solution was always precipitated, irrespective of the nature of the solute or of the amount in solution.

TABLE VIII.

Substance.	Poorer solvent.	Better solvent.	$K = \frac{C_1 - C_2}{C_1}$.
Lithium chloride (42)	Benzene (78)	Acetone (58)	0.35
Acetanilide (135)	Ether (74.1)	Chloroform (119.4)	0.28
Strychnine (334)	Ether (74.1)	Chloroform (119.4)	0.32
		Av.,	0.32

There have been only a few cases of nonaqueous solvents observed where the simple relationship given above can be applied. It will take more work of a very accurate nature to establish such a point and to develop a more general relationship for the more complicated cases.

COLUMBIA, MO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 290.][1]

THE WATER CORRECTION IN CONDUCTIVITY DETERMINATIONS.[2]

BY JAMES KENDALL.

Received November 13, 1916.

When we speak of measuring the "conductivity of an electrolyte" in aqueous solution, we are liable to overlook the fact that the quantity actually derived from our experimental results is the specific conductivity of the *solution*. The physical properties of a solution may always be resolved into two factors, functions of the solvent and the solute respectively. These two quantities are in this case not directly additive, but will influence one another to an extent that cannot be calculated unless we know the nature and the concentration of *all* the ions present. The exact evaluation of the specific conductivity of an electrolyte is therefore by no means a simple problem.

In the study of concentrated and moderate dilute solutions, however, the solvent factor is often negligible. The specific conductivity of carefully prepared "conductivity water" is so small in comparison with the

---

[1] A paper presented at the Seattle meeting of the American Chemical Society, August, 1915.

[2] This article consists of an examination and extension of the existing conductivity data for electrolytes of various types in very dilute aqueous solution, and aims at establishing the exact correction necessary in each case for the elimination of the conductivity of the solvent. The experimental work preliminary to the investigation has already appeared in recent communications (Kendall, THIS JOURNAL, 38, 1480 and 2460 (1916)), to which reference should be made for numerical data.

specific conductivity of the dissolved electrolyte that neither its direct nor its indirect effect needs to be taken into account. For all practical purposes, the conductivity of the solution is identical with the conductivity of the solute.

Nevertheless, when we come to the exact investigation of more dilute solutions, the specific conductivity of the solvent finally becomes appreciable, since it remains constant while the specific conductivity of the solute (whether a strong, transition or weak electrolyte) decreases rapidly. The ratio of the solvent conductivity to the total conductivity may thus, even though special precautions are taken, reach a value of several per cent. The most accurate measurements at very high dilutions at present available are probably those of Kohlrausch and Maltby[1] for the chlorides of potassium and sodium. The specific conductivity of the water employed in these determinations bore the following percentage ratios to the total observed conductivity of the solutions:

Dilution of the solute in liters	100	200	500	1000	2000	5000	10000
% water conductivity (KCl)	0.1	0.2	0.4	0.7	1.3	3.2	6.2
% water conductivity (NaCl)	0.1	0.2	0.4	0.8	1.6	3.9	7.4

It will be evident from this one illustration that if we wish to obtain the *exact* specific conductivity of *any electrolyte* at such high dilutions we must know how to apply to our experimental results an accurate correction, which will eliminate entirely not only the *direct* but also the *indirect* effect of the specific conductivity of the solvent.

The importance of such an accurate water correction will be recognized at once by all who are familiar with recent work in the field of very dilute solutions. It is absolutely essential, before we can put to a strict test any of the various formulas—empirical and otherwise—that have been proposed for the expression of the dissociation equilibrium of strong electrolytes, that we have perfectly trustworthy values for the specific conductivities of these electrolytes at very high dilutions. Until the question of an exact water correction is satisfactorily settled, all measurements at high dilution are open to suspicion. Even the results of Kohlrausch and Maltby for potassium chloride have recently been challenged by Kraus and Bray,[2] who discovered that their general dissociation formula did not reproduce these results at very high dilutions. Kraus and Bray make the following statement:

> There is always a possibility that the discrepancy in these dilute solutions is due to experimental error, such as uncertainty in the correction for the conductance of the solvent. An increase of 10% in the correction for the solvent would bring the conductance between 0.001 N and 0.0001 N into agreement with Equation III.[3] It should

---

[1] Kohlrausch and Maltby, *Wiss. Abhandl. Phys.-Techn. Reichsanstalt*, **3**, 156 (1900).

[2] Kraus and Bray, THIS JOURNAL, **35**, 1413 (1913).

[3] The four-constant empirical equation proposed by Kraus and Bray in the above investigation as applicable to all solutions of electrolytes.

be borne in mind that in these dilute solutions we have a highly complex equilibrium between the solute, the solvent and its ions, and an unknown constituent which, in part, probably consists of carbonic acid. Taking all these factors into account, it may well be expected that the corrections made for the solvent are in error by as much as 10%.

The only comment that can be made upon the above quotation is that if the results of Kohlrausch and Maltby are *not* trustworthy, then there exist no reliable data at all for strong electrolytes in very dilute solution, and our present knowledge as to their dissociation equilibria at high dilutions is just *nil.* The problem of the abnormality of strong electrolytes[1] becomes, therefore, a problem which cannot possibly be solved so long as we are forced to apply an uncertain water correction to our otherwise accurate experimental results.

The examination of this "water correction" is taken up in the following sections. Needless to say, the subject is one which has been frequently attempted by previous investigators, since all who have performed conductivity work in the region of very dilute solutions have suggested *some* means of correcting for the specific conductivity of the water employed, in order to standardize their results. In nearly all cases the corrections proposed, however, have admittedly been only approximate. The effort has been made here to establish quantitatively exact corrections.

There are two methods available for attacking this problem. One is to obtain water of such a high degree of purity that its specific conductivity will be quite negligible even at the highest dilutions to be examined. The other is to discover the nature and concentration of the conducting impurities in the water employed and to calculate their total influence upon the specific conductivity of the solute. The present impracticability of the first method has been pointed out in a preceding paper;[2] the second method is considered below. Since the subject has not previously been *systematically* examined,[3] the work of former investigators and the bearing of their particular results upon the general problem may be briefly discussed.

Previous Work.

The earliest efforts are scarcely entitled to be called more than rule-of-thumb methods. The first general procedure appears to have been to subtract the whole of the specific conductivity of the water. This answered fairly well in the case of neutral salts, but for acids and bases the results so obtained were obviously incorrect, since the molecular con-

---

[1] See Wegscheider, *Z. physik. Chem.*, **69**, 603 (1909); Partington, *J. Chem. Soc.*, **97**, 1158 (1910); Kendall, *J. Phys. Chem.*, **19**, 197 (1915) and previous papers.

[2] Kendall, THIS JOURNAL, **38**, 2460 (1916).

[3] Exact data necessary for the calculations not being available. See, however, Arrhenius, *Meddel. K. Vetenskapsakademiens Nobelinstitut*, Band **2**, No. 42 (1913).

ductivity, instead of tending towards a maximum, showed values decreasing with increasing dilution.[1] The empirical procedure of applying either half of the water correction or none at all was adopted to obviate this. The classical investigations of Arrhenius,[2] Ostwald,[3] and Bredig[4] are examples of early accurate work upon the three types of electrolytes (salts, acids and bases), respectively. The most exact measurements at high dilutions, however, are those made by Kohlrausch.[5]

Kohlrausch recognized that the main impurities in conductivity water are carbonic acid (derived from the atmosphere) and ammonia (derived from the organic impurities present in the water). The presence of *neutral salts* would not be expected to change the ionization of these at all appreciably, hence practically correct values are obtained by direct subtraction of the whole of the "water conductivity." This procedure was followed by Kohlrausch and his co-workers in all investigations.[6] Kohlrausch admits, however, that the method cannot be quite exact. It is more probable that values so corrected are too low than too high, but uncorrected values are certainly far too high.[7]

With regard to *acids* and *bases*, Kohlrausch was of the opinion that it is quite impossible to investigate these successfully at high dilutions in view of the disturbing influence of the acidic and basic impurities present. The various suggestions made for these, to subtract half or none of the water conductivity, he rejected as meaningless, since even if by chance they should give true values occasionally, the procedure adopted was quite without foundation.[8]

A further disturbing note was struck by Arrhenius,[9] in a research on the effect of neutral salts upon the strength of weak acids. Arrhenius concluded from his experimental results that the ionization constant of a weak acid is increased by the addition of a neutral salt. The bearing of this upon the "water correction" is important, for if the neutral salt under examination increases the dissociation of the carbonic acid present as impurity in the water, it is evident that a greater correction than a simple subtraction will be necessary. Different conclusions, however, have been drawn from the results of Arrhenius by later investigators.[10]

[1] Kohlrausch, *Wied. Ann.*, **26**, 195–7 (1885).

[2] Arrhenius, *Bihang. Svensk. Vet.-Akads. Handl.*, **8**, Nos. 13 and 14 (1884).

[3] Ostwald, *Z. physik. Chem.*, **3**, 418 (1889).

[4] Bredig, *Ibid.*, **13**, 289 (1894).

[5] Kohlrausch, *Loc. cit.*

[6] Kohlrausch, "Gesammelte Abhandlungen," Vol. 2, Leipzig, 1911.

[7] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," pp. 91–93, Leipzic, 1898.

[8] Kohlrausch and Holborn, *Loc. cit.*

[9] Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899).

[10] McBain and Coleman, *J. Chem. Soc.*, **105**, 1517 (1914).

From a recent paper[1] it appears that Arrhenius himself has now abandoned his original view.

The suggestion that, in carefully prepared water, carbonic acid is the preponderating conducting impurity has led to several efforts to construct an exact correction. The principle involved is that if we employ in conductivity measurements water from which all other impurities generally present (*e. g.*, ammonia and soluble silicates) have been completely removed, then it will be possible to apply to the results obtained a "*carbonic acid correction*" according to the law of mass action.

The first real advance along this line was made by Walker and Cormack[2] in an article already discussed in detail.[3] The conductivity of the purest water obtainable in contact with air was found to be equal to that calculated for a saturated solution of carbonic acid under atmospheric conditions. The conclusion was drawn that "carbon dioxide is the only substance in the atmosphere which confers conductivity on water." Furthermore, the method of calculating, under this assumption, the *true* conductivity of phenol in decinormal solution, where the "water conductivity" amounted to one-half of the total observed value. was indicated.[4]

It is strange that the results of this research have not been more widely utilized, since we have here a method for obtaining exact conductivity results for any electrolyte at high dilutions without the necessity of preparing ultra-pure water. Investigators have persisted, however, in following more or less empirical and approximate methods (sometimes of great complexity) for the correction of their experimental data.[5] It is only recently that Arrhenius[6] has made use of the conclusions of Walker and Cormack for a general discussion of the problem: "Die Berechnung des electrischen Leitvermögens in sehr verdünnten wässerigen Lösungen."

The most significant deduction of Arrhenius from this investigation arises from his examination of the data of Kohlrausch and Maltby[7] for sodium and potassium chlorides. The true correction for these salts is found to be slightly less[8] than the total "water conductivity," the difference varying with the dilution. From the final values obtained the conclusion is drawn that *both electrolytes, at very high dilutions, obey the Ostwald dilution law.*

The importance of this deduction cannot be too strongly emphasized,

---

[1] Arrhenius, *Meddel. K. Vetenskapsakademiens Nobelinstitut*, Band 2, No. 42 (1913).

[2] Walker and Cormack, *J. Chem. Soc.*, **77**, 5 (1900).

[3] Kendall, This Journal, **38**, 1480 (1916).

[4] This is discussed more fully on page 17.

[5] Compare Goodwin and Haskell, *Phys. Rev.*, **19**, 373 (1904).

[6] Arrhenius, *Loc. cit.*

[7] Kohlrausch and Maltby, *Loc. cit.*

[8] Compare Kohlrausch and Holborn, "Leitvermögen der Electrolyte," p. 92.

since, while most chemists recognize that the mass action law must be universally applicable in exceedingly dilute solutions,[1] no direct evidence of its validity for any strong electrolyte has yet been accepted. Biltz[2] claimed to have showed, from freezing-point depression measurements, that caesium nitrate followed the dilution law; these results, however, have not been confirmed.[3] Bogdan[4] concluded, from conductivity determinations, that hydrochloric and nitric acids obeyed the law of mass action; these deductions were shown by Kohlrausch[5] to be unwarranted. It is therefore unfortunate that the data available to Arrhenius in his calculation of "carbonic acid corrections" at high dilutions were only approximate and incomplete.

Exact concentration and ionization values for carbonic acid solutions in equilibrium with the atmosphere have been established in a preceding paper.[6] With their use, it is now possible for us to apply accurate "carbonic acid corrections" to our conductivity data.

The calculation in certain examples becomes tedious, inasmuch as a series of approximations must be made to solve the equations involved. Nevertheless it is possible to establish finally an exact correction for each case.[7] It may be noted that the ionization of the water itself in the presence of the carbonic acid is entirely negligible. Consequently hydrolysis effects will not enter into our calculations unless we deal with solutions in which the hydrogen-ion concentration of this acid is reduced considerably, *i. e.*, solutions of salts of exceedingly weak acids.

Instructive comparative values regarding the variation in the magnitude of the correction with electrolyte and concentration are to be found in the paper by Arrhenius quoted above, and need not be recalculated in detail here. It can be readily seen from inspection of the following tables how the correction varies for the different cases examined.

Application of the Correction to Strong Acids.

Hydrochloric and sulfuric acids will be taken up in this section as typical examples of monobasic and dibasic strong acids. In each case we have available very careful experimental work at very high dilutions. For hydrochloric acid the data of Goodwin and Haskell[8] may first be em-

---

[1] For a full discussion of this question see Wegscheider, *Z. physik. Chem.*, **69**, 603 (1909); also Kraus and Bray, This Journal, **35**, 1423 (1913).

[2] Biltz, *Z. physik. Chem.*, 40, 218 (1902).

[3] See Wegscheider, *Loc. cit.;* also Washburn and MacInnes, This Journal, **33**, 1707 (1911).

[4] Bogdan, *Z. Elektrochem.*, **13**, 596 (1907).

[5] Kohlrausch, *Ibid.*, **13**, 645 (1907).

[6] Kendall, This Journal, 38, 1480 (1916).

[7] See Arrhenius, *Z. physik. Chem.*, **5**, 1 (1890).

[8] Goodwin and Haskell, *Phys. Rev.*, **19**, 380 (1904).

ployed. The results for a series of dilutions with water of specific conductivity 0.85×10^{-6} at 18° are given below.[1]

TABLE IA.—HYDROCHLORIC ACID 18°. (GOODWIN AND HASKELL.)

Conc. of solution (millimols per liter).	Spec. cond. (reciprocal ohms $\times 10^{-6}$).	Molecular conductivity.	
		(a) Uncorrected.	(b) Water subtracted.
1.6176	607.18	375.4	374.8
0.8834	332.11	376.0	374.9
0.7117	267.99	376.5	375.3
0.5351	201.47	376.5	374.9
0.3722	140.12	376.5	374.2
0.2583	97.38	377.0	373.7
0.1219	45.74	(375.3)	(368.3)
0.04526	16.47	(364.0)	(345.1)
0.00	0.854	[379.1]	[379.1]

Throughout the whole range of concentrations considered, the acid is almost entirely ionized. The molecular conductivities tabulated in Columns 3 and 4 are therefore very near to the value 379.1 for the acid at infinite dilution.[2] In Column 3 these molecular conductivities are not corrected at all, in Column 4 the "water conductivity" has been directly subtracted.[3]

These results may be compared with a series made with the same acid by the present author for a similar range of dilutions at 25°. Details of the experimental procedure need not be given here, since the apparatus and methods employed were essentially as described in previous papers.[4] The water used in the dilutions possessed a specific conductivity of 0.80×10^{-6} throughout.

TABLE IB.—HYDROCHLORIC ACID 25°. (KENDALL.)

Conc. of soln. (millimols per liter).	Spec. cond. (reciprocal ohms $\times 10^{-6}$).	Molecular conductivity.[5]	
		(a) Uncorr.	(b) H_2O subtracted.
1.0084	422.42	418.9	418.1
0.5042	211.51	419.5	417.9
0.3616	151.87	419.8	417.6
0.2521	105.90	420.1	416.9
0.1808	75.95	420.1	415.7
0.1260	52.77	(418.8)	(412.5)
0.0904	37.55	(415.4)	(406.6)
0.00	0.80	[422.7]	[422.7]

---

[1] The assumption is made in the following sections that, for water of specific conductivity below 1×10^{-6}, the whole of the conducting impurity consists of carbonic acid. The concentrations of any other electrolytes present must be so minute that the conclusions obtained cannot, in any case, be *significantly* affected.

[2] Obtained by summation of the ionic velocities at 18°; $H^+ = 313.9$ (Kendall, *J. Chem. Soc.*, **101**, 1293 (1912)), $Cl^- = 65.25$ (Bates, THIS JOURNAL, **35**, 534 (1913)).

[3] Goodwin and Haskell discuss two other methods for deriving the *true* molecular conductivity at high dilutions. For details the original paper should be consulted.

[4] Kendall, *J. Chem. Soc.*, **101**, 1281 (1912).

[5] For the molecular conductivity at infinite dilution we have $H^+ = 347.2$, $Cl^- = 75.5$ (Kohlrausch, *Z. Elektrochem.*, **14**, 129 (1908); Johnston, THIS JOURNAL, **31**, 1015 (1909)).

From the above tables it will be seen that the uncorrected values (except for the last two concentrations,[1] are quite regular in their tendency towards the maximum at infinite dilution. The application of any "water correction" gives results which are obviously too low. This is exactly what is to be expected, since the ionization of the (weak) carbonic acid present will be so reduced by the (strong) hydrochloric acid that its effect upon the measured conductivity will be infinitesimal. Direct application of the law of mass action[2] shows that the "carbonic acid correction" amounts to only 0.04×10^{-6} reciprocal ohms at the highest dilution recorded above; for all other dilutions it vanishes entirely.

For strong acids, therefore, we have the rule that *no correction is to be applied to the experimental values.* It is important to note that this rule could result only if the conducting impurity present consisted entirely of a weak acid such as carbonic acid. Neutral salts would necessitate a large negative correction, basic impurities a large positive one.

Confirmation of the above conclusion is obtained from a series of determinations for sulfuric acid by Whetham,[3] which yields results precisely similar. Whetham subtracted the water conductivity (0.903×10^{-6} reciprocal ohms in this series) in its entirety; the following table shows the inaccuracy of such a procedure:

TABLE II.—SULFURIC ACID 18°. (WHETHAM.)

Conc. of soln. (milli-equivalents per liter).	Spec. cond. (reciprocal ohms $\times 10^{-6}$).	Equivalent conductivity.	
		(*a*) Uncorr.	(*b*) H_2O subtracted.
1.872	654.9	349.8	349.3
0.9304	341.7	367.3	366.3
0.4298	161.1	374.8	372.7
0.2446	92.95	379.9	376.3
0.1097	41.77	380.7	372.7
0.04613	17.14	(371.5)	(352.0)
0.02487	9.024	(362.8)	(326.9)
0.00	0.903	[381.5]	[381.5]

The final dissociation of the acid is almost complete at the high dilutions here examined. The value for the equivalent conductivity at infinite dilution is obtained from the results of Kendall and of Bates[4] as before.

Again it is evident that the ***uncorrected*** results, for concentrations greater than 0.1 milli-equivalent, tend regularly towards the maximum value, 381.5. The subtraction of the "water correction" leads to anomalous figures. If any correction is to be made it is obviously not a subtraction, but an ***addition***, for at the very highest dilutions there is (as for HCl) a marked decrease even in the uncorrected values.

---

[1] See note 2, page 15.

[2] See Equation 2, page 15.

[3] Whetham, *Z. physik. Chem.*, **55**, 204 (1906).

[4] $^1/_2SO_4^- = 67.65$ (Bates, *Loc. cit.*).

This abnormal behavior at exceedingly high dilutions might well be ascribed to experimental errors, which here affect the results considerably even in most accurate work. Such an explanation is not satisfactory, however, since the results of Kohlrausch[1] indicate that the decrease for strong acids at very high dilutions is a general phenomenon. There must therefore exist some general disturbing influence not yet taken into consideration.[2]

Application of the Correction to Weak Acids.

The method to be followed in applying the "carbonic acid correction to very dilute solutions of weak acids is best illustrated by particular examples. We have two cases to consider:

(*a*) the acid under examination is not so weak that its dissociation constant cannot be determined at higher concentrations, where the correction is negligible.

(*b*) the acid is so exceedingly weak that the carbonic acid correction is large at all concentrations.

The first case includes the transition acids and weak acids stronger than carbonic. Acetic acid ($k = 1.85 \times 10^{-5}$ at 25°)[3] may be taken as an example. Suppose we have determined the specific conductivity of a 0.0001 *N* solution. Then, if we represent the concentrations of acetate and hydrogen carbonate ions by x and y respectively, we have[4]

$$(x + y)x/(0.0001 - x) = 1.85 \times 10^{-5} \qquad \text{(I)}$$

$$(x + y)\, y/(0.0000140 - y) = 3.50 \times 10^{-7}. \qquad \text{(II)}$$

Solving these equations for x and y, we obtain the concentration of the hydrogen carbonate ion, and from this we can calculate what part of the specific conductivity of the solution is due to carbonic acid. It is not legitimate, however, to subtract this from the observed value and call the result the specific conductivity of 0.0001 *N* acetic acid. What we require is this quantity not in presence of, but in *absence* of H_2CO_3. If we represent the concentration of acetate ions under these ideal conditions by z, then we have

---

[1] Kohlrausch, *Ann. Physik*, 26, 161 (1885).

[2] The abnormality of the conductivity results obtained with strong acids at the highest dilutions that can be examined with accuracy has been the subject of several important investigations (see particularly, Whetham and Paine, *Proc. Roy. Soc.*, 81A, 58 (1908) and Paine and Evans, *Proc. Camb. Phil. Soc.*, [1] 18, 1 (1914)). An adequate discussion of the results of these papers and of the conflicting conclusion drawn from them that the conducting impurity in "pure water" consists mainly of a *salt* (ammonium carbonate) cannot be entered into here. The matter will be taken up more in detail in a subsequent article, in connection with experimental work at present in progress.

[3] Any inaccuracy in this value (due to uncertainty in Λ_∞, the equivalent conductivity at infinite dilution) will not affect the correction appreciably.

[4] See Kendall, This Journal, 38, 2465 (1916).

$$(x + y)\, x/(0.0001 - x) = z^2/(0.0001 - z). \qquad \text{(III)}$$

Hence, x and y being known, z can be calculated.

The correction in general will be very small, even at high dilutions, as will be seen in Table III below. The application of an exact correction, however, provides particularly valuable information regarding the true value of Λ_∞ for the acid and the *true* dissociation constant.[1]

Table III.—Acetic Acid (Kendall)[2] 25°.

V.	Conc. HCO_3^-.	Λ (uncorrected).	Λ (corrected).	$k \times 10^5$ (uncorrected).	$k \times 10^5$. (corrected).
217.12	0.17×10^{-7}	23.81	23.81	1.849	1.849
434.24	0.25×10^{-7}	33.22	33.22	1.848	1.848
868.5	0.36×10^{-7}	46.13	46.12	1.848	1.848
1737.0	0.52×10^{-7}	63.60	63.58	1.851	1.850
3473.9	0.76×10^{-7}	86.71	86.67	1.852	1.850
6947.8	1.12×10^{-7}	116.75	116.62	1.865	1.856
∞	1.40×10^{-7}	[387.9]	[387.9]	...	...

It will be evident from the above table that the small "carbonic acid correction" is effective in rendering the dissociation constant somewhat more satisfactory at very high dilutions (assuming $\Lambda_\infty = 387.9$ is correct) than when no correction is applied. The slight deviations still existent may be ascribed either to experimental errors or to an inaccuracy in the assumed value for Λ_∞.[3]

For acids stronger than acetic (*i. e.*, the whole series of the transition acids) the "carbonic acid correction" will be negligible up to the highest available dilutions.[4] Hence for these acids also we have the rule that

[1] Derick, This Journal, **36**, 2268 (1914).

[2] Kendall, *J. Chem. Soc.*, **101**, 1283 (1912). The water employed in this series possessed a specific conductivity of 0.86×10^{-6} at 25°. Since a careful examination by Derick (*Loc. cit.*) has indicated that these results are rather more accurate than was originally assumed, values in the above table are given (in certain cases) to one more place of decimals than previously. The value for Λ_∞ is obtained from $H^+ = 347.2$ (Kendall, *Loc. cit.*) and $CH_3COO^- = 40.7$ (Bredig, *Z. physik. Chem.*, **13**, 218 (1894)). The latter value may well be ±0.5 unit in error, the total uncertainty is therefore about ±1.0.

[3] Derick has recently elaborated upon the author's indirect method for the determination of Λ_∞ (Kendall, *Loc. cit.*, p. 1279) by deducing a general formula for the requisite calculations and applying it critically to the above results (Derick, This Journal, **36**, 2270 (1914)). The value thus obtained for Λ_∞ is 398 ± 6. If Derick's procedure is followed *after* the application of the carbonic acid correction, the value resulting is 390 ± 3. The correction has therefore brought the values derived from different dilutions into better agreement, and the limits indicated by the final results now include the "probable value" 387.9 given in Table III. It should be noted, however, that conductivity determinations with so weak an acid as acetic are ill-suited for establishing the exact value of Λ_∞, since experimental errors become enormously magnified in the course of the calculations. From the transition acids much more trustworthy results are obtained (see Kendall, *Loc. cit.*, p. 1280).

[4] Since their dissociation will here be, as with the strong acids, almost complete.

no correction is to be applied to the experimental values.[1] For acids much weaker than acetic, however, the correction becomes considerable even at ordinary concentrations. The method for deriving the ideal specific conductivity in such a case may be indicated by an example taken from Table IV, which shows the results obtained for phenol.[2]

TABLE IV.—PHENOL[3] 25°. (KENDALL.)

Conc. of soln. (mols per liter).	Spec. cond. $\times 10^{-6}$. Uncorr.	Corr.	Mol. cond. Corr.	$k \times 10^{10}$. Uncorr.	Corr.
0.1240	1.62	1.40	0.0113	1.47	1.10
0.0894	1.43	1.18	0.0132	1.59	1.08
0.0620	1.30	1.02	0.0164	1.87	1.15
0.0447	1.15	0.82	0.0184	2.07	1.05
0.0310	1.06	0.68	0.0220	2.53	1.04
0.00	0.81	0.00	[380.0]	..	..
				Mean,	1.08

For the first concentration given (0.1240 *N*) the observed specific conductivity is 1.62×10^{-6}; that of the water used to prepare the solution was 0.81×10^{-6}.

Let x and y represent the concentrations of the ions $C_6H_5O^-$ and HCO_3^- in the solution. If we assume (as a first approximation) that the mobilities of these ions are the same,[4] then the addition of the phenol to the water has increased the total ionic concentration (conc. H^+) in the ratio $1.62/0.81 = 2$. This involves a decrease to one-half[5] in conc. HCO_3^-. Hence the specific conductivity due to H_2CO_3 in the solution is $0.5. (0.81 \times 10^{-6}) = 0.40 \times 10^{-6}$. The specific conductivity due to phenol will thus be 1.22×10^{-6}. If now we take z to represent the ideal concentration of $C_6H_5O^-$ in the solution, we have the relation[6] $(x + y)\, y = z^2$. Hence the *ideal* specific conductivity of a 0.1240 *N* solution of phenol at 25° is $(1.62 \times 1.22 \times 10^{-12})^{1/2} = 1.40 \times 10^{-6}$. From this we obtain the molecular conductivity 0.0113, and the dissociation constant 1.10×10^{-10}. The constant calculated from the uncorrected value is 1.47×10^{-10}.

It will be clear that the "carbonic acid correction" is in this case considerable.[7] At the highest dilution given above (approximately *N*/30)

---

[1] Compare Derick, *Loc. cit.*, pp. 2201–3. It may again be noted that this rule could hold only if the whole of the conducting impurity consisted of a weak acid.

[2] Compare Walker and Cormack, *J. Chem. Soc.*, 77, 18 (1900).

[3] The phenol was purified by repeated distillation and used immediately after preparation. For the molecular conductivity at infinite dilution the (approximate) value 380.0 was derived by the method of Ostwald (*Z. physik. Chem.*, 2, 840 (1888)).

[4] The overwhelmingly large mobility of H^+ renders any existent difference of small importance.

[5] Again an approximation, since we are neglecting the change in nonionized H_2CO_3 (see Equation II, p. 15).

[6] Since the change in nonionized phenol is negligible (see Equation III, p. 16).

[7] The *exact* correction (calculated with the use of the values $\Lambda_\infty H_2CO_3 = 393.4$, $\Lambda_\infty C_6H_5OH = 380.0$, and the full equations on p. 15) leads to substantially the same

it exceeds 30% of the total conductivity. That its application leads to accurate results is evident from the last column of the table, the deviation of the *corrected* constants from the mean value[1] (1.08×10^{-10}) being wholly within the limits of experimental error. The *uncorrected* constants, on the other hand, increase rapidly with the dilution.[2]

Application of the Correction to Bases.

Practically no exact data are available for these at high dilutions. The results even at moderate dilutions are so anomalous, whether the water correction is subtracted or neglected, that the field has been left almost untouched.

The most extensive work is that of Bredig.[3] Measurements were carried out only as far as $v = 256$, beyond this dilution (often also before it) the dissociation constants obtained for the weak bases investigated showed a rapid decrease. Similarly Kohlrausch[4] found that the equivalent conductivity of a strong base reached a maximum at about this point, and subsequently began to fall off.

The explanation again lies, of course, in the fact that the conducting impurity in the water employed for dilution consists of a weak acid. The combination of this with the base (even though the salt produced may be highly dissociated) involves a considerable reduction from the *true* conductivity. Kohlrausch[5] has observed, indeed, that the specific conductivity of "pure water" *decreases* on first addition of very minute amounts of NaOH.

The "carbonic acid correction" here will therefore be large and positive. In the absence of any reliable data to which they may be applied, the equations necessary for the calculation of the ideal specific conductivity from an observed value may for the present be omitted.

Application of the Correction to Salts of Strong Acids.

This constitutes the most important part of the whole field. Careful measurements upon a great number of neutral salts at very high dilutions have been carried out by Kohlrausch and his co-workers and, in recognition of the accuracy of these determinations, a great amount of theo-

---

result. The approximate corrections for some other weak acids have recently been tabulated by Arrhenius (*Loc. cit.*, p. 3).

[1] Interesting confirmation as to the accuracy of this value is obtained from the hydrolysis experiments of Lundén (*Z. physik. Chem.*, **70**, 251 (1910)) and of Boyd (*J. Chem. Soc.*, **107**, 1540 (1915)) which indicate dissociation constants at 25° of 0.97×10^{-10} and 1.15×10^{-10}, respectively.

[2] It appears inconceivable that the calculations, in such an extreme case, could furnish such consistent agreement if the "carbonic acid correction," as applied above, were *not* fundamentally valid.

[3] Bredig, *Z. physik. Chem.*, **13**, 289 (1904). See especially p. 292.

[4] Kohlrausch, *Wied. Ann.*, **26**, 202 (1885).

[5] Kohlrausch, *Loc. cit.*, p. 203.

retical speculation has been founded upon them. Unfortunately the plan of attack has too often consisted merely of an attempt to induce the data for some particular salt to reproduce some particular dissociation formula. If the attempt succeeded, the formula was vindicated; if it failed, the data were not sufficiently accurate.[1]

With regard to the data themselves, the only uncertainty that needs consideration lies in the "water correction." Errors at very high dilutions introduced hereby will, however, also affect the value for Λ_∞, which is obtained either by calculation or by graphical extrapolation from the experimental data. An exact value for Λ_∞ is all-important in the interpretation of the results. The method of Kohlrausch[2] for the estimation of Λ_∞ was long accepted without question, but of late years a great variety of alternative procedures[3] have been proposed to obtain a more definite "end-value" for each salt. Kraus and Bray[4] have suggested that Kohlrausch's values for Λ_∞ in the case of neutral salts may be in error by as much as 0.5%.

Meanwhile, with all this work on accurate end-values, no attempt has been made until recently[5] to establish the *exact* water corrections necessary for the experimental data from which these end-values are derived. Arrhenius has considered the data of Kohlrausch and Maltby for $NaNO_3$ and NaCl, and has fully discussed the method for calculating the ideal specific conductivity of the salt in such cases. We may proceed directly here to an examination of the results obtained. Those for NaCl[6] are given in Table V.

TABLE V.—SODIUM CHLORIDE 18°. (KOHLRAUSCH AND MALTBY.)

Conc. of solution (millimols per liter).	Λ (water corrected) (Kohlrausch and Maltby).	Λ (H_2CO_3 corrected) (Arrhenius).	Difference in corrections.	Possible error in Λ (Kohlrausch and Maltby).
0.4981	107.32	107.30	0.02	0.14
0.2054	108.03	107.99	0.04	0.23
0.1038	108.40	108.33	0.07	0.32
0.04283	108.75	108.67	0.08	>0.32
0.02164	108.97	108.91	0.06	>0.32
0.01088	108.86	108.86	0.00	>0.32
0.00	(108.87)	(108.87)	0.00	>0.32

The figures given in the third column are reproduced more closely (for concentrations less than 0.2 millimolar) by the Ostwald dilution

---

[1] Opposite conclusions could, of course, just as readily be drawn. Compare G. Jones, THIS JOURNAL, 37, 251 (1915).

[2] Kohlrausch, *Z. Elektrochem.*, 13, 333 (1907).

[3] For example see Noyes and Falk, THIS JOURNAL, 34, 462 (1912); Bates, *Ibid.*, 35, 519 (1913); Kraus and Bray, *Ibid.*, 35, 1410 (1913); Randall, *Ibid.*, 38, 788 (1916).

[4] Kraus and Bray, *Loc. cit.*, p. 1432.

[5] Arrhenius, *Loc. cit.*, p. 10.

[6] The *magnitude* of the "water correction" for these solutions has already been indicated on p. 8.

law than by the empirical formula of van't Hoff. The results for $NaNO_3$ are exactly similar, the dissociation constant obtained for both salts being 0.024. Arrhenius has consequently drawn the conclusion that all electrolytes, at sufficiently high dilutions, follow the mass-action law exactly.

While this conclusion is in all probability correct, it must be pointed out that the results of Arrhenius, in themselves, afford no decisive evidence. In the first place, as will be seen from the figures in the last two columns of the above table, the correction applied by Arrhenius to Kohlrausch and Maltby's results is only a small fraction of the experimental error at these high dilutions (the values given are the differences between two separate series at equivalent concentrations).[1] Where the possible errors are (relatively) so large, agreement with any formula may be possible, but still not significant.

In the second place, the end-value employed by Arrhenius is the old figure of Kohlrausch and Maltby. This was obtained by extrapolation[2] from the figures given in Column 2. If now these figures are modified (as in Column 3) then the value for Λ_∞ is left entirely unsupported and must certainly also be modified. Even a small change in Λ_∞ will suffice to destroy all traces of "agreement" of the figures in Column 3 with the Ostwald dilution law.

The real value of the results obtained by Arrhenius lies in the fact that they indicate that *the method of Kohlrausch of directly subtracting the water conductivity for neutral salts is substantially accurate.* Only for very refined work at exceedingly high dilutions need any further correction be considered. The accepted values for Λ_∞ also require only slight modification.

Another fact which now becomes apparent is that, since the Kohlrausch corrections and end-values are valid, the equation of Kraus and Bray (which leads to much lower values) must be inapplicable to neutral salts in very dilute aqueous solution.[3] The recent work of Bates,[4] however, shows that a somewhat similar equation (also empirical, with three variables)[5] can be made to apply.

Application of the Correction to Salts of Weak Acids.

The "carbonic acid correction" for these salts diverges considerably from the directly subtracted "water correction;" in fact, it will be seen

---

[1] Kohlrausch and Maltby, *Loc. cit.*, p. 207. The specific conductivity of the water employed in the series given in Table V is not stated, but it is inferred that it was not a satisfactory value. Hence both the "water corrected values" in Column 2 and the "carbonic acid corrected values" in Column 3 may be affected by appreciable errors. For this reason no effort is made here to amend the H_2CO_3 correction by means of the more accurate data now available.

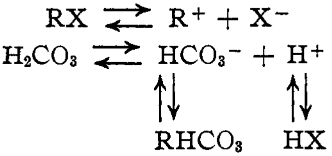
[2] By the method of Kohlrausch, *Loc. cit.*

[3] See Kraus and Bray, THIS JOURNAL, **35**, 1432 (1913).

[4] Washburn, "Principles of Physical Chemistry," p. 215–6.

[5] The *fourth* variable in the Kraus and Bray equation, Λ_∞, is here a fixed quantity.

below that in certain cases the *uncorrected* values are more accurate. This is due to the effects of double decomposition in the solution. The complete reaction occurring may be written:



$$\begin{array}{lcl} & \mathrm{RX} \rightleftharpoons & \mathrm{R^+ + X^-} \\ & \mathrm{H_2CO_3} \rightleftharpoons & \mathrm{HCO_3^- + H^+} \\ & & \updownarrow \qquad\quad \updownarrow \\ & & \mathrm{RHCO_3} \quad \mathrm{HX} \end{array}$$

and the point of equilibrium reached may be determined from the respective dissociation constants and concentrations involved. Since no fewer than eight substances are concerned in the equilibrium, it will be evident that the calculation of the *ideal* specific conductivity of the solute RX from the observed specific conductivity of the solution is a very complex problem. The equations involved can be solved only by a series of approximations.[1]

While the exact measurements of Kohlrausch and his co-workers do not include any salts of the true weak acids, the recently published investigations of Kohlrausch and von Steinwehr[2] give us the necessary accurate data for several fluorides at very high dilutions. Hydrofluoric acid is, in aqueous solution, a typical "transition electrolyte," and approximates to a weak acid at high dilutions. The dissociation equilibrium of the acid at 25° may be established from the results of Ostwald,[3] which are given in Table VI.

TABLE VI.—HYDROFLUORIC ACID 25°. (OSTWALD.)

V.	Λ.	100 α.	$k \times 10^4$ (expt.).	$[k_\infty + c(1-\alpha)/\alpha] \times 10^4$ (calc.).
16	44.3	11.04	8.55	8.52
32	59.5	14.82	8.06	7.94
64	78.6	19.58	7.44	7.53
128	104.7	26.08	7.19	7.21
256	138	34.38	7.03	6.98
512	177	44.10	6.79	6.82
1024	224	55.80	6.92	6.70
∞	[401.5]	...	..	[6.50]

$k_\infty = 0.000650$; $c = 0.000025$

The first three columns show the dilution, the equivalent conductivity and the percentage ionization, respectively. (The equivalent conductivity at infinite dilution is obtained from the values $H^+ = 347.2$; $F^- = 54.3$.)[4]

---

[1] See Arrhenius, *Z. physik. Chem.*, **5**, 1 (1890), and *Meddel. K. Vetenskapsakakemiens Nobelinstitut*, Band **2**, No. 42 (1913).

[2] Kohlrausch, "Gesammelte Abhandlungen," 1911 (Barth, Leipzic), Vol. 2, p. 1255.

[3] Ostwald, "Allg. Chemie," Leipzic, 1893. The more recent measurements of Hill and Sirkar (*Proc. Roy. Soc.*, **83A**, 130 (1910)) show widely divergent values, from which no constant can be deduced.

[4] Kohlrausch, *Z. Elektrochem.*, **14**, 129 (1908).

The fourth column gives the "dissociation constant;" it will be seen that this decreases throughout, but tends towards a constant value as the dilution increases. The last column shows that the calculated values for the dissociation constant according to the formula for transition electrolytes:[1]

$$\alpha^2/(1-\alpha)v = k_\infty + c(1-\alpha)/\alpha$$

agree with the experimental values for the whole range of dilutions. Hydrofluoric acid may therefore be regarded, in very dilute aqueous solution, as a monobasic weak acid (ionizing into H^+ and F^-) with a dissociation constant of 0.00065.

This value has been employed in the calculation[2] of the *ideal* specific conductivities of dilute solutions of sodium fluoride in Table VII.

TABLE VII.—SODIUM FLUORIDE 18°. (VON STEINWEHR.)

V.	Spec. cond. × 10^{-6}. Observed.	Ideal.	Λ (equivalent cond.). Uncorr.	Water corrected.	H_2CO_3 corrected.	H_2CO_3 correction (in % of water correction).
100	835.85	835.57	83.58	83.48	83.56	27.0
200	427.30	426.92	85.46	85.25	85.38	35.9
500	174.99	174.44	87.49	86.97	87.22	52.8
1000	88.89	88.22	88.89	87.84	88.22	64.2
2000	45.282	44.483	90.56	88.47	88.97	76.3
5000	18.859	17.937	94.29	89.06	89.69	88.0
10000	9.982	9.004	99.82	89.35	90.04	93.4
∞	1.047	0.000	...	90.15	91.01	..

It will be seen that the ideal values in this case differ considerably both from the observed values and from the "water corrected" values. The magnitude of the "carbonic acid correction" as compared with the "water correction" is given, for each dilution, in the last column of the above table.

The change involved in Λ by the application of an exact correction is large throughout the whole series and, since the dilutions are less than in the case of NaCl, quite beyond the limits of experimental error. The modified value[3] of Λ_∞ is also higher (by almost one per cent) than the original value.

For salts of weak acids, therefore, we have the rule that *the ideal specific conductivity is intermediate between the uncorrected and the water corrected values.* The variation from each is dependent upon the concentration of the solution and the strength of the acid; interesting comparative tables on these two factors are to be found in the work of Arrhenius.

---

[1] Kendall, *J. Chem. Soc.*, 10, 1275 (1912).

[2] The change in the dissociation constant of the acid between 25° and 18° will not be large enough to affect the calculations appreciably.

[3] Obtained by graphical extrapolation according to the method of Kohlrausch, *Z. Elektrochem.*, 13, 333 (1907).

In general, it may be stated that, for the ordinary range of dilutions, the divergence of the ideal from the water-corrected value increases as the strength of the acid decreases. For salts of true weak acids (*e. g.*, potassium acetate) the observed values, except at very high dilutions, are substantially valid without any correction.

One special case remains to be noted, where the salt is a hydrogen carbonate. Here the high concentration of HCO_3^- present cuts down the ionization of the carbonic acid practically to zero throughout the whole available dilution range. This may be seen by application of the conductivity data for sodium and calcium hydrogen carbonates[1] to Equation II on page 15. It will be found that the concentration of hydrogen ion is reduced to such an extent that it cannot influence the conductivity values appreciably, even at the highest dilutions examined. At the same time, however, the hydrogen-ion concentration remains always large enough to preclude the possibility of hydrolysis affecting the results of all. The observed values for the salts are therefore to be employed without any correction.

Summary.

The significance of the water correction in conductivity determinations at very high dilutions has been discussed and the previous work on the subject summarized. The derivation of an exact "solvent correction," under the assumption that the water employed is in equilibrium with atmospheric carbon dioxide, has been demonstrated. It has been shown that the following conclusions may be drawn from the different examples examined:

1. **Strong Acids.**—No correction is to be applied to the observed values throughout the ordinary range of dilutions. The abnormal values obtained at exceedingly high dilutions are being further investigated.

2. **Weak Acids.**—Acids stronger than acetic require no correction. With acetic acid the correction begins to become appreciable at very high dilutions. The correction in the case of exceedingly weak acids (*e. g.*, phenol) is considerable throughout.

3. **Bases.**—The correction necessary is large and positive.

4. **Salts of Strong Acids.**—Substantially accurate values are obtained by the procedure of Kohlrausch—direct subtraction of the water conductivity. The *ideal* correction is slightly less than this, but only within the present limits of experimental error.

5. **Salts of Weak Acids.**—The true results lie between the uncorrected and the water corrected values. The exact correction necessary varies with the concentration of the solution and the strength of the constituent acid. Hydrogen carbonates alone require no correction.

---

[1] Kendall, THIS JOURNAL, 38, 1489 (1916).

The accepted values for Λ_∞ (as given by Kohlrausch) are, in the case of *neutral salts*, practically unaffected by the application of a "carbonic acid correction" to the conductivity data from which they are derived. Whether these salts follow the simple dilution law at exceedingly high dilutions is a point which cannot be satisfactorily established until more accurate measurements are available.[1] The confirmation of the figures of Kohlrausch, however, indicates that the equation of Kraus and Bray is inapplicable to neutral salts in very dilute aqueous solutions.[2]

The values for Λ_∞ derived by Kohlrausch for *salts of weak acids* are decidedly too low (almost one per cent. in the case of sodium fluoride). Our present figures for the ionization of such salts and for the mobility of their anions stand, therefore, in need of recalculation.

In conclusion, it is necessary to emphasize the fact that we sadly require considerable additions to our *exact* experimental data for all types of electrolytes. We have now a large number of rival dissociation formulas[3] in the field, with theoretical foundations awaiting discovery, confirmation or rejection. In order to test or to interpret these formulas, any except the most accurate conductivity measurements are absolutely valueless.[4] At present one can but feelingly repeat the statement of Kraus and Bray:[5] "No one can fully appreciate the hopeless inconsistency and inaccuracy of the major portion of the work done on solutions, particularly by the conductivity method, unless he has had occasion to utilize the results in a quantitative way."

It is hoped that the present series of articles will prove of general aid in future investigations by the removal of that one universal bugbear—the uncertainty of the water correction.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK CITY.

---

[1] It must be mentioned that a large number of these salts were examined by Kohlrausch and his students with water of rather inferior quality, *i. e.*, specific conductivity above 1.0×10^{-6} at 18°. The data in such cases cannot be altogether satisfactory.

[2] Compare Bates, THIS JOURNAL, **37**, 1431 (1915).

[3] For examples, see Partington, *J. Chem. Soc.*, **97**, 1159 (1910); MacDougall, THIS JOURNAL, **34**, 855 (1912); Kendall, *J. Chem. Soc.*, **101**, 1275 (1912); Kraus and Bray, THIS JOURNAL, **35**, 1315 (1913); Bousfield, *J. Chem. Soc.*, **105**, 1809 (1914); Snethlage, *Z. phys. Chem.*, 90, 1 and 139 (1915); Bates, Washburn's "Principles of Physical Chemistry," pp. 215–6.

[4] A repetition of the work of Kohlrausch and Maltby with the more refined apparatus now available (see Washburn, THIS JOURNAL, **38**, 2432 (1916), also Leeds and Northrup catalog, No. 48) would be especially desirable.

[5] Kraus and Bray, THIS JOURNAL, **35**, 1317 (1913).