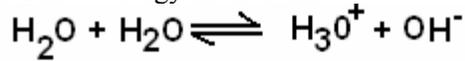


Water Conductivity – A Review

Narlin B. Beaty, Ph.D.

It is interesting to entertain the notion of charged particles moving under the influence of an electric field. Particularly, when the average separation between charges is such that they are unlikely to encounter one another, their movement is dictated by the applied field. The theoretical derivation of the molecular motion is complex, but the macro description of events needed to understand conductivity measurement is tractable. Pure water ionizes and is described in standard terminology as follows.



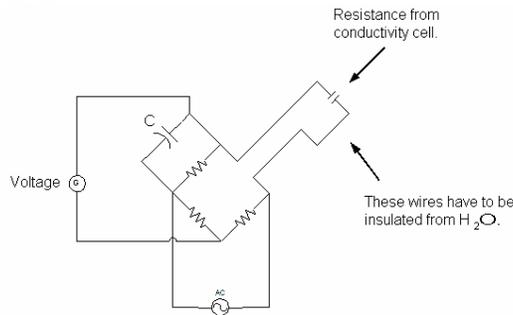
$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

$$K[\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \{\text{EQ\#1}\}$$

The term on the left in equation 1, for all practical purposes, is a constant, and is given the name K_w .

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

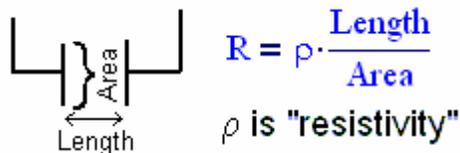
Conductance of electricity is a simple way to measure the mobility of ions, and indeed conductivity meters are nothing more than a Wheatstone bridge with bells and whistles. One of the whistles is a necessity to use alternating current to avoid electrolysis, which might lead to interference. Certainly we want the electric field to move the ions, but a DC current would cause them to plate out on the electrodes. The AC frequency needs to be at least about 1 kHz, and the zero balance involves voltage magnitude and voltage phase. See figure 1. The conductivity cell is a set of plates that are a fixed distance apart. Modern cells are not actually parallel plates, but tend to be concentric cylinders.



The AC circuit is a requirement.
The capacitor is needed to balance both voltage magnitude and phase.

Figure 1- Simplest Bridge circuit for conductance

Resistance in the conductivity cell is proportional to Length/Area¹.



$$R = \rho \cdot \frac{\text{Length}}{\text{Area}}$$

ρ is "resistivity"

When we record the resistance of a volume of water between the two plates, we are recording the value of ρ , which is called "resistivity" or "specific resistance". Since resistance, R , is measured in ohms (Ω), the units of resistivity are Ω -meters.

$$\rho = \frac{R \cdot \text{Area}}{\text{Length}} = \frac{\Omega \cdot \text{m}^2}{\text{m}} = \Omega \cdot \text{m}$$

Conductance is merely the inverse of resistance and conductivity is the inverse of resistivity. Conductance is not conductivity and resistance is not resistivity. Conductivity is seemingly the more fundamental concept, since it addresses the quantity and mobility of ions. In current terminology, conductivity (κ) is in units of Sieman/meter = S/m.

$$\kappa = \frac{1}{\rho} = \frac{1}{\Omega \cdot \text{m}} = \frac{\text{S}}{\text{m}} \quad \frac{1}{\Omega} = \text{S}$$

Manufacturing a conductivity cell with sufficiently precise measurements to enable the calculation from dimensions alone is impractical. Consequently, standards are employed for calibration of probes. Molar conductivity is the ion specific common unit of expression and is conductivity per unit concentration.

$$\frac{\kappa}{\text{Conc}} = \frac{\frac{\text{Siemens}}{\text{meter}}}{\frac{\text{mol}}{\text{meter}^3}} = \frac{\text{S} \cdot \text{m}^2}{\text{mol}}$$

These ion specific molar conductivities are not the values measured by a conductivity meter. Meters display conductivity, κ , or resistivity, ρ , in units of $\mu\text{S}/\text{cm}$ or $\text{M}\Omega \cdot \text{cm}$.

Friedrich Kohlrausch (1840-1910) was able to show that if one extrapolated the molar conductivity to a measurement at infinite dilution, the following expression was true, where the superscript indicates extrapolated values. This is called the law of independent migration of ions.

$$S^0 = n_{\text{cat}} \cdot \lambda_{\text{cat}}^0 + n_{\text{anion}} \cdot \lambda_{\text{anion}}^0$$

In this expression, λ^0 ($\text{S} \cdot \text{cm}^2/\text{mol}$) is identified as a fundamental number, the molar conductivity of an ion at infinite dilution. " n_{cat} " and " n_{anion} " (dimensionless) are the integer equivalence numbers needed to form one mole of the salt. S^0 ($\text{S} \cdot \text{cm}^2/\text{mol}$) is the extrapolated (to infinite dilution) molar conductivity. These results established that ions which do not encounter other ions in their travels proceed at a characteristic speed in a defined electric field. Since mobility of ions through a fluid is governed by the usual natural laws, we expect that fluid viscosity exerts frictional force on the ions and greater viscosity retards mobility and thus conduction. Heat also affects mobility because it changes both viscosity and internal energy. An increase in temperature causes marked increases in ion mobility and hence conductivity.

The conductivity that is measured, κ , is equal to the concentration of ions times the total molar conductivity, S^0 . From tables of $\lambda_{cat}(T)$ and $\lambda_{anion}(T)$ and $K_w(T)$, since $K_w(T)$ in moles/liter is the concentration of ions in water, one can conveniently calculate the limiting conductivity for water at any temperature.

$$\kappa = \sqrt{K_w} \cdot (\lambda_H + \lambda_{OH})$$

Conductivity, κ , is in units of Siemens/meter and all variables are temperature dependent.

Cell Calibration

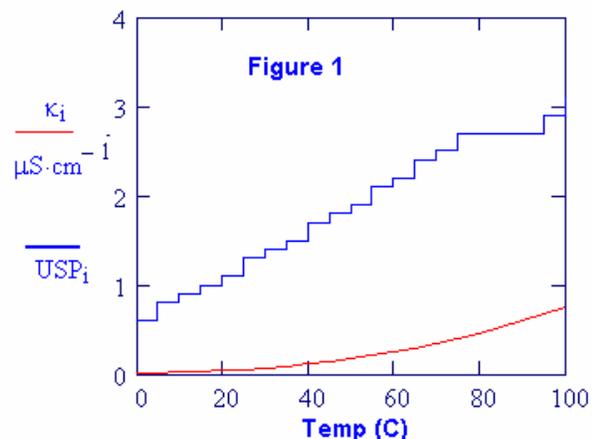
For measurement of conductivity, it is critical that the cell be calibrated. Potassium chloride can be dried and accurately prepared as a standard solution and its specific conductance in mS/cm is tabulated in reference compendia over a reasonable range. Unfortunately, it is not typically the range of interest for water. In order to be in the correct range of measurement, sensors for pure water must be calibrated in an ultra-pure water loop, which in turn is calibrated by more sensitive methods, such as ion chromatography or mass spectrometry. Calibration entails determining a cell constant, K , where $\kappa = K/R$. Cell constants have units of cm^{-1} . For meeting the USP specification, laboratory cells (probes) can be calibrated in the range of the specification using KCl. Do not confuse the calibration of cells with the calibration of meters. The meters are easily calibrated with standard resistors.

The FDA and Conductivity Testing

FDA regulations for “Purified Water”, and all of their water types which reference purified water permit online measurement of conductivity to be part of the official testing and release criteria for water, thus replacing much offline chemical testing. The specification is for conductivity, not resistivity, and is a ‘not to exceed’ specification at each particular temperature. Table 1 and Fig 1 show the USP requirement for online measurement at different temperatures as well as the limiting conductivity for that temperature.^{2,3}

	Theory	USP		Theory	USP
Temp	$\mu S/cm$	$\mu S/cm$	Temp	$\mu S/cm$	$\mu S/cm$
0	0.012	0.6	55	0.204	2.1
5	0.017	0.8	60	0.244	2.2
10	0.023	0.9	65	0.289	2.4
15	0.031	1.0	70	0.339	2.5
20	0.042	1.1	75	0.394	2.7
25	0.055	1.3	80	0.455	2.7
30	0.071	1.4	85	0.522	2.7
35	0.090	1.5	90	0.594	2.7
40	0.112	1.7	95	0.672	2.9
45	0.139	1.8	100	0.756	3.1
50	0.169	1.9			

Table 1.



Note that the USP excludes temperature compensation algorithms, temperature rounding, and interpolation between tabulated values. These criteria seem unreasonably restrictive, but are offset by permitting offline laboratory testing with considerably lessened specifications. Notably, even the most restrictive specifications are well above conductivity for pure water.

FDA/USP excludes temperature compensation because vendors have implemented multiple and different algorithms and none of them can theoretically be correct unless the water is indeed pure.

If the measured conductivity is more than that for pure water, one must assume the presence of ions other than H_3O^+ and OH^- . Since every type of ion has a unique and characteristic molar conductivity, and since we do not know which ions are contaminating, it is theoretically incorrect to compensate for temperature.

Most pharmaceutical Water for Injection loops run at about 80°C , and thus online testing is done at that temperature. The stepped slope of the specification graph in Figure 1 (USP), when compared to the theoretical limit for conductivity, favors a hot measurement. That is, the specification is more lenient at warmer temperatures. Secondly, the specification is flat between 75°C and 94.9°C , since rounding is excluded. That could discourage running a hot loop at anything more than 80°C , since the lowest conductivity reading in that range will always be at 80°C .

References

1. Atkins, P.W. Physical Chemistry W.H. Freeman and company, San Francisco, 1978, p820.
2. Light, Truman S., Licht, Stuart, Bevilacqua, Anthony C. Morash, Kenneth R. Electrochemical and Solid-State Letters, 8(1), 2004, pp E16-E19.
3. United States Pharmacopoeia, 28, <645>Water Conductivity. Online Version.