



The Fundamental Conductivity and Resistivity of Water

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The most accurate values to date were determined for conductivity of water from 0-100°C, permitting new determination of high-temperature hydroxide ion equivalent conductance. These values were incorporated into a fundamental water coefficient table including hydroxide and hydrogen ion mobilities, water ionization constant, density, conductivity, and resistivity. The conductivity/resistivity values were measured with a multiple-pass, closed, recirculating flow conductivity system, with improved multiple resistance temperature device measurement, and improved analysis of temperature and impurity effects. An accurate conductivity knowledge is necessary to understand water-limiting processes and to facilitate the analysis of trace ionic impurities in water.

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Pure water has a very low, but not quite zero, electrical conductivity. This conductivity provides a probe into fundamental properties of water, including the electrochemical mobility of the hydrogen and hydroxide ions. Deviation from this value is a measure of trace ionic impurities. Ultrapure water (UPW), with impurities at or below the sub-parts-per-billion range, is used extensively in many critical applications. Applications include chip fabrication for semiconductors, intravenous solutions for pharmaceuticals, and in high-pressure boilers for power generation.

We report here correction to a considerable error in the values for water conductivity and hydroxide mobility. In 1987, data was collected to establish the conductivity of pure water over a wide temperature range.¹ In 1989, Thornton and Light measured the intrinsic resistivity of ultrapure water from 0 to 100°C.² The results exhibited agreement within 0.25% to other values below 30°C, but showed the uncertainty rose to almost 3% at temperatures approaching 100°C. This discrepancy implied that at elevated temperatures, the resistivity change for impurity levels below about 1 µg/L (or part-per-billion, ppb) could not be calculated. This is an unacceptable limitation for modern conductivity instrumentation, necessitating a new study with detailed attention to the known issues that affect conductivity measurement and calculation accuracy.

The theoretical conductivity of pure water, κ , and its reciprocal, resistivity, ρ , are related to its basic physical chemical properties according to

$$\kappa(\text{S/cm}) = 1/\rho = 10^{-3}d(C_{\text{H}^+}\lambda_{\text{H}^+}^+ + C_{\text{OH}^-}\lambda_{\text{OH}^-}^-) \quad [1]$$

where d is the water density (g/cm^3), $\lambda_{\text{H}^+}^+$ and $\lambda_{\text{OH}^-}^-$ are the specific conductances of H^+ and OH^- ($\text{S}\cdot\text{cm}^2/\text{mol}$), and $C_{\text{H}^+}^+$ and $C_{\text{OH}^-}^-$ are the respective concentrations of these ions (mol/kg water). In pure water, the only source of ions is due to auto-dissociation, which, are determined from the H_2O dissociation constant K_w and from Eq. 1

$$\kappa(\text{S/cm}) = \rho^{-1} = 10^{-3}dK_w^{1/2}(\lambda_{\text{H}^+}^+ + \lambda_{\text{OH}^-}^-) \quad [2]$$

The 1980 measurements of Strong provide a reproducible source of specific conductance of the hydrogen ion.³ We estimate that the accuracy of this data is $\sim 0.25\%$ at 25°C, but the accuracy is less at higher and lower temperatures. Uncertainties of the specific conductance of the hydroxide ion are much larger. The density of water is known to relatively high accuracy. In particular, the data prepared by Schmidt,⁴ given for 1°C intervals over the 0 to 374°C range, is sufficiently accurate as to not cause even a 0.1% error in the resistivity calculation. For the water dissociation constant, recent re-

searchers have used data from a 1974 paper by Sweeton, Mesmer, and Baes, which agree with other studies to within about ± 0.004 pK units,⁵ hence conductivity errors introduced from this source are less than 0.5%. At 25°C the accepted values with their uncertainties for conductivity, κ and its reciprocal, resistivity, ρ , are²

$$\kappa = 0.05501 \pm 0.0001 \mu\text{S/cm} \quad \text{at } 25.00^\circ\text{C}$$

$$\rho = 18.18 \pm 0.03 \text{ M}\Omega\text{-cm} \quad \text{at } 25.00^\circ\text{C} \quad [3]$$

In this study, accurate values are determined through 100°C for water conductivity, and used to build a fundamental water coefficient table including hydroxide and hydrogen ion mobilities, ionization constant, density, conductivity, and resistivity.

Experimental

Ultrapure water is reproducibly prepared by continuously passing water through semiconductor grade mixed-bed ion-exchange columns in a closed loop system as shown in Fig. 1. As indicated, an array of conductivity sensors and platinum resistance temperature devices (RTDs) are situated in the deionizing loop. The source of water to charge the system consisted of reverse osmosis purified (R/O) water with organics removed by ultraviolet lamp oxidation and resulting CO_2 absorption. The water circulation system consists of a RTDE-220 Neslab Vaponics heat exchanger to maintain constant temperature, a closed, recirculating water loop (polyvinylidene fluoride (PVDF) valves, fittings, and insulated plumbing) with multiple sets of nuclear/semiconductor grade mixed-bed ion exchangers (Barnstead Nanopure D080 UPW Deionization Cartridges) to produce 25°C 18.18 MΩ-cm equivalent water. One challenge is that the resistivity of ultrapure water varies by two orders of magnitude over the temperature range of interest, 0 to 100°C. At temperatures above 50°C, a sealed titanium heat exchanger and electric heater was used to rapidly heat the water to the measurement temperature, and then, as indicated following the conductivity measurement, cooled to a temperature suitable for the resins in the ion exchange purification equipment via a second heat exchanger.

Each conductivity cell consisting of a Thornton 230-11 conductivity sensor and Thornton 770 MAX, was calibrated to 18.18 MΩ-cm at 25°C and resistivity was measured to an accuracy of $\pm 0.1\%$. To measure the temperature accurately we used RTD sensors, at each end of the array, and were able to interpolate to find the precise temperature of each conductivity sensor. The entire loop was wrapped with insulation, although there was still a measurable temperature drop, always less than a degree from the first sensor to the last. High-precision, calibrated resistance measuring equipment was used to measure the RTD resistance and the conductivity sensors. Repeated measurements at 25°C were used to verify that no changes occurred between successive measurement runs. An additional con-

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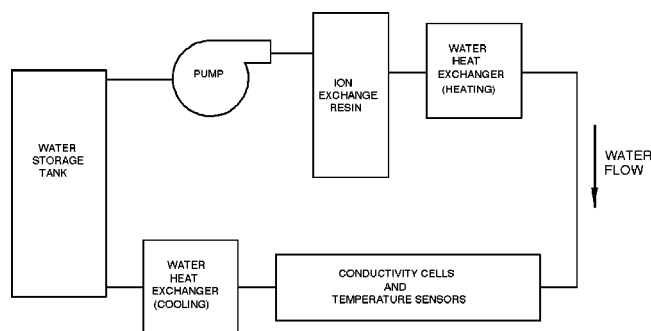


Figure 1. Schematic of the UPW multipass conductance determination.

ductivity sensor was installed, located after the cooling heat exchanger, to verify the water purity. The water resistivity at this point remained at 18.18 M Ω -cm when the water at the cell bank was at high temperatures, verifying that the heating process did not introduce any impurities into the water. After a stable measurement environment was established, all measurements were repeatedly logged for several hours and averaged over each of the conductivity sensors.

It is preferable to use a platinum RTD because of its chemical, mechanical, and electrical stability and dynamic range rather than the alternate, semiconductor based thermistors. The NIST standard platinum RTD has temperature accuracy quantified by the International Electrochemical Commission (IEC). The IEC has described the allowed deviation between measured and actual temperature of $\pm(0.15 + 0.002[T(^{\circ}\text{C})])^{\circ}\text{C}$ for the Class A (IEC 751 standard) for 100 Ω platinum RTDs. In practice, a class A 100 Ω Pt RTD can generally produce a temperature error of 0.35 $^{\circ}\text{C}$ at 100 $^{\circ}\text{C}$, still large for the requisite ppb conductivity analysis. However, temperature sensors can be individually calibrated to provide better accuracy than found in the IEC standards. Furthermore, the inherent temperature sensitivity may be accurately compensated for by incorporation of multiple averaged, standardized RTDs. An RTD resistance measurement to a temperature deviation of less than 0.2 $^{\circ}\text{C}$ was accomplished by individual RTD calibration using a 1000 Ω Pt RTD, instead of a 100 Ω RTD, to reduce the effect of the lead wire resistance and resistive self-heating, with certificates traceable to NIST, and averaging redundant measurements with multiple RTDs.

Results and Discussion

An important property of pure water is its conductivity-temperature dependency, S_T , given by

$$S_T = 100 \left(\frac{\partial \kappa}{\partial T} \right)_T \left(\frac{1}{\kappa} \right)_T \quad [4]$$

Over the temperature range from 0 to 100 $^{\circ}\text{C}$, the objective was to obtain improved conductivity measurements with errors of less than 0.5%. To achieve this level of accuracy required isolation of error sources. As described in the experimental section, RTD temperature measurement to a deviation of less than 0.2 $^{\circ}\text{C}$ was utilized. Figure 2 shows the importance of precise temperature measurement. As seen in the figure, at 0 $^{\circ}\text{C}$ the sensitivity of conductivity (or resistivity) of ultrapure water to temperature is 7.4% per $^{\circ}\text{C}$. At 100 $^{\circ}\text{C}$ this sensitivity drops by a factor of three, to 2.3% per $^{\circ}\text{C}$; that is, an error of 0.1 $^{\circ}\text{C}$ in temperature measurement is equivalent to a conductivity error of 0.23%. The issue is more complex than this, and the sensitivity of the measurement to impurity concentration has to be incorporated into the consideration.

In water containing impurities, such as due to the dissolution of NaCl, a lower bound to the water conductivity can be determined from the additional known conductivity of the impurities. This is given for the NaCl example by

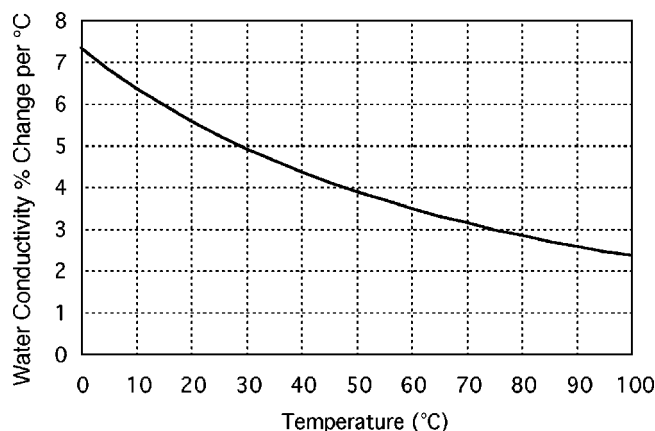


Figure 2. Sensitivity of pure water conductivity to changes in temperature as determined from the differential temperature variation of the inverse of the data in Table I.

$$\kappa = \rho^{-1} = \kappa_{\text{H}_2\text{O}} + 10^{-3}(\lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-}) \frac{w}{FW_{\text{NaCl}}} \quad [5]$$

where w is the weight of NaCl in grams, and FW is the molecular weight of NaCl. The temperature dependence of the conductivity of the impurity also has a major effect on temperature compensated, conductivity measurements. Assume that we have NaCl impurities measured in the $\mu\text{g/L}$ domain (ppb of NaCl). Using the data from Ref. 2, Fig. 3 illustrates the manner in which this sensitivity changes with temperature, and exhibits a factor of 12 decrease in sensitivity when the temperature increases from 0 to 100 $^{\circ}\text{C}$. Most important, at 25 $^{\circ}\text{C}$ the sensitivity is 4% per ppb, while at 85 $^{\circ}\text{C}$ it is 1% per ppb. Hence, to determine a trace impurity, a conductivity methodology must be four times as accurate to be as useful at 85 $^{\circ}\text{C}$ as it is at 25 $^{\circ}\text{C}$, and in turn cell constant calibration, instrument and sensor accuracy, and calculation procedures must each be four times as accurate.

It might be inferred from Fig. 2 and 3 that, as conductivity change is flatter and less sensitive to temperature variation at elevated temperature, accurate measurement is less important at high temperature. The opposite is the case, due to the increasing deviations of temperature measurements at elevated temperature, as delineated in the experimental section. This increases temperature and conductivity uncertainty by a factor of two to three in the temperature range studied. However, this is successfully compensated for by averaging multiple measurements, with the uncertainty in the mean decreasing with the square root of the number of measurements. Measurements of the ultrapure water conductivity were conducted from 0-100 $^{\circ}\text{C}$. At each temperature, a mean conductivity value was determined from redundant measurements performed over multiple,

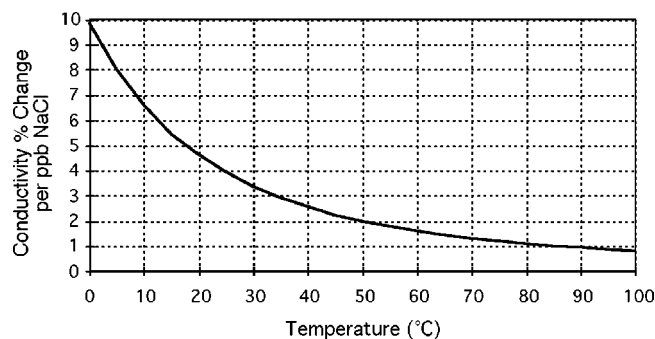


Figure 3. Sensitivity of conductivity change to NaCl impurities as a function of temperature.

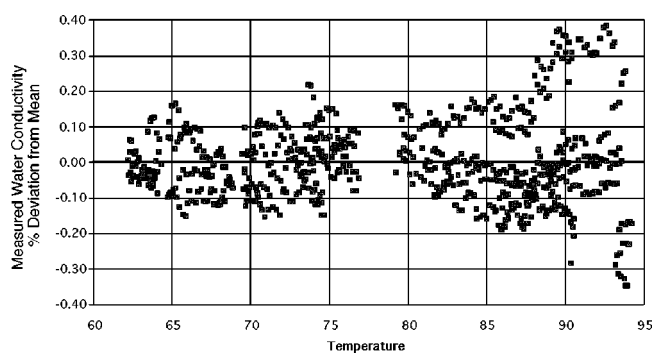


Figure 4. Deviations of individual measurements of pure water conductivity from the mean conductivities vs. temperature.

individually calibrated 1000 Ω RTDs as described in the previous sections. The deviation from the mean of the individual RTD measurements is shown in Fig. 4. It is evident that the individual deviation increases with temperature; however, the resultant mean deviation is low, permitting substantial improvement in accuracy over previous measurements, particularly in the high temperature region.

The mean determined values of the ultrapure water conductivity are summarized from 0-100°C in the second column of Table I. The experimental resistivity methodology, incorporating multiple pass flow, and redundant, individually calibrated sensors leads to improved accuracy. From temperatures to 60°C the measured values of the ultrapure water conductivity, ρ_{exp} , are estimated to be accurate to about $\pm 0.25\%$, rising to $\pm 0.5\%$ in the 80 to 100°C range. In the last two columns of the table, these values are compared to our 1987 values for water resistivity.¹ It is seen that deviations are 0.5% or less through 60°C, and then compared to the prior values rapidly rise with temperature to over 3% at 100°C.

As determined by multiple regression, the natural log of the measured resistivity of pure water, $\ln(\rho_{\text{exp}})$ can derived as a polynomial expansion as a function of temperature, $T(^{\circ}\text{C})$. This function is summarized in Eq. 6. Resistivities calculated by ρ_{fit} are tabulated in the third column of Table I, as seen, expressing the measured resistivity of pure water to within an accuracy of $\pm 0.02\%$

Table I. Comparison of measured and calculated, and prior values of pure water resistivity.

T	This work		Ref. <i>Anal. Chem</i>	% Diff
	ρ_{exp}	ρ_{fit}	1987 ρ_{1987}	
0	86.19	86.19	86.14	0.06%
5	60.48	60.48	60.21	0.45%
10	43.43	43.44	43.21	0.51%
15	31.87	31.87	31.71	0.50%
20	23.85	23.85	23.78	0.29%
25	18.18	18.18	18.15	0.17%
30	14.09	14.09	14.09	0.00%
35	11.09	11.09	11.10	-0.09%
40	8.849	8.85	8.88	-0.35%
45	7.154	7.155	7.18	-0.36%
50	5.853	5.853	5.88	-0.46%
55	4.840	4.840	4.86	-0.41%
60	4.042	4.042	4.06	-0.45%
65	3.407	3.407	3.43	-0.68%
70	2.896	2.896	2.93	-1.17%
75	2.482	2.481	2.51	-1.13%
80	2.142	2.142	2.18	-1.77%
85	1.862	1.862	1.90	-2.04%
90	1.630	1.630	1.67	-2.45%
95	1.436	1.436	1.48	-3.06%
100	1.274	1.274	1.32	-3.61%

Table II. Physical parameters and calculated conductivity and resistivity. λ_{OH^-} literature values are interpolated from Ref. 4.

T	λ_{OH^-}	λ_{OH^-} re	Deviation (%)	λ_{OH^-} 1987	Deviation (%)
0	118.59	118.30	0.2	117.8	0.7
5	133.11	133.81	-0.5	133.6	-0.4
10	148.73	149.71	-0.7	149.6	-0.6
15	165.07	165.94	-0.5	165.9	-0.5
20	182.03	182.45	-0.2	182.6	-0.3
25	199.24	199.18	0.0	199.2	0.0
30	216.62	216.09	0.2	216.1	0.2
35	234.00	233.11	0.4	233.0	0.4
40	251.49	250.20	0.5	250.1	0.6
45	268.92	267.30	0.6	267.2	0.6
50	286.07	284.35	0.6	284.3	0.6
55	303.44	301.31	0.7	301.4	0.7
60	321.08	318.21	0.9	318.5	0.8
65	338.77	335.07	1.1	335.4	1.0
70	356.76	351.93	1.4	352.2	1.3
75	374.78	368.82	1.6	388.8	-3.7
80	393.64	385.78	2.0	385.2	2.1
85	412.50	402.85	2.3	401.4	2.7
90	431.27	420.05	2.6	417.3	3.2
95	450.32	437.42	2.9	432.8	3.9
100	468.28	455.00	2.8	448.1	4.3

$$\ln(\rho_{\text{fit}}, \text{M}\Omega - \text{cm}) = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 + a_5T^5 \quad [6]$$

where $a_0 = 4.45656$, $a_1 = -7.3309 \times 10^{-2}$, $a_2 = 5.0273 \times 10^{-4}$, $a_3 = -2.5792 \times 10^{-6}$, $a_4 = 6.6206 \times 10^{-9}$, and $a_5 = 7.0484 \times 10^{-13}$

The improved determination of pure water resistivity at elevated temperature, leads to significant corrections to the fundamental conductivity of the hydroxide ion in the temperature range from 60 to 100°C. There has been considerable uncertainty of hydroxide ion conductivity in this temperature range. Reviewing the available literature, Iverson discussed in detail, values of λ_{OH^-} in the range of 5-55°C.⁶ From 70-90°C, these hydroxide values were determined from the Walden approximation to no better than an uncertainty of 5%.^{7,8} Quist and Marshall *et al.* gave elevated temperature data at 100 and 300°C for limiting ionic conductances.^{8,9} A good determination for λ_{OH^-} is found in a 1964 paper by Marsh and Stokes,¹⁰ and these values are summarized in the third column of Table II. This data was reported for temperatures of 15, 25, 50, and 75°C, and intermediate values may be estimated by interpolation. The only other data for 100°C appears to be a recomputation of data reported by Noyes in 1907.¹¹ Marsh and Stokes give a value of 455 S-cm²/mol, but others have recomputed Noyes data to arrive at values as low as 427.

The next to last column of Table II summarizes λ_{OH^-} conductivities from our 1987 paper.¹ Although low-temperature data is scarce, it is less important to start with, as the intrinsic conductivity of low-temperature water is very low. Furthermore, the contribution of the hydroxide ion to the total conductivity increases with temperature. λ_{OH^-} is only 53% of λ_{H^+} at 0°C, but rises to 73% at 100°C. Hence, uncertainties in λ_{OH^-} are increasingly dominant at elevated temperatures.

In this study we determined the hydroxide ion conductivity from our measured values of water resistivity, upon rearrangement of Eq. 2 to yield

$$\lambda_{\text{exp OH}^-} = 1000(\rho_{\text{exp}}(\text{S/cm})dK_w^{1/2})^{-1} - \lambda_{\text{H}^+} \quad [7]$$

In this equation, the values we have used are the best available data for water's density, dissociation constant, and λ_{H^+} as summarized in the introduction and tabulated in Table III. These values for

Table III. Physical parameters and calculated conductivity and resistivity. Values of λ_{H^+} , K_w , and d are, respectively, from Ref. 3-5.

T	λ_{H^+}	λ_{OH^-} exp	$\log(K_w)$	d	$\kappa_{\text{H}_2\text{O}}$	$\rho_{\text{H}_2\text{O}}$
0	225.04	118.59	14.9412	0.99980	0.01160	86.19
5	250.27	133.11	14.7287	0.99990	0.01653	60.48
10	275.38	148.73	14.5286	0.99970	0.2303	43.43
15	300.29	165.07	14.3400	0.99920	0.03138	31.87
20	324.92	182.03	14.1618	0.99830	0.04193	23.85
25	349.19	199.24	13.9933	0.99711	0.05501	18.18
30	373.03	216.62	13.8337	0.99572	0.07097	14.09
35	396.38	234.00	13.6823	0.99404	0.09017	11.09
40	419.18	251.49	13.5385	0.99226	0.1130	8.849
45	441.39	268.92	13.4019	0.99020	0.1398	7.154
50	462.98	286.07	13.2718	0.98804	0.1709	5.853
55	483.90	303.44	13.1480	0.98571	0.2066	4.840
60	504.13	321.08	13.0301	0.98319	0.2474	4.042
65	523.67	338.77	12.9176	0.98049	0.2935	3.407
70	542.49	356.76	12.8103	0.97771	0.3453	2.896
75	560.60	374.78	12.7019	0.97475	0.4029	2.482
80	578.00	393.64	12.6102	0.97163	0.4669	2.142
85	594.71	412.50	12.5169	0.96843	0.5371	1.862
90	610.75	431.27	12.4279	0.96516	0.6135	1.630
95	626.14	450.32	12.3429	0.96163	0.6964	1.436
100	640.92	468.28	12.2618	0.95813	0.7849	1.274

λ_{OH^-} are improved based on the higher accuracy of the measured conductivity. The accuracy for determining λ_{OH^-} by this method is limited by the accuracy of K_w and λ_{H^+} . As evident in the last column of Table II, at temperatures below 60°C the experimental values of hydroxide conductivity deviated from the prior values by 0.7% or less. Above 60°C, the deviation of λ_{OH^-} increases rapidly with temperature, to 3% compared to the Marsh and Stokes value¹⁰ and to over 4% at 100°C compared to the 1989 value.

Table III incorporates the highest accuracy fundamental values, for ultrapure water, from 0°C to 100°C, for λ_{H^+} , λ_{OH^-} , K_w , d , $\kappa_{\text{H}_2\text{O}}$, and $\rho_{\text{H}_2\text{O}}$. The improved conductivity and resistivity values of pure water are summarized in the last two columns of Table III. These values have been used to determine improved values for the hydroxide ion conductivity as also summarized in the table.

Conclusions

The resistivity and conductivity of ultrapure water have been determined experimentally with particular emphasis on temperatures

in the range 50 to 100°C. Measurement results are the most accurate reported to date to about $\pm 0.25\%$ through 60°C, rising to $\pm 0.5\%$ in the 80 to 100°C range. The results are presented in both tabular and equation form suitable for calculation of compensated resistivity. These measurements of water conductivity agree with prior values to about $\pm 0.5\%$ accuracy through 60°C but differ by over 3.0% approaching 100°C. It is believed that the difference at high temperature is due to the prior difficulty of making accurate measurements at elevated temperatures. Sources of error are discussed and include accurate calculation of the temperature dependence of resistivity, conductivity measurement method, and impurity effects. Calculations show the sensitivity of the measurement to the error sources, and it is shown that both temperature and resistivity must be measured with much higher accuracy at 75-100°C than is necessary at 25°C to achieve the same accuracy in impurity determination. With careful attention to detail it is possible to detect impurities at levels less than 1 ppb at elevated temperatures, but it is significantly more difficult than to make the same determination at low temperatures.

Accurate values have been tabulated for water, from 0°C to 100°C, of λ_{H^+} , λ_{OH^-} , K_w , d , $\kappa_{\text{H}_2\text{O}}$, and $\rho_{\text{H}_2\text{O}}$. The specific conductance of the hydroxide ion is determined to a substantially improved precision. These values for λ_{OH^-} are improved based on the higher accuracy of the measured conductivity. Below 60°C the experimental values of hydroxide conductivity deviated from the prior values by 0.7% or less. Above 60°C, the deviation of λ_{OH^-} to the previous values increases rapidly with temperature, to over 4% at 100°C.

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