How a pH Meter Works

A pH meter is actually quite a complicated device. It consists of two basic parts: a pH electrode and the electronics of the meter itself. Often these are different devices attached with a cable, as shown in Figure 1 for a meter and probe sold by American Marine (Pinpoint Brand). Alternatively, less expensive models often combine the probe and meter into a single device, such as the Oakton pHTestr^{TM} 1 shown in Figure 2.

Combination pH electrodes used in both of these systems actually contain two different electrodes inside of them (hence the word combination). One is a reference electrode that does not change voltage, but just sets a standard voltage level to which the sensing electrode is compared. This reference electrode is described in more detail below. The second electrode is sensitive to pH. It is the voltage difference between these two electrodes that the meter reads and converts into pH.

The pH Sensing Electrode

The usual glass pH sensing electrode consists of a nonconductive glass or epoxy cylinder with a conductive glass bulb on its end. When the glass bulb is placed into a solution it becomes more or less charged on the outside, depending on the pH. The exact details of this process are unimportant for aquarists to understand, but some discussion is provided below for folks that like to really understand how things work.

Figure 2
A typical handheld pH meter where the probe is incorporated into the meter itself. In this case, it is a pHTestrTM 1 sold by Oakton.

There are also other types of pH electrodes that are now available. One type, for example, involves an ion-sensitive field effect transistor (ISFET). These are fairly uncommon today but may become more common in the future. They have the advantage of being more rugged than glass electrodes, and can respond to pH changes much faster. They require power to work, and so require a special power adaptor to use with a normal pH meter. They are also fairly expensive, and not likely to be encountered by hobbyists, except in scientific supply catalogs.

In preparing this article, I was frustrated that I had such a hard time understanding something that I thought should be fairly straightforward: glass pH electrodes. In the end, it appears that truly understanding pH electrodes on a molecular level is still an active area of investigation. So despite their widespread use, the detailed physicochemical processes taking place are still fairly unclear.

The glass used in a pH electrode has a composition that includes certain metals in addition to the usual silicon and oxygen of SiO_2 glass. These metals can include lithium, barium, lanthanum, sodium, and calcium, among others. At both the inside and outside surfaces of the glass bulb (and also in a thin (50 nm) swollen region of hydrated glass on each side), there is some substitution of H^+ for these cations. How much substitution depends on how much H^+ is in solution, and hence on pH. The internal pH does not change, but the external pH does, so the amount of substitution on the outer surface changes while on the inside it does not, setting up a potential difference across the glass membrane that depends on pH.

How exactly this substitution happens and translates into a potential across the glass membrane is where the uncertainties begin. Mechanisms were first proposed in the 1960's, but our understanding of the process continues to evolve today.[12-16] The discussion that follows represents my marginal understanding of this complex process.

Some of the oxygen atoms in the glass are not fully bound to silicon. The siloxy group that remains (Si-O⁻) can either be bound to a cationic metal (sodium, lithium, etc), or it can be bound to a proton (H^+). When bound to a proton, it forms a neutral silanol, (Si-OH). When it is bound to other cations, it forms an ionic complex, such as Si-O⁻ Na⁺ . This ionic complex, when exposed at the surface of the glass can partially dissociate into a negatively charged surface, and a positively charged "layer" of ions just off of the solid surface. This separation is shown schematically in Figure 3.

This dissociation leaves the surface with a net negative charge. The extent to which this happens depends on the concentration of Si-O⁻ Na⁺ and related species. Since the pH changes the relative concentration of these species, the potential is related to the pH in solution.

This charge separation between the surface and the ions in solution (often called an electrical double layer) results in a potential that can be read as a voltage. Think of it this way. Imagine having one long wire passing through the membrane. At the point where it crosses the glass surface, there is an electric field that is positive in the water layer, and negative in the glass due to the preponderance of the charged ions present in each location. The wire experiences this field as the field acts upon the electrons present in it, pushing them away from the negative charges, and toward the positive charges
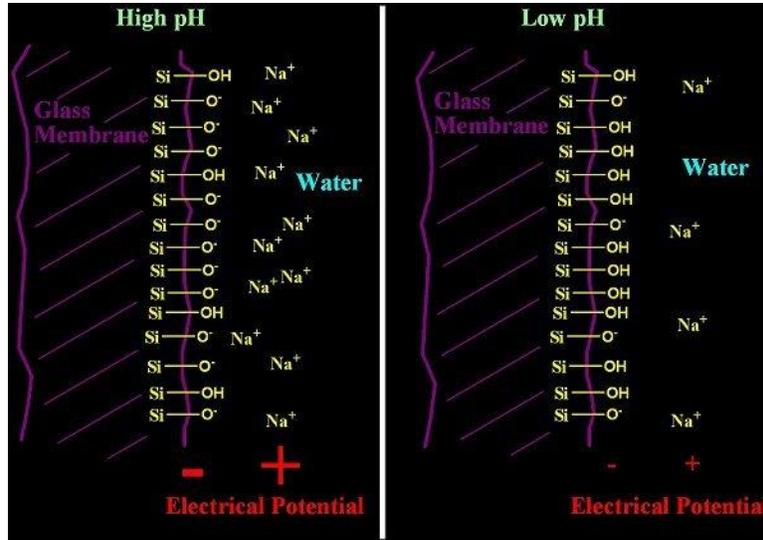
Figure 3
A schematic diagram of a glass pH electrode. The electrical potential at the glass/water surface caused by separation of the Si-O- and Na+ ions is shown in red for both low and high pH.

A voltmeter attached to the two ends of this wire would then be able to record a voltage. In this description, there is another interface on the inside of the glass membrane (where it contacts the electrode filling solution), but that one is fixed and does not respond to pH since pH is unchanging there.

In reality, there is no wire. But there is an incredibly small current passing through the glass membrane. That is why the glass membrane must be somewhat conductive. The external reference electrode is really just a way of sending this tiny current out into the water being measured, through the glass membrane, and back through the internal wire of the pH sensing electrode. This is also one reason why normal pH electrodes do not do a good job of determining pH in very pure (low conductivity) fresh water: there are not enough ions to support even this tiny current.

The Reference Electrode

There are a variety of different reference electrodes that can be used in a combination pH electrode. The most common type is the silver/silver chloride electrode (Ag/AgCl electrode). Inside of such an electrode is a silver wire coated with silver chloride and surrounded by a solution saturated with potassium chloride. The reaction setting the potential for this reference electrode is:

3. $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$
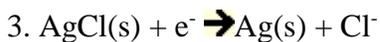
The potential for this reaction only depends on the concentration of chloride in the internal filling solution. Using a saturated potassium chloride (KCl) solution keeps the chloride concentration steady (at a given temperature), making this a good choice as a reference electrode. If the fluid filling the glass sensing pH electrode is saturated KCl (as

it usually is), then the reference electrode can be kept inside of the glass shell and the electrode looks like a single unit.

Temperature Effects on pH Measurement

There are two different ways that temperature impacts pH measurement. The first involves actual chemical changes in the solution that you are measuring. Acids can, for example, become stronger or weaker as the temperature is changed. This is how calibration standards change their pH as a function of temperature (which is discussed in more detail in the calibration section below). If the solution has solids in contact with it (as is the case with saturated limewater in the presence of excess solids), the temperature can also impact how much acid or base is in solution impacting pH, and how much is just solid sitting on the bottom of the container. These effects are specific for every solution that you will encounter, and there is nothing general that one can or should do about this, except be aware that it happens.

The second impact of temperature is on the pH electrode itself. pH electrodes change their response in a very clear way as temperature is changes. They respond more strongly to pH changes at higher temperature than at lower ones. At 100 ℃, they change their output potential by 74 mV/pH unit, and at 0 ℃, they change by 54 mv/pH unit. Because pH meters are typically standardized at pH 7 (that is, zero mv = pH 7), the error from temperature differences gets greater and greater as the pH being measured gets further from 7. So it may be trivial when measuring something with a pH of 7.1, but very important when measuring something with a pH of 10 (or when calibrating with a pH 10 buffer).

There are usually three different ways of taking temperature into account. One is to make measurements close to the temperature at which you calibrated the meter (say, within a few degrees). The second is to "tell' the meter what the temperature is (digitally or with a dial). The third is that some meters have a temperature probe, usually called an ATC, which you stick into the measuring solution. This probe reports the temperature back to the meter, and the meter makes any necessary corrections (for this type of temperature effect).

As long as you use one of these three ways of dealing with temperature issues, you will get reasonably accurate readings.