been checked by both men and it is believed that the values given are correct.

URBANA, ILLINOIS.

REVIEW: THE PREPARATION OF CONDUCTIVITY WATER.[1]

By James Kendall.

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Water so nearly corresponds to the universal solvent sought by the alchemists that it is a matter of extreme difficulty, whatever methods of purification are adopted, to obtain a sample which may be shown to be practically free from all conducting impurities. Still more onerous is the task of preserving such a specimen when once prepared, since solution from the containing vessel inevitably introduces some contamination. The final and practical object—to maintain the sample at its original purity while actually in use in conductivity determinations—borders closely upon the unattainable.

By repeated distillations *in vacuo* Kohlrausch and Heydweiller,[2] working in Strasbourg,[3] succeeded in obtaining, in a glass conductivity cell, water with a specific conductivity of 0.043×10^{-6} reciprocal ohms at 18°, or 0.015×10^{-6} reciprocal ohms at 0°.[4] These values are certainly very near to those which would be given by perfectly pure water at the corresponding temperatures. This has been proved by the employment of several distinct indirect methods for determining the ionization constant of water.[5] Kohlrausch and Heydweiller themselves estimate the specific conductivity of absolutely pure water at 18° to be 0.0384×10^{-6} reciprocal ohms.[6]

If it were possible to reproduce this work conveniently and, after obtaining in quantity water of such extreme purity, to employ it in actual conductivity work, then it is obvious that we should never need to apply to our results any water correction at all.[7] In order to do this, however,

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[1] Nearly all chemists have occasion at some time to employ especially pure water in their investigations, and find that the usual methods often fail to give the anticipated results. It is difficult to collect from the references in the literature (since the work is generally only incidental) satisfactory suggestions in such a case. Perhaps the most frequent mistake made is to persist in the attempt to prepare water beyond the laboratory's limit of purity. In the following pages the previous work on the subject is summarized and the utmost degree of purity attainable under ordinary conditions indicated.

[2] Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 326 (1894).

[3] After each reference which follows, the place where the investigation was carried out will be indicated. The difficulty in obtaining good conductivity water varies considerably in different localities, as will be seen below.

[4] One millimeter of this water at 0° possessed a resistance equal to that of forty million kilometers of copper wire of the same sectional area, or a length of wire capable of encircling the earth a thousand times.

[5] Landolt-Börnstein, *Tabellen*, **1912**, p. 1187.

[6] This is often incorrectly quoted as *the experimental value* of Kohlrausch and Heydweiller. The results are also usually given without conversion from the Siemens units in which they were published to the units now employed.

[7] A general discussion of the water correction in conductivity determinations will

it would be essential to carry out all the manipulations (preparation of solutions and measurement of conductivities) in evacuated vessels. This is a feat which has been frequently attempted but, owing to the extraordinary experimental difficulties involved, not yet successfully concluded.

The necessity for carrying out the whole of the work *in vacuo* arises from the fact that water, on exposure to the atmosphere, immediately loses its purity. Thus Kohlrausch and Heydweiller[1] give the following values from their experiments with two separate specimens:

Original spec. cond. of water *in vacuo*........	0.05×10^{-6} to 0.11×10^{-6}
Spec. cond. after 20 min. exposure to air.....	0.34×10^{-6} to 0.40×10^{-6}
Spec. cond. after long exposure to air........	0.66×10^{-6} to 0.65×10^{-5}

The final values obtained for different samples in equilibrium with the atmosphere were practically constant at 0.65 to 0.70×10^{-6} reciprocal ohms at 18°. Subsequent investigators have recorded uniformly similar results; it is impossible to maintain, for more than a short interval of time, any sample of water in contact with air at a much lower value. All existent conductivity data have consequently been obtained with the use of water of this order of purity.

While, therefore, Kohlrausch and Heydweiller accomplished the preparation of small quantities of exceedingly pure water, the main problem—the preparation of pure water in large quantity for actual conductivity determinations—was left unsolved. In later experimental work, indeed, Kohlrausch and Maltby,[2] recognizing the futility of preparing extremely pure water which would be sure to become contaminated before use, did not attempt any further refinements of method, but employed water which was obtained in bulk from Kahlbaum in Berlin with a specific conductivity of 0.8 to 1.0×10^{-6} reciprocal ohms at 18°. The water correction for such a sample at high dilutions is considerable.[3]

The endeavors of subsequent investigators have been almost entirely directed towards the facile preparation of large quantities of water of as low a specific conductivity as is possible *in contact with air*. The uncertain water correction consequent upon the employment of such water for conductivity work at high dilutions has come to be regarded as an unavoidable evil. The main investigations of this nature, the methods followed and the results obtained are summarized below.

Walker and Cormack,[4] in Dundee, prepared water of specific conductivity 0.75×10^{-6} at 18° by three successive distillations—with alkali, with phosphoric acid, and without the addition of any chemical. No lower permanent value, it was shown, could be obtained for water in contact with air.

Kohlrausch,[5] in Berlin, found that the specific conductivity of water at 18° was lowered from 0.9×10^{-6} to 0.5×10^{-6} by long standing in an

appear in a subsequent communication, to which this and a former article (Kendall, THIS JOURNAL, 38, 1480 (1916)) are preliminary.

[1] Kohlrausch and Heydweiller, *Ann. Physik*, **53**, 209 (1894).

[2] Kohlrausch and Maltby, *Wiss. Abhandl. Physik-Techn. Reichsanstalt*, **3**, 188 (1900).

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

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

[5] Kohlrausch, *Z. physik. Chem.*, **42**, 193 (1902).

atmosphere free from carbon dioxide. When CO_2-free air was passed through such water in the conductivity cell, the specific conductivity fell further to 0.2–0.3 × 10^{-6} but reverted soon to the higher value if the water was again exposed to the atmosphere.

Bousfield,[1] at Hendon (near London), prepared water of specific conductivity 1.0 × 10^{-6} at 18° by a process of continuous fractional distillation. The most favorable results were obtained by addition of a trace of $KHSO_4$ to keep back ammonia and basic impurities. Later improvements[2] gave water of specific conductivity 0.8 × 10^{-6} in one distillation from tap-water without the use of any chemicals.

Hartley, Campbell and Poole[3] have described an apparatus which supplies water of specific conductivity 0.75 × 10^{-6} (at 18°) in a single distillation from Oxford tap-water. Bourdillon,[4] also working at Oxford, has improved greatly upon this and has obtained water of specific conductivity less than 0.2 × 10^{-6} (part of the yield being as low as 0.09 × 10^{-6}) by a single distillation into an air-tight cell. So long as the water was kept in this cell, its specific conductivity increased only slowly (for example, from 0.12 × 10^{-6} to 0.4–0.45 × 10^{-6} in 2–3 weeks), but if the cell was not air-tight the conductivity rose rapidly.

Paul,[5] in Munich, has also recently described a method of obtaining water of specific conductivity 0.8 × 10^{-6} at 18° by one distillation.

In this country the chief conductivity work at high dilutions has been carried out at the Massachusetts Institute of Technology by A. A. Noyes and his cöworkers. Noyes and Coolidge[6] have described a very efficient still for the preparation of high-grade conductivity water. Washburn,[7] using this still at Urbana, has obtained water of specific conductivity 0.4 × 10^{-6} at 0° and 0.6 × 10^{-6} at 25° by distillation from an alkaline permanganate solution. The purest water employed by Goodwin and Haskell,[8] at Boston, in their work on hydrochloric and nitric acids at high dilutions, possessed a specific conductivity of 0.8 × 10^{-6} at 18°.

Experimental.

The general results of previous workers indicate that, while it is a comparatively easy matter to obtain water of specific conductivity 0.7–0.8 × 10^{-6} at the ordinary temperature (18°), special apparatus and stringent precautions are necessary to effect any further purification. The significance of the constancy of the values obtained for water in contact with air by different observers working in different laboratories and using different methods has been discussed in a preceding paper.[9]

Sufficient attention does not seem to have been called to the fact that

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[1] Bousfield, *J. Chem. Soc.*, **87**, 740 (1905).

[2] Bousfield, *Ibid.*, **101**, 1443 (1912).

[3] Hartley, Campbell and Poole, *Ibid.*, **93**, 428 (1908).

[4] Bourdillon, *J. Chem. Soc.*, **103**, 791 (1913).

[5] Paul, *Z. Elektrochemie*, **20**, 179 (1914).

[6] Noyes and Coolidge, *Proc. Am. Acad.*, **39**, 190 (1908).

[7] Washburn and MacInnes, THIS JOURNAL, **33**, 1688 (1911); Washburn and Williams, *Ibid.*, **35**, 751 (1913); The above are average results. The specific conductivity at 25° increased from an initial value of 0.19 × 10^{-6} to a final value of 0.60 × 10^{-6} on exposure to air.

[8] Goodwin and Haskell, *Phys. Rev.*, **19**, 271 (1904).

[9] Kendall, THIS JOURNAL, **38**, 1480 (1916).

a method for the preparation of conductivity water which answers extremely well in one laboratory may not work at all in another. The reason lies presumably in the difference in the nature of the impurities present in different water supplies.[1]

While engaged in conductivity determinations at Edinburgh, in 1911–12, the present author found that several of the standard methods (*e. g.*, distillation from alkaline permanganate or repeated distillation without chemicals) failed to give water below 1.2×10^{-6} at 25° in spite of all precautions taken. The Edinburgh water supply was at that time notoriously contaminated with objectionable impurities,[2] the atmospheric conditions in the city are also not of the best.[3] Professor Walker suggested the addition of Nessler's solution to the water under distillation as a method for the simultaneous elimination of the two volatile conducting impurities most to be apprehended—ammonia and carbon dioxide. It was found that one distillation from tap-water to which a few cc. of Nessler's solution had been added provided water of specific conductivity 0.9×10^{-6} at 25°.

This distillation was carried out in the open air with Jena glass vessels and a block-tin condenser, specially modified to ensure thorough washing of the steam on the way to the receiver. By redistillation in silica vessels (connected with a ground-on silica hood),[4] no chemicals being added and the distillate being collected hot, water of specific conductivity 0.2–0.6×10^{-6} at 25° was obtained. Such low values could be observed, however, only when the distillate was tested at once, for its specific conductivity increased rapidly on standing until values of 0.8–0.9×10^{-6} at 25° were attained. The following series of measurements upon a sample of water transferred to a conductivity cell immediately after collection will illustrate this.[5]

Time after transference to cell........	0.5 min.	2 min.	10 min.	1 hr.	2 hrs.	6 hrs.
Specific conductivity $\times 10^{-6}$..........	0.22	0.30	0.39	0.55	0.69	0.80

On longer standing no appreciable change occurred; even after the water had remained in the cell for three weeks the specific conductivity was only 0.85×10^{-6}.

The same method of purification was subsequently employed successfully in other laboratories—in Stockholm, Petrograd and New York City.[6] It may therefore be recommended as an easy and general method for the preparation of high-grade conductivity water.

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[1] Ostwald found that his measurements upon dilute solutions of acids, made in Riga, were in error owing to the presence of ammonia in the conductivity water employed. In Leipzic this difficulty vanished (*Z. physik. Chem.*, **2**, 280 (1888)).

[2] The purely scientific results obtained from a consequent examination of the water supply are to be found in a paper by Walker and Kay, *J. Soc. Chem. Ind.*, **31**, 1013 (1912).

[3] As its familiar name, "Auld Reekie," testifies.

[4] A still of this type can now be obtained from the Thermal Syndicate, Ltd., New York City.

[5] Specific conductivities have been reduced to 25° throughout to give comparable results.

[6] Results are tabulated in the preceding paper (Table XI). It may be noted that at Petrograd, also, other methods of water purification failed.

The results obtained throughout have been in entire agreement with those of previous investigators in confirming the conclusions of Kohlrausch. Water in contact with air possesses a specific conductivity of at least 0.7–0.8 $\times 10^{-6}$ at 18°, and the correction for this in conductivity determinations at high dilutions must be considerable. The elimination of the water correction by the preparation of perfectly pure water is therefore doomed to remain impracticable unless the whole work is carried out in air-tight vessels. In this connection, present investigations by Washburn at Urbana and by Hartley at Oxford may be mentioned. Hartley and Bassett[1] have already described an "intermediate" type of apparatus for use with very dilute solutions—successive small quantities of solute being added to a large volume (300 cc.) of solvent contained in a special cell which protects it from contamination with the air. The cells designed by Washburn[2] are simpler and serve the same purpose.

The Carbonic Acid Concentration of "Pure Water."

In the preceding article[3] it has been shown that the purest distilled water of the laboratory is, in point of fact, a saturated solution of carbonic acid under the partial pressure of the carbon dioxide in the atmosphere, and contains no other conducting impurities in appreciable amount. Some additional evidence from the work of other observers as to the validity of the above conclusion may be considered here.

Caldwell,[4] in an examination of the Letts and Blake method for the determination of CO_2 in air, made the following observations: "To ordinary distilled water more than sufficient KOH was added to make it alkaline. It was then distilled, and portions of the distillate examined from time to time. They were at first alkaline, no doubt from ammonia, but then became acid, and eventually of a *constant* degree of acidity. This degree of acidity was found to correspond with the amount of carbonic anhydride in the laboratory in which the water was distilled." Solubility measurements follow which confirm these statements.[5]

A recent paper by Fales and Nelson[6] also affords interesting results. According to theory, the hydrogen-ion concentration of *pure* water at 25° is a little less than 10^{-7} normal. The purest distilled water of the laboratory[7] gave a hydrogen-ion concentration of $10^{-5.8}$. A saturated solution of carbonic acid under atmospheric conditions at 25° possesses a calculated ionic concentration of 2.05×10^{-6} (see the table on p. 2465). The hydrogen-ion concentration of such a solution, $10^{-5.7}$, is clearly in very close agreement with the observed value.

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[1] Hartley and Bassett, *J. Chem. Soc.*, 103, 789 (1913).

[2] "The Measurement of Conductivity of Electrolytes," Leeds and Northrup Co., Catalogue 48.

[3] Kendall, *Loc. cit.*

[4] Letts and Blake, *Proc. Roy. Soc. Dublin*, 9, 222–3 (1900).

[5] The calculations as carried out by Caldwell are not accurate, since it is assumed that Henry's law in its simple form can be applied (see Kendall, *Loc. cit.*, page 1493). The true calculated values are in slightly better agreement with the observed.

[6] Fales and Nelson, THIS JOURNAL, 37, 2782 (1915).

[7] The author's method of distillation from Nessler's solution was employed. It may be noted that the hydrogen-ion concentration of the indicator used (*p*-nitrophenol) would, under the conditions of experiment, be almost entirely suppressed in the presence of the stronger carbonic acid.

The results of the previous communication may be summarized in the following table:

SYSTEM: CO_2–H_2O (ATMOSPHERIC CONDITIONS).

Temp.	Conc. of satd. soln. (mols per liter).	Ionization constant of H_2CO_3.	Conc. of ionized solute.	Spec. cond. of satd. solution.
0°	2.94×10^{-5}	2.24×10^{-7}	2.46×10^{-6}	0.65×10^{-6}
18°	1.67×10^{-5}	3.12×10^{-7}	2.13×10^{-6}	0.75×10^{-6}
25°	1.40×10^{-5}	3.50×10^{-7}	2.05×10^{-6}	0.80×10^{-6}

The agreement of the values given in the last column with those directly obtained by conductivity measurements is evident from Table XI of the preceding paper. Their agreement with the general results of other observers may be seen on examination of the values given in the review of previous work above. The fact that pure distilled water is a saturated solution of carbonic acid may therefore now be regarded as definitely established. If due precautions are taken, no other conducting impurity (such as ammonia from the original water supply or dissolved salts from the containing vessel), can be present in appreciable amount.[1]

It will be impossible to obtain *permanent* conductivity values for water in contact with air lower than those given in the above table. Many investigators have certainly employed "purer water" (*i. e.*, water of lower conductivity) in their measurements, but it is questionable whether any increase in accuracy has been gained thereby. Such water (prepared by passing CO_2-free air through good distilled water) will be *unsaturated* with respect to the carbon dioxide content of the atmosphere, and will therefore slowly absorb CO_2 and consequently change in conductivity during the necessary manipulations. It is preferable to use a stable sample of water for which we can make an *exact* correction,[2] than to strive after a purer but unstable sample for which the correction is smaller but unknown.

This conclusion may be emphasized by a quotation from Kohlrausch:[3] "The purer the water, the more the difficulties of keeping it constant accumulate. Vessels with quite tight stopcocks would be necessary, if the employment of a purer water than that existing in contact with air (specific conductivity = 0.8×10^{-6} [at 18°] in the most favorable circumstances) is not to entail more dangers than advantages."

Summary.

The results of previous work upon the preparation of conductivity water have been collected and discussed. A method has been described for obtaining a standard product of specific conductivity 0.9×10^{-6} at 25° by one distillation from tap-water. This method has been found to afford satisfactory results in four different laboratories.

It has been shown that the above specific conductivity value is the same as that given by a saturated solution of carbonic acid under atmospheric conditions. A permanent lower value for water in contact with air is not possible, since slow absorption of CO_2 must take place—unless airtight vessels are employed—until equilibrium is attained.

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[1] If other impurities *are* present, then the observed conductivity will be in excess of that indicated above.

[2] As will be shown in a following paper.

[3] Kohlrausch, *Z. physik. Chem.*, **42**, 200 (1902). See also Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," pages 111–112 (Leipzig, 1898).

It is, indeed, quite unnecessary in conductivity work to invite the troubles involved in the preparation of purer water than the saturated H_2CO_3 solution. The aim should rather be to exclude all other conducting impurities except H_2CO_3, and make for this an *exact* correction. The application of such a correction to electrolytes of different types at very high dilutions will be discussed in a succeeding article.

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THE HYDROLYSIS OF HEXAHYDROPYRIMIDINE.

By Gerald E. K. Branch.

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Introduction.

The study of the catalytic action of hydrogen ion has been recently extended to many cases in which the hydrogen ion decreases instead of increasing the speed of the reactions. The most notable of these investigations have been carried on by Biddle and his co-workers.

It appears that it is by no means uncommon for hydrogen ion to have a retarding effect. In fact in the case of additions to a nitrogen-carbon linkage, it might be expected from theoretical grounds that H^+ should act as a negative catalyst when there is a tautomeric change involving the nitrogen atom. An example of such a reaction was found by Titherley and Branch[1] in the hydrolysis[2] of hexahydropyrimidine. It was there shown that this substance is tautomeric with methylene-α,γ-diaminopropane and that its hydrolysis to formaldehyde and trimethylenediamine is negatively catalyzed by hydrogen ion. Although they did not study this reaction quantitatively, they suggested that the effect of hydrogen ion was due to its favoring the less readily hydrolyzable ring form, a suggestion which has been verified by the author.

When an allelotropic mixture undergoes a reaction which is slow enough to allow equilibrium to be maintained between the isomers, any change in conditions which affects this equilibrium must have a corresponding influence on the reaction. In cases which involve a tautomeric shift about a nitrogen atom the isomers will show very different tendencies to form ions of the type of ammonium ion. The ability to add by virtue of a change of valence of the nitrogen varies inversely with the ability to add at the carbon nitrogen bond. Thus pyridine is a weaker base than piperidine but stronger than imines, just as benzene shows greater powers of addition than cyclohexane, but less than ethylenes.

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[1] *J. Chem. Soc.*, 103, 330 (1913).

[2] In this paper hydrolysis is assumed to be preceded by an addition. For the argument, however, it is only necessary that it be a reaction which takes place more readily at a double than at a single bond.