

The Everyman's Guide To The Miraculous But Misunderstood ORP Sensor

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Everyone in the water and wastewater industry knows and measures pH. Conductivity is a concept we all readily grasp. Dissolved oxygen and free chlorine are easy to understand since they refer to actual chemicals.

But ORP is another matter. If you know that it stands for oxidation-reduction potential then you are already in a select minority. And if you can really explain what it means then you are eligible.

It's precisely because ORP is so poorly understood that we sell about 8 pH sensors for every ORP sensor. Yet, if more people understood just how powerful this 3-letter parameter is we would triple our sales. There is a good chance that you may be one of the many who are missing out on the power hidden in an ORP measurement.

1. What ORP Means

Chemicals are like people. There are givers and there are takers. In the chemical universe the givers are chemical compounds or elements that give electrons to those in need. The takers are those compounds that need and take electrons. In the human race, for every giver there has to be a taker. So it is in chemistry. Electrons don't just float around in water. For every molecule, atom or ion that coughs up an electron there must be another species that can grab it for its own selfish purpose.

The process of giving an electron is called "oxidation" and the process of grabbing an electron is "reduction." One molecule is especially famous for being a "taker"—oxygen. O_2 molecules are ruthless in their pursuit of taking electrons from any poor chemical capable of giving it one or—more frequently—two. A schematic of an oxidation-reduction reaction is shown in Figure 1. In this drawing compound B could be oxygen.

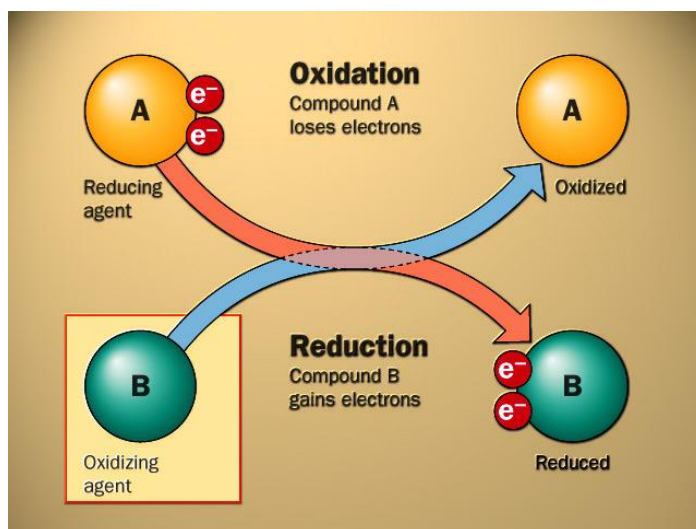
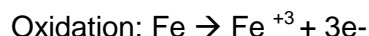


Figure 1 - Schematic of Oxidation Reduction. Compound A gives up two electrons and compound B takes the two electrons

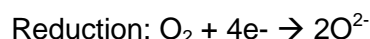
The giver is very often a metal such as iron or sodium. In one case known to us all 4 oxygen atoms gang up on 3 iron atoms and steal a total of 8 electrons. The two elements then form a merger as Fe_2O_3 —or good old rust. Even though iron and oxygen make rust in one fell swoop we like to pretend that the chemical reaction is the result of two reactions—one oxidation reaction and one reduction reaction.

On the oxidation side is selfless iron (Fe), which gives up 3 electrons for the good of the world:

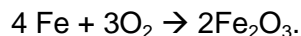


Most trade journals shy away from writing out chemical reactions like the one above. They don't think you can handle them. I think you can. The chemical symbol for iron is Fe and it's form on the left side of the reaction means that it has neither lost nor gained electrons prior to this reaction. We say it is "neutral." But when the oxidation reaction occurs the iron atom gives up 3 electrons. Since each electron has a charge of -1, the loss of three electrons means that poor iron now has a charge of +3. This is denoted by the "+3" superscript.

On the other side of the swap is greedy oxygen in which each O_2 molecule takes four electrons to form 2 oxygen atoms each with a doubly negative charge.



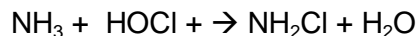
We call these reactions "half reactions" because neither one can proceed by itself. We know that, in real life, they always proceed together and the number of electrons that the iron atoms give up has to equal the number of electrons that the oxygen molecules take. That's why 2 iron atoms link up with 3 oxygen atoms and we combine both half reactions to give us the following full reaction:



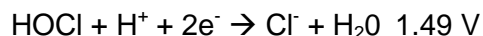
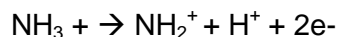
If you wonder how we get 4 Fe atoms reacting with 3 O_2 molecules just do the arithmetic: Four Fe atoms giving up 3 electrons each give up a total of 12 electrons. Three O_2 molecules grabbing 4 electrons each steal a total of 12 electrons. Twelve electrons are given up and twelve are taken. The world is in balance.

Our knowledge of oxygen stealing electrons dates back over two centuries to the great French scientist who lost his head in the French Revolution—Antoine Lavoisier. Tony both discovered oxygen and its propensity to cause rust. Hence the term "oxidation." Since oxidation was originally intended to mean the addition of oxygen then it's easy to see that the term "reduction" comes from opposite process of removing or reducing oxygen. Since the eighteenth century chemists have uncovered thousands of reactions that combine elements or compounds that give up electrons and others that gobble them up but we still use the terms "oxidation" for the former and "reduction" for the latter.

Let's take an example that is near and dear to us in both the water and wastewater industry: the formation of monochloramine (NH_2Cl) from hypochlorite (HOCl) and ammonia (NH_3).



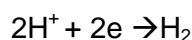
If we bubble ammonia through water nothing happens. If we add HOCl to a container of pure water nothing happens. But add the two ingredients together and you get monochloramine. If we break this reaction into a sum of half-reactions we get:





The last reaction is just a little clean-up to let us know that NH Since oxidation and reduction reactions always occur together we term the pair of reactions as oxidation-reduction or “redox” for short. If you know how a battery works then it should be immediately apparent that, as long as the oxidation reaction is physically separated from the reduction reaction and we force electrons to flow on a wire then we have a battery, or “Galvanic” device. We characterize batteries by their voltage output—or “potential”—and that is exactly how we measure a redox reactions. Instead of volts we use millivolts (mV)—hence the name oxidation-reduction potential (ORP).

We would like to attach a mV reading to just the oxidation or the reduction part of a redox pair but we know we can never measure one without the other. It's like one hand clapping. So we create a standard reaction to which we arbitrarily assign an ORP value of 0 mV. That reaction is the reduction of hydrogen ions to hydrogen gas—the “standard hydrogen electrode” (SHE):



This should sound familiar to anyone who has studied pH electrodes. Standard hydrogen electrodes require bubbling hydrogen gas through a 1 Molar solution of hydrochloric acid (i.e. pH 0). Figure 2 is a schematic of galvanic cell in which nickel oxidizes (i.e. is the reducing agent) and a standard hydrogen electrode serves as the oxidizing agent.

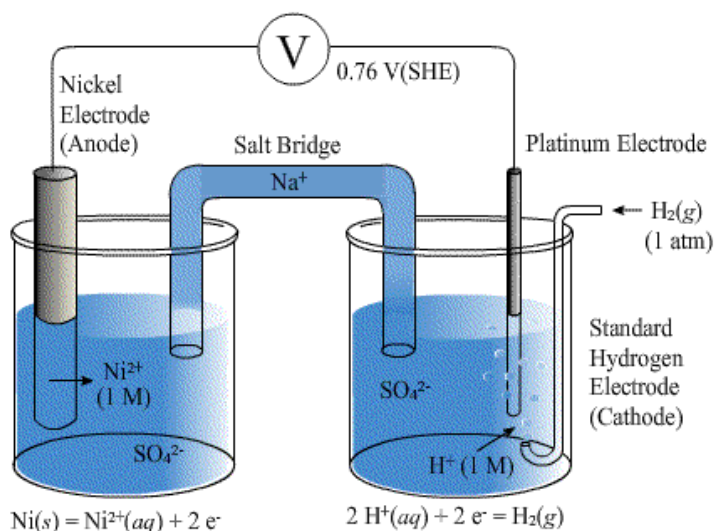
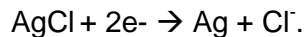


Figure 2 - Oxidation of Nickel with a standard hydrogen electrode

You don't have to be an experienced chemist to realize that using a hydrogen electrode in a working sensor is not very convenient. For this reason electrochemists have largely switched over to a more benign standard reference electrode that is created by immersing a silver wire in a saturated potassium chloride solution. Simple chemistry inside this electrode results in the pure silver in the wire being in equilibrium with silver chloride in solution. This redox reaction is:



This should also look familiar because the silver/silver chloride electrode is the reference electrode in virtually every combination pH probe sold today. Now you can see why an ORP probe and a pH probe differ only by virtue of their process electrode and have the same reference electrode.

The question you should be asking yourself is just what the ORP value of the Ag/AgCl reaction to the H^+/H_2 reaction. The answer is 230 mV at 25 °C. So if a redox reaction is reported relative to the Ag/AgCl reaction and you want to know what the redox value is relative to the SHE just add 230 mV. (Remember though that this is true only at 25 °C.) The sad truth is that authors who report ORP values in the literature, more often than not, do not state which zero reference they are assuming. Fortunately for us practitioners who live in the real world and use real probes with real Ag/AgCl reference electrodes the values we read on our ORP analyzers are the ones we report. Adding 230 mV is just one act of mental drudgery that we would rather not add to our complicated lives. So when you see ORP values of, say 650 mV, that is recommended for disinfection you can assume that this is the value you will measure with your ORP probe consisting of a Pt process electrode and Ag/AgCl reference electrode.

Now we are primed and ready to understand how an ORP probe works. The reference electrode a silver wire in a KCl electrode that undergoes the reaction above in either direction, i.e. it be a reduction reaction and go from left to right or an oxidation reaction and go from right to left. The direction it goes depends on what happens with the process electrode. If the process electrode sits in a solution that has an overall positive oxidation potential the reference electrode will accommodate by undergoing reduction (left to right). If the solution has an overall positive reduction (or negative oxidation) voltage then the reference electrode undergoes oxidation, i.e. the reaction above goes backwards.

The reference electrode is therefore armed and ready to balance whatever the solution throws at the probe. However, just because the potentials add up favorably doesn't mean that the redox reaction will occur. The situation is analogous to a car facing a hill. On the other side of the hill is a decline that is even longer than the uphill it faces but it still has to go up the hill first. What is needed is for someone to bore a tunnel through the hill so the car can make it to the other side.

For an ORP probe that tunnel is the platinum or gold band. These metals are catalysts. They make reactions go faster by providing a tunnel through what we call a reaction barrier. A familiar example is combining hydrogen and oxygen. They want to make water but they can't until a spark provides the boost they need to get started. One little spark and the reaction is a veritable explosion.

The combination of a reference electrode and process electrode is common to all electrochemical sensors. We are all familiar with the pH probe. The only difference between an ORP probe and a pH probe is that we replace the pH process electrode with a simple platinum (or gold) band to make redox reactions go. The reference electrode for an ORP probe is unchanged. The silver wire in a KCl solution saturated with AgCl just becomes a reference for ORP measurements instead pH measurements. For a combination probe the reference electrode is a silver (Ag) wire immersed in KCl-AgCl solution. For a differential probe the reference electrode is a fully enclosed electrode containing the Ag/AgCl system, which is then immersed in pH 7 buffer. Figure 3 shows the front end of a differential ORP probe. You can see the platinum band that surrounds the glass electrode.

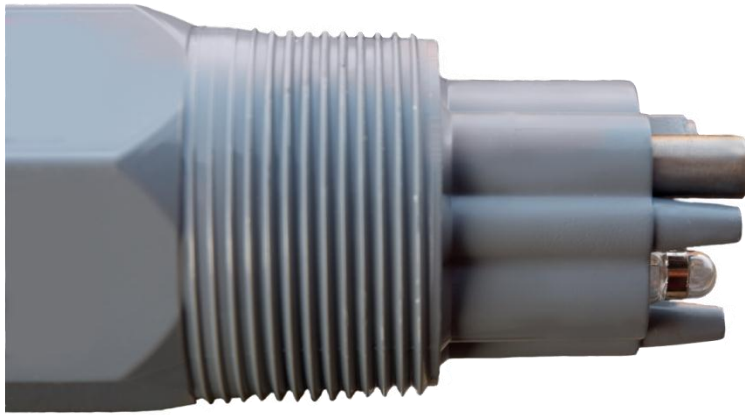


Figure 3 - This front end of an Aquamatrix differential probe shows the process electrode, which consists of nothing more than a Platinum band and a lead wire that connects to the pre-amp.

An ORP sensor may appear to be a minor variation of a pH probe but the ramifications of changing the process electrode to a catalytic Pt surface wired to the reference electrode brings about profound and uniquely powerful consequences.

The ORP probe is a “bottom line” instrument. It doesn’t care about specific chemicals in the water. It simply measures the redox potential of everything in the water. Whether it’s ozone, chlorine, sodium metabisulfite dissolved oxygen or gas it doesn’t care. It only “cares” that whatever is in the water do the job whether that job is breaking down the organic matter, turning nitrates into nitrogen or any of the many other chemical reactions that occur in a water or wastewater treatment facility.