta_B = \Delta_A = \frac{(1 - \alpha)[H^+]_S}{2 - \alpha}\left[1 - \frac{\Delta_B}{\alpha C}\right] =$$

$$\text{(approx.)} \ \frac{(1 - \alpha)([H^+]_W - \Delta_H)}{2 - \alpha} \quad (31)$$

$$\Delta_{HCO_3} = \frac{[K_I(1 - \alpha) - \alpha\Delta_H]([H^+]^2_W - K_W)}{[K_I + \alpha([H^+]_W - \Delta_H)][H^+]_W} \quad (32)$$

and

$$\Delta_{OH} = \frac{- K_W\Delta_H}{[H^+]^2_W - [H^+]_W\Delta_H}. \quad (33)$$

By means of these equations and Equation 7 the value of ΔL, the total metathesis correction, can now be calculated for any uni-univalent salt of a strong acid and base.

For conductivity water in contact with atmosphere Δ_{OH} will be entirely negligible and we can write Equation 8 in the form

$$1000 \ \Delta L = (\Lambda_H + \Lambda_{HCO_3}) \ \Delta_H + (\Lambda_B + \Lambda_A) \ \Delta_B \quad (34)$$

or

$$1000 \ \Delta L = \Lambda_{H_2CO_3}\Delta_H + \Lambda_{BA}\Delta_B. \quad (35)$$

This shows that the total carbonic acid metathesis correction for conductivity water in contact with the atmosphere can be regarded as made up of two parts, one part representing the decrease in the conducting power of the carbonic acid, the other the decrease in the conducting power of the dissolved salt.

The value of the metathesis correction expressed in terms of per cent. of the conductance of the salt will be

$$P_M = \frac{100\Delta L}{L_E} = \frac{\Lambda_{H_2CO_3}}{10L_E} \ \Delta_H + \frac{\Lambda_{BA}}{10L_E}\Delta_B \quad (36)$$

$$= \frac{\Lambda_{H_2CO_3}}{\Lambda_{BA}} \times \frac{100\Delta_H}{\alpha C} + \frac{100\Delta_B}{\alpha C} = P_I + P_S. \quad (37)$$

Curve A in Fig. 2 shows values of $P_I \times \Lambda_{BA}/\Lambda_{H_2CO_3}$ as a function of C, for "equilibrium water" at 18°. In order, therefore, to find the value of the

metathesis correction due to the decrease in the conducting power of the carbonic acid, we have only to multiply the abscissa of the desired point on Curve A by the ratio $\Lambda_{H_2CO_3}/\Lambda_{BA}$. Thus for example, for a 0.0001 N solution of KCl at 18° this part of the metathesis correction would be

$$P_I = 0.54 \; 353/129 = 0.0015\%.$$

Curves B and E in the same figure show, directly, values of P_S (in thousandths of a per cent.) as a function of C. Curve E is simply the lower portion of Curve B with the ordinate scale magnified 100-fold. From Curves A and B it is evident that the total metathesis correction increases with dilution and approaches a constant limiting value at high dilutions. Curve D shows the *total* metathesis correction, P_M, (in thousandths of a per cent.) as a function of the concentration in the case of KCl at 18°. The correction amounts to only 0.004% at 0.003 N and increases with dilution at first gradually and then more rapidly, reaching a limiting value of 0.016 % at high dilutions.

Owing to the fact that P_I is such a small part of the total correction P_M, an approximate expression may be substituted for its influence with-
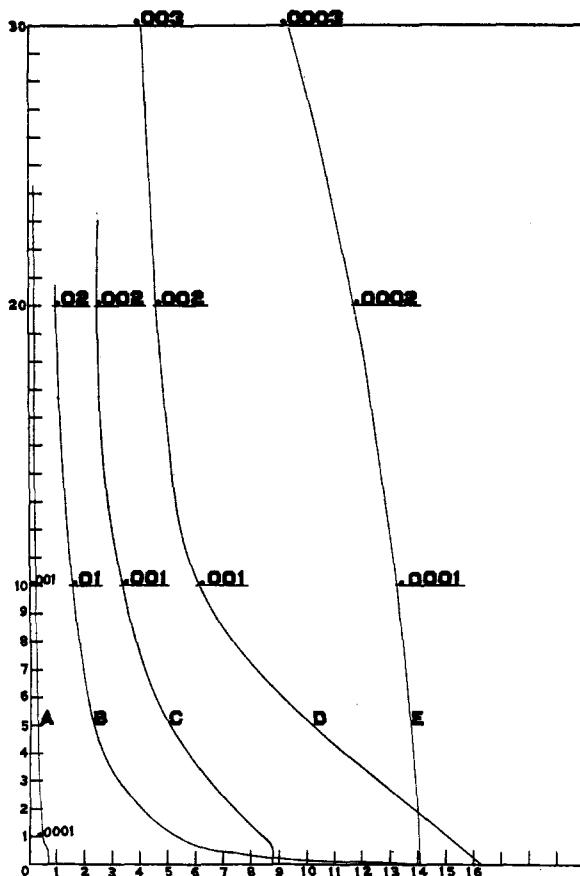

Fig. 2.—Curves illustrating the metathesis corrections for conductivity water. The abscissa scale represents thousandths of a per cent. in the case of Curves A, B, D and E, and hundredths of a per cent. in the case of Curve C. The ordinate scales represent concentration of the electrolyte and are indicated on each curve.

out significant loss of accuracy. From a study of Curves A, B, and D, and the equations upon which they are based, we find that for P_M we

can write with sufficient exactness, in place of Equation 37, the approximate expression

$$P_M = 1.15(2 - \alpha)P_S = \frac{115\Delta_B(2 - \alpha)}{\alpha C}. \tag{38}$$

Combining this with Equation 31 and neglecting Δ_H we have

$$P_M = \frac{115(1 - \alpha)}{\alpha C}[H^+]_W. \tag{39}$$

Substituting for $[H^+]_W$ from Equation 3 gives finally

$$P_M = \frac{1.15 \cdot 10^6 \alpha L_W}{\Lambda_{H_2CO_3} K_E}, \tag{40}$$

an expression from which one could calculate the metathesis correction for any uni-univalent salt of a strong acid and base dissolved in any conductivity water containing only carbon dioxide as an impurity. The expression is applicable for room temperatures, and values for K_E and α may be obtained from Table VII. The quantity P_M thus calculated represents the correction *in per cent.* which must be *added* to the ordinary "water corrected" value of the specific conductance (*i. e.*, to $L_S - L_W$) in order to obtain the *true specific conductance of the salt*, assuming all the time that CO_2 is the only impurity in the conductivity water. For example, for a 0.00005 N solution at 18° we have (Table VII) $K_E = 0.0210$, $\alpha = 1$, and $\Lambda_{H_2CO_3} = 353$. Substituting we find if $L_W = 1 \times 10^{-6}$, $P_M = 0.016\%$.

Before closing this discussion reference should be made to the work of previous investigators on this subject. For a fuller presentation and discussion of such work, together with a bibliography, the reader is referred to the papers by Kendall already mentioned.[1] The first important contribution to the subject, insofar as it concerns salts of strong acids and bases, was made by Arrhenius[2] about four years ago in connection with a general discussion of the "carbonic acid correction." Arrhenius computed the values of this correction for some dilute solutions of sodium chloride and sodium nitrate and obtained results and conclusions which directly contradict those of the writer. If the writer correctly interprets him, Arrhenius concludes that the "carbonic acid correction" for the salt of a strong acid and base (sodium chloride) dissolved in equilibrium water at 18°, is *negative in sign*, starting at zero for high dilutions, reaching a maximum of -0.1% at about 0.0001 N and then falling away to zero again at higher concentrations. This is a complete contradiction of the writer's conclusion that this correction should be *positive in sign* and should *increase continuously* with dilution reaching a maximum value of only +0.016% at high dilutions.

Kendall in his own discussion of this question apparently reaches the

[1] *Loc. cit.*, **39**, 18.
[2] Arrhenius, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, No. 42 (1913), especially p. 10.

same conclusion that Arrhenius does[1], since he reproduces Arrhenius' calculations for sodium chloride as an illustrative example and states finally in his summary that the present "water corrected" values are slightly *too large*.[2] Neither Arrhenius nor Kendall gives any details of the calculations from which his conclusions were reached.

8. **Influence of Saline Impurities upon the Metathesis Correction.**— Let us assume in the following calculation that the conductivity of the "conductivity water" is due entirely to the presence of a strong electrolyte $B'A'$ whose equivalent conductance is Λ'. The products of metathesis will be the un-ionized molecules BA' and $B'A$ which, in the case under consideration, will be produced in equal amounts. The total concentration of the salt $B'A'$ will be $\dfrac{1000\,L_W}{\Lambda'}$

The decrease Δ_I in the concentration of each ion species owing to metathesis will evidently be the same for all the four ions involved and will be practically equal to the number of equivalents of BA' formed, which is given with sufficient accuracy by the following expression:

$$[BA'] = \Delta_I = \frac{\alpha C \times \alpha' C'}{K_E}. \tag{41}$$

The percentage decrease in the conductance due to the metathetical removal of the ions of each salt will therefore be

$$0.01 P_{BA} = \frac{\Lambda\,\Delta_I}{1000\,L_E} \tag{42}$$

or

$$P_{BA} = \frac{100\Lambda\alpha C\alpha'C'}{K_E\dfrac{C\Lambda}{1000} \times 1000} = \frac{100\alpha C'}{K_E} \tag{43}$$

for the ions for the salt BA; and similarly

$$P_{B'A'} = \frac{\Lambda'\alpha\alpha'C'}{K_E\,\Lambda} \tag{44}$$

for the ions of the salt $B'A'$.

Putting $C' = \dfrac{10^3 L_W}{\Lambda'}$ and adding, we find the total percentage metathesis correction to be

[1] Or else he accepts Arrhenius' conclusions without having given the subject any study himself. It is not entirely clear from his treatment of the subject just what is the real basis for his attitude on this point.

[2] His contradictory statement near the bottom of page 11 of the same paper is assumed by the writer to be unintentional and his true views on the subject are assumed to be those stated in the latter part of his paper which are in accord with those of Arrhenius.

$$P'_M = \frac{10^5 L_W \alpha}{K_E}\left(\frac{1}{\Lambda'} + \frac{\alpha}{\Lambda}\right)$$ (45)

in which α has been written for α', and $\Lambda_C = \Lambda_0$ for both salts.

Curve C in Fig. 2. shows how P'_M varies with C in the case of potassium chloride, for $L_W = 10^{-6}$ and Λ' taken as 100. For this curve the abscissa scale represents *hundredths of a per cent.* instead of thousandths. By comparing Curves C and D it is evident that the metathesis correction due to a salt impurity in the conductivity water would be about *twenty times as large* as that due to a carbon dioxide impurity, for the same value of L_W.

In view of our lack of knowledge concerning the exact natures and amounts of the impurities present in the conductivity water employed by Kohlrausch, the following somewhat arbitrary method of correcting his data is proposed: From Curve D in Fig. 2 we find that the "carbon dioxide corrections" at 0.0001 N and 0.0002 N would be 0.015 and 0.016%, respectively. Since, however, the water employed by Kohlrausch contained some traces at least of basic or saline impurities (see below, Sec. 11), the true metathesis correction would be somewhat larger than the above figures. In lieu of any exact information, the writer proposes the round value 0.02% as the metathesis correction for these two concentrations, and the round value 0.01% for the concentrations 0.0005 N and 0.001 N, respectively, with no correction for higher concentrations. These corrections are at all events not too large and may be safely regarded as having all the accuracy that Kohlrausch's data themselves justify; in fact they are within the experimental error of Kohlrausch's measurements. The above corrections apply only to salts of strong acids and bases.

9. **Salts of Weak Acids and Bases.**—If the conductivities of solutions of sodium acetate could be studied at low concentrations (0.0001 N and below) with *absolutely pure water*, then in addition to a very appreciable "water correction" which would be *subtracted* in the usual manner, there would also be a comparatively large (*e. g.*, about 0.4% at 0.0001 N) metathesis correction which would have to be *added*. This metathesis correction would be the larger, the weaker the acid and it would be greatly increased by the presence of carbon dioxide in the water. In the case of absolutely pure water, however, practically no error would be involved in applying this correction since it could be accurately calculated, provided that the ionization constant of the acid were known with sufficient accuracy.

In the case of "equilibrium water," however, considerable uncertainty would be attached to the calculation of the metathesis correction owing: (1) to the magnitude of the correction; (2) to the uncertainty as to how much of the conductivity of the water could be ascribed to the carbonic acid; (3) to the uncertainty as to the natures of the other impurities and

the metatheses which they would produce; and (4) to the already mentioned difficulty of maintaining a sufficient degree of constancy in the composition of equilibrium water under working conditions, owing to the variability of the atmosphere. For these reasons it seems to the writer that the only possible method for securing really dependable Λ_0 values in the case of salts of weak acids or bases (and consequently for determining the anion conductances of these weak acids and bases) is to employ "ultra-pure conductivity water" in making the measurements at high dilutions. Undoubtedly much more accurate conductance values than those at present accepted for salts of strong bases with weak acids can be obtained by applying a "carbonic acid correction" to the data now available,[1] but the weaker the acid involved, the greater will be the uncertainty attached to this procedure.

In the case of a salt of a weak base with a strong acid the presence of carbonic acid in the conductivity water tends to reduce the hydrolysis, and if the base is not too weak, a salt of this kind would behave very much like the salt of a strong acid and base. It is perhaps for this reason, for example, that the conductivity data given for thallous chloride and thallous nitrate appear to be substantially correct.

10. Salts of Higher Valence Types.—Owing to the presence of intermediate ions in solutions of salts of mixed valence types, such as K_2SO_4 and $MgCl_2$, the conductances of bi- and poly-valent ions are best obtained from the Λ_0 values for salts of unmixed valence types; for example, the conductance of magnesium ion could probably be most reliably calculated by determining the Λ_0 value for magnesium sulfate rather than from attempting to determine directly the Λ_0 value of magnesium chloride. In all cases the metathesis corrections for salts of the higher valence types are *very much larger*[2] than they are for uni-univalent salts and furthermore there would always exist some uncertainty in applying a "carbonic acid correction" to a salt such as $MgSO_4$, owing to the formation in unknown amounts of the un-ionized molecules $MgCO_3$, $Mg(HCO_3)_2$, H_2SO_4 and $Mg(HSO_4)_2$. The present Λ_0 values for all salts of higher valence types must therefore be regarded as of *very doubtful accuracy*.

11. Acids and Alkalies.—A very considerable degree of uncertainty exists at the present time regarding the values of the conductances of hydrogen ion and hydroxyl ion owing to the entire lack of accurate values for the true specific conductances of dilute solutions of acids and alkalies. It has been noticed by numerous investigators that the measured values of the equivalent conductances of strong acids reach a maximum at about 0.0001 to 0.0002 N thereafter decreasing again. This so-called "abnormal

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[1] Cf. Kendall's recalculation of the data for NaF, THIS JOURNAL, **39**, 22 (1917).

[2] For example, if $MgSO_4$ is 90% ionized at $C = 0.0001$ N, the "carbonic acid" correction for equilibrium water would be more than 0.3%, possibly as much as 0.5%, as compared with only 0.015% for a uni-univalent salt.

behavior" is also exhibited even after a "carbonic acid correction" has been applied to the data, as Kendall discovered.[1]

Because of this behavior Kendall considers that "there must exist some general disturbing influence not yet taken into consideration," and he promises a more detailed discussion of this matter in a later paper. With this statement of Kendall's the writer finds himself in complete accord, with, however, the added conclusion[2] that the "general disturbing influence" referred to is the presence of basic or saline impurities, or both, in the conductivity water, in amounts which are far from being negligible. The influences of such impurities are much more apparent when studying solutions of acids than in the case of neutral salt solutions because metathesis is larger and results in the removal of the ion to which 80% or more of the conductance of the electrolyte is due. It seems, therefore, to the writer than the above so-called "abnormal behavior" of acids should be taken as conclusive proof that the whole of the conducting impurity in ordinary conductivity water cannot in general be regarded as carbonic acid and hence that any proposal to employ equilibrium water and to calculate "exact" metathesis corrections cannot be approved as a general and primary method for obtaining true specific conductances at high dilutions.[3]

URBANA, ILL.

THE EQUIVALENT CONDUCTANCE OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION.

II. THE EXTRAPOLATION OF CONDUCTIVITY DATA TO ZERO CONCENTRATION.

BY EDWARD W. WASHBURN.

CONTENTS.—1. Introduction. 2. The Method of Kohlrausch. 3. The Method of A. A. Noyes. 4. The Equation of Kraus. 5. The Equation of Bates. 6. A New Graphical Method of Extrapolating. 7. Bates Method for Computing Λ_o.

1. **Introduction.**—In order to determine the value of Λ_o and also the limiting value K_o of the Mass-Action expression

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[1] THIS JOURNAL, **39**, 13 (1917). The "carbonic acid correction" in this instance was, within the experimental error of the data employed, equal to the water correction, which it, therefore, canceled.

[2] Frequently suggested in the past by various investigators.

[3] In footnote 1, page 13, of his second paper, Kendall makes the statement that "The concentrations of any other electrolytes present must be so minute that the conclusions obtained cannot, in any case, be significantly affected." It seems to the writer that such a statement fails to give sufficient weight to the fact that in many cases saline or alkaline impurities are much more effective than carbon dioxide. This is true even, for example, in the simple case of neutral salts as explained in Sec. 8 above. Cf. Kohlrausch and Holborn, *Leitvermögen*, p. 92.