

Conductivity Measurements

Conductance, resistance, conductivity, and resistivity: A summary for people who weren't paying attention in PChem or who had PChem long ago

The ability of a solution to conduct electricity is determined by the concentration and mobility of ions in the solution and by the charges carried by those ions. Conductivity is a measure of the number of mobile ions per unit volume in a solution. Aqueous solutions can have a wide range of conductivity, spanning a factor of more than ten million from ultra pure water to concentrated ionic solutions.

At first glance, one might consider this a simple measurement and with the advanced technology of modern cells and meters, it outwardly it appears to be. Once conductivity probes are calibrated, students simply stir their solution gently, immerse the probe and record the result on the PC. The MicroLab conductivity cell in conjunction with the MicroLab FS522 lab interface is no exception. The real trick with conductivity comes in getting accurate readings, sifting through the bewildering array of units and explaining the vocabulary used to describe conductivity in a cohesive manner.

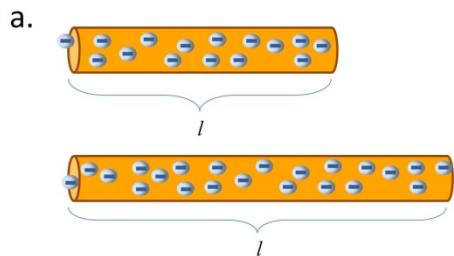
Many undergraduates have taken physics, but not all. Of those who have taken physics, many have some trouble conceptualizing the concept of electricity and dealing with even simple circuits such as those used to measure conductance. Some chemistry faculty are in the same boat. This may be, in part, due to how circuit boards are drawn, tracking the ion flow in terms of positive charge; while other concepts concerning electricity, such as electrochemistry and magnetism, are defined with respect to electron flow. The purpose of the following is to make sure that the terms and concepts are as clear as can be for the chemist or chemistry student.

In physics and chemistry, resistance and conductance are both bandied about. Both are a measure of a material's ability to transfer current. Electrical **resistance**, measured in **ohms** (Ω), describes the ability of current to pass through a device or solution when a given voltage is applied. Again, this depends on the concentration, mobility and charge of ions present. An ideal conductor is a material whose resistance, R , is constant over a wide range of applied voltages. Conductors obey **Ohm's Law**:

$$V = IR$$

in which V is a voltage applied across the conductor and I is the current it carries. Because the resistance is constant in an ideal conductor, the current is directly proportional to the voltage and it is this property that engineers use in selecting building materials. Conventionally, students are primed to think of conductors in terms of resistance and for materials rather than a solution.

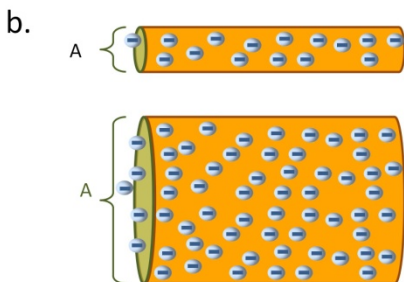
If you were to ask your students what materials are good conductors, one answer would likely be copper. While copper is a good conductor, it is not a superconductor. A superconductor has no resistance at all so the current is large at any voltage and does not diminish through the device. The resistance of a length of copper wire at a particular temperature depends on two things: its length, l , and its thickness or cross section area, A . A wire's resistance increases in proportion to its length and decreases in proportion to its thickness (Figure 1). That is to say, a wire's **resistance is an extensive property** that depends on size. Measure the resistance of a short piece of wire and it will approach zero. Measure the resistance of a 100 meter length of wire and it will be significant (Figure 1a). As you increase the length of the wire, you increase the number of atoms involved in transferring the electron and each interaction steals a bit of energy and converts it to heat (which is why wires with high resistance



become hot). Increasing the thickness decreases the resistance since a thicker wire can accommodate more electrons. This is why the power companies use very thick wires in the power grid.

Sometimes, like when discussing properties of solutions, it makes sense to talk about the ability of a material to conduct a current rather than its resistance to current. The **conductance, L**, of a material or a solution is just the inverse of resistance:

$$L = \frac{1}{R} = \frac{I}{V}$$



The units of conductance used to be Ohm spelled backwards (Mho), but conductance is now expressed in Siemens (S), or micro Siemens, uS.

Another term encountered is **specific resistance**, also known as **resistivity, ρ**. It is a measure of the material's resistance, R, when the length, l, is one meter and its cross section area, A, is 1 m². In other

words, it is a measure of the current loss as a function of length and cross section area. The resistivity of a wire of any dimension can be given by the general formula:

$$\rho = \frac{RA}{l}$$

Resistivity has the units (ohm) × (m²) ÷ m = ohm·m.

Resistivity is an intensive property of a material, independent of the size and shape.

[Another example of an intensive property is solution concentration - it doesn't matter how much solution you have or what container it is in; it's concentration is the same. Any other solution you would prepare of the same material to the same concentration in the same solvent at the same temperature and pressure would have identical properties.]

We can extend this concept to solution resistance. We define the **resistivity of a solution** as the resistance between of a pair of platinum electrodes, each of area A = 1m² separated by a distance l = 1 meter.

We mentioned that solutions tend to be characterized by their conductance, not their resistance. So we define **conductivity, κ**, as the inverse of ρ.

$$\kappa = \frac{1}{\rho} = \left(\frac{l}{A}\right) \times \left(\frac{1}{R}\right) = \left(\frac{l}{A}\right) \times L = K \times L$$

Conductivity has the reciprocal units of resistivity, ohm⁻¹m⁻¹ ≡ siemens·m⁻¹ in the SI system. The constant K is called the **cell constant** and takes into account the specific dimensions of the cell used to take the measurement.

Conductivity is an intensive property of a solution, independent of the amount of solution present and of the nature of the cell used to measure the conductance.

Though siemens is the SI unit and is preferred, you will often see the conductivity given as microsiemens/cm or millisiemens/cm – reverting to the old centimeter-gram-second (“cgs”) units – in order to avoid excessively small numbers. Sometimes you will even see the conductivity improperly reported as just some factor of siemens, the

unit of conductance, ignoring the distance unit altogether. It can be very confusing. So it is best to keep a pencil handy when you are reading the literature or following directions when making standards.

The **molar conductivity** is given by the equation:

$$\Lambda_m = \frac{\kappa}{c}$$

in which *c* is the concentration in the SI units of mol/m³. Since κ has the units siemens·m⁻¹, the units of Λ_m are siemens·m⁻¹/mol·m⁻³ or siemens·m²·mol⁻¹.

OK, so usually concentration is given in molarity, mol/L (represented below as *M*). A liter is also a cubic decimeter so molarity can be written as mol/dm³. Concentrations in molarity have to be converted to SI units to take measured conductance to molar conductivity.

$$c \left(\frac{\text{mol}}{\text{m}^3} \right) = M \left(\frac{\text{mol}}{\text{dm}^3} \right) \times \left(\frac{10 \text{ dm}}{\text{m}} \right)^3 = 1000 M$$

Putting it all together, we get an expression relating molar conductivity to molarity and κ :

$$\Lambda_m = \frac{\kappa}{c} = \frac{\kappa}{1000M} = 10^{-3}(\kappa/M)$$

Making the Measurement: The Conductance Electrode

Let's discuss how the conductance cell measures the conductivity. Consider two conducting plates in a solution, connected to a battery, and current meter to read the current passed through the solution. This is an expanded version of a conductivity probe. The conducting plates represent the electrodes, which are connected to a power supply and current meter. (Figure 2a). By measuring the current, the resistance of the solution can be calculated by Ohm's law: $R \text{ (Ohms)} = \text{Voltage (Volts)} / \text{Current (Amps)}$.

The problem with this model is that ions in a solution are free to move, and will quickly migrate – positive ions to the negative plate and negative ions to the positive plate, as shown in Figure 2b. Once the ions are all pulled to one side or the other, and their charges neutralized, the current in the circuit will fall to zero.

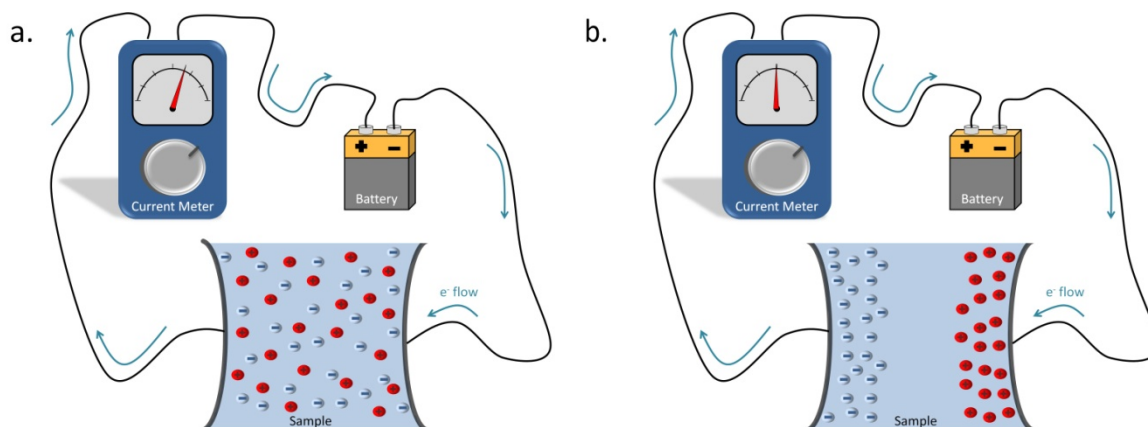


Figure 1: (a) An ionic solution has equal numbers of positive ions (red) and negative ions (blue). This models solution resistance by giving electrons to positive ions and picking them up from negative ions. (b) Because ions are mobile, they will quickly gather at the oppositely charged plate. Once the ions are separated and the charge neutralized, current stops in the external circuit and you can't make a measurement.

This problem is solved by rapidly alternating the polarity of the “battery” voltage. In the MicroLab FS-522, the voltage is changed from + 100 millivolts to – 100 millivolts about 1000 times per second. This keeps the ions mixed up.

Once, right at the end of each voltage cycle, the MicroLab very quickly measures the current caused by ions against the plates accepting or giving up electrons (Figure 3). This measurement, made on a randomly mixed group of ions, is a good measure of the number of ions per unit volume of the solution, or the ionic concentration of the solution.

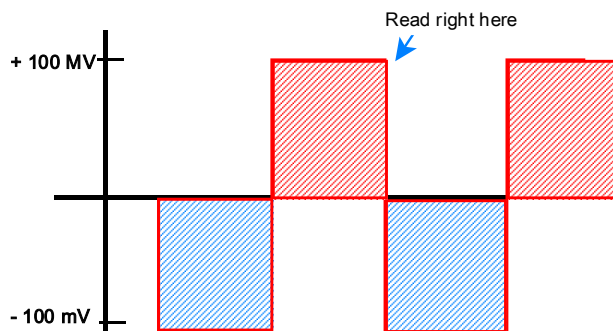


Figure 3: MicroLab provides a small alternating voltage to the electrodes. Because this voltage spends exactly as much time positive as negative, at the end of each "cycle" of applied voltage, the ions are completely mixed up. The current measurement is made exactly at this point of maximum randomness.

Conductance electrodes are quite simple. They consist of two parallel conducting plates made of a material that will not chemically react with the ions or solvent in the solution. This limits the materials that can be used for conductivity electrodes basically to platinum or gold and carbon (graphite).

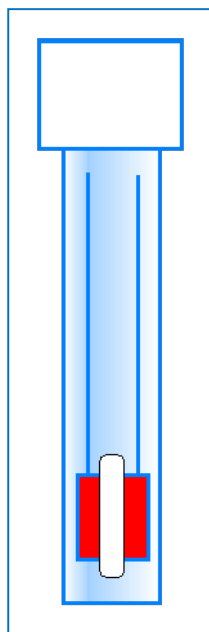


Figure 4: The two graphite electrodes are embedded in an epoxy tube. The milled slot exposes the face of the electrode to the solution.

The MicroLab Model 160 conductance electrode uses two parallel graphite electrodes. They are imbedded in a ½” epoxy rod, with a slot milled near the end to allow the solution to contact the bare graphite.

Here’s where care of the electrode is important. The manufacturing process produces graphite electrode surfaces that are clean and within about ± 10% in area from electrode to electrode. This means that, if one wants to compare measurements, you have to calibrate the electrode by immersing it in several standard solutions and making a calibration graph.

Operational information

For quantitative work, it is necessary to calibrate the sensor with a solution of known conductivity. The CRC Handbook of Chemistry has recipes (Table 1), and most chemical supply houses carry pre-mixed conductivity standards covering a wide range of conductivity. It is very easy and inexpensive to make your own standards using NaCl and DI water. It is important to dry the NaCl at 110°C for an hour or two before weighing and also to measure the conductance of the DI water used to make the solutions. Conductivity values for various concentrations of NaCl are given in the table below. The calibration step relates the conductivity to the measured conductance to obtain the cell constant. **Thus all measurements made with the MicroLab system after calibration are conductivities in uS/cm**

Table 1: CRC Handbook of Chemistry Conductivity Standards Recipe

<u>Concentration of NaCl (g/1000.0 mL)</u>	<u>Conductivity ($\mu\text{S/cm}$)</u>
0.000	0.05
0.050	105
0.100	210
0.150	315
0.200	415
0.500	1020
1.000	1990
1.500	2930
2.000	3860

All conductivities are given at 25°C

The units used in entering the solution conductivity values into the calibration screen in the MicroLab software determine the units of conductivity in the measurement. MicroLab chooses to use microsiemens/cm ($\mu\text{S/cm}$) as the default rather than SI units in order to avoid having to enter (and possibly mistype) lots of zeroes in the calibration process. You will also find that many manufacturers of conductivity standards use $\mu\text{S/cm}$ units.

One word of caution: many suppliers of conductivity standards use μS to specify the conductivity of their standard solutions when in fact they should be using $\mu\text{S/cm}$ (or some factor of these units). This practice understandably leads to confusion. It is analogous to saying that bench top HCl is 6 moles instead of 6M. Just as the number of moles of HCl depends on the volume taken, so the number of μS one measures depends on the specific cell – with its cell constant - used to carry out the measurement. The conductivity κ in $\mu\text{S/cm}$ is an intrinsic property of the solution just as much as its concentration.

If molar conductivities are desired for an unknown, it is an easy matter to convert μS to siemens and cm to meters to get κ in SI before converting to $\Lambda_m = 10^{-3} \kappa/\text{M}$

Cleanliness: The electrode surface has to be very clean. This means that it has to be well rinsed with distilled water before it is used and before it is stored. If ionic compounds (salts) are allowed to dry on the electrode, it can be cleaned by soaking for several hours in dilute HCl, at room temperature. Then rinse very well with distilled water. It won't work if it is not clean.

Hydration: The surface of the electrode has to be covered with water molecules prior to placing it in the test solution. You can do this by soaking the electrode in distilled water for several minutes before use.

Bubbles: Air bubbles can form on the surface of the graphite electrode as you transfer it from one solution to another. You can stir with the electrode or even tap it gently against the side of the beaker to get rid of the bubbles.

We hope that this helps. For more detailed review of solution conductivity, you may need to refer to a PChem lab manual or text book. Or call us for a nice conversation about it all!