## What is ORP?

ORP stands for *oxidation reduction potential*, which is a measure, in millivolts, of the tendency of an atom or chemical to oxidize or reduce another atom or chemical.

Oxidation

Oxidation is the loss of electrons by an atom, molecule, or ion. Oxygen, which is the origin of the term, is but one of several oxidants that can accomplish this task. Other common oxidants are free chlorine, ozone and peroxides. Common examples of oxidation-reduction reactions are iron rusting and wood burning.

When an atom has been oxidized, its oxidation state increases. Many atoms can exist in a number of oxidation states. A good example is sulfur, which can exhibit oxidation states of: -2 in H_2S; 0 in S; +4 in SO_2; and +6 in SO_4^{-2}. Thus, atoms with multiple oxidation states can be sequentially oxidized from one oxidation state to the next higher. Two different oxidation states of a particular atom or chemical are referred to as redox couples. In Equation 1, an iron atom, which has an oxidation state of 0, is oxidized to form ferrous ion, which has an oxidation state of +2, and two electrons are released.

Equation 1:

$$\underset{\text{iron}}{Fe} \quad = \quad \underset{\text{ferrous ion}}{Fe^{+2}} \quad + \quad \underset{\text{electrons}}{2e^-}$$
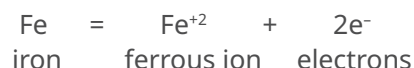
The chemical equation shown in Equation 1 is called the half-reaction for oxidation of iron. Electrons lost by the iron atom cannot exist freely in solution. They have to be accepted by another atom. Thus, an additional equation will need to be written, which represents the reduction of a second atom. The oxidation reaction shown for iron is, therefore, only half of the total reaction that takes place.

Reduction

Reduction is the net gain of electrons by an atom, molecule, or ion.

When a chemical atom is reduced, its oxidation state is lowered. For example, in Equation 2, the chlorine atom has an oxidation state of 0, and is reduced by acquiring two free electrons, to form chloride ion, which has an oxidation state of -1. Thus as was the case with oxidation, atoms or chemicals that can exhibit multiple oxidation states can also be sequentially reduced from one oxidation state to the next lower oxidation state.

The chemical equation shown in Equation 2 is the half-reaction for the reduction of chlorine gas:

Equation 2:

$$\underset{\text{chlorine}}{Cl_2} \quad + \quad \underset{\text{electrons}}{2e^-} \quad = \quad \underset{\text{chloride ion}}{2Cl^-}$$

The redox couple in the above case is Cl_2/Cl^- (chlorine/chloride). Here the chlorine atoms in chlorine gas are reduced by the free electrons to form chloride ions.

Thus oxidation reactions are always accompanied by reduction reactions. The electrons lost in oxidation must have another atom, ion or molecule as a destination, and the electrons gained in reduction reactions have to come from a source.

Equation 3:

Oxidation:
(Half-Reaction)

$$Fe \quad = \quad Fe^{+2} \ + \ 2\,e^-$$

Equation 4:

Reduction:
(Half-Reaction)

$$Cl_2 \ + \ 2\,e^- \ = \ 2\,Cl^-$$

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Equation 5:

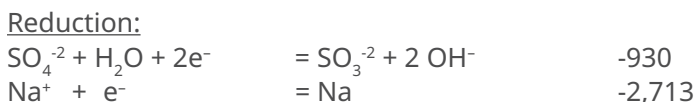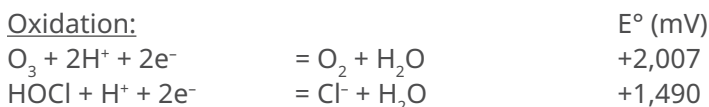**Overall Reaction:** $Fe + Cl_2 => FeCl_2$

When two half-reactions are combined to yield the overall reaction, the electrons lost in the oxidation reaction must equal the electrons gained in the reduction reaction

In Equations 3 to 5, iron (Fe) reduces chlorine (Cl_2) and is called a *reductant* or *reducing agent*.

Conversely, chlorine (Cl_2) oxidizes iron (Fe) and is called an *oxidant* or *oxidizing* agent.

Standard Potential

How easily an atom or chemical is oxidized or reduced is given by the *standard potential* of its redox couple, symbolized by E°. The standard potentials of many half reactions are tabulated in reference books. All are referenced to the redox couple for hydrogen ion/hydrogen (H+/H_2), which is assigned a standard potential of 0 millivolts. Examples of half reactions with their standard potentials are given below:

Oxidation:		E° (mV)
$O_3 + 2H^+ + 2e^-$	$= O_2 + H_2O$	+2,007
$HOCl + H^+ + 2e^-$	$= Cl^- + H_2O$	+1,490

Reduction:		
$SO_4^{-2} + H_2O + 2e^-$	$= SO_3^{-2} + 2\ OH^-$	-930
$Na^+ + e^-$	$= Na$	-2,713

The standard potential for a half-reaction is based on the assumption that the concentrations of all components in the half-reaction are at 1 molar concentration. In a process, however, the concentrations of each component can vary independently of one another. So, to arrive at the ORP of a particular solution, it is necessary to use the Nernst equation to calculate the ORP for each case.

The Nernst Equation for ORP

The ORP of a general half-reaction can be written in terms of molar concentrations as follows:
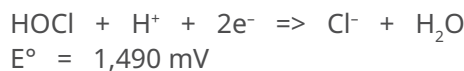
Equation 6:

$$aA+bB+cC+ \ ... + ne^- = xX+yY+zZ + ...$$

$$E = E° - \frac{59.16}{n} \log \frac{[X]^x\,[Y]^y\,[Z]^z\,...}{[A]^a\,[B]^b\,[C]^c\,...}$$

Hypochlorous acid (chlorine in water) provides a useful example of the Nernst equation:

Equation 7:

Half-Reaction:

$$HOCl + H^+ + 2e^- => Cl^- + H_2O$$
$$E° = 1,490\ mV$$

Equation 8:

Nernst Equation (25 °C):

$$E = 1,490 - (29.58) \log \frac{[Cl^-]}{[HOCl]\,[H^+]}$$

Examining Equations 6, 7 and 8 shows some important properties of ORP:

1. *The ORP depends upon the concentrations of all the components in the half-reaction (except water).* Therefore, the ORP of hypochlorous acid depends as much on chloride ion (Cl^-) and pH (H^+) as it does on hypochlorous acid (HOCl).
2. The ORP is a function of the *logarithm* of the concentration ratio.
3. The logarithm of the concentrations is multiplied by a coefficient. This coefficient is -59.16 mV divided by the number of electrons in the half reaction. In this case, n = 2; therefore, the coefficient is -29.58. *A 10-fold change in the concentration of Cl^-, HOCl, H_+ will only change the ORP by ±29.58 mV.*
4. There is no specific temperature dependence shown. Temperature can affect an ORP reaction in a variety of ways, so no general ORP temperature behavior can be characterized Therefore, *ORP measurements are almost never temperature compensated*.

The Measurement of ORP

An ORP sensor consists of an ORP electrode and a reference electrode, in much the same fashion as a pH measurement.

The ORP Electrode

The principle behind the ORP measurement is the use of an inert metal band such as platinum or gold. Because platinum and gold have several oxidation states, they will give up electrons to an oxidant or accept electrons from a reductant. The ORP band will continue to accept and/or give up electrons until it develops a potential, which is equal to the ORP of the solution. The typical accuracy of an ORP measurement is ±10 mV.

The Reference Electrode

The reference electrode in ORP sensors typically uses the same silver-silver chloride wire as pH sensors.

The Application of ORP

ORP can be used to determine the oxidizing strength of a solution. Oxidizers like oxygen, free chlorine, ozone, and peroxide will yield a very positive ORP value. While solutions with organic material will yield negative ORP values.

Concentration Measurement with ORP

Many customers try to establish a correlation between ORP and oxidizer concentration. When the equation for the ORP of a hypochlorous acid solution (Equation 8) is considered, the problems associated with calculating a concentration measurement can be outlined:

1. The ORP depends upon chloride ion (Cl^-) and pH (H^+) as much as it does hypochlorous acid (HOCl). Any change in the chloride ion concentration or pH will affect the ORP. Therefore, to measure free chlorine accurately, chloride ion and pH must be measured to a high accuracy or carefully controlled to constant values.
2. Furthermore, one can plug in the millivolt value read by the sensor into Equation 8 to calculate the hypochlorous acid concentration. The typical accuracy of an ORP measurement is ±10 mV. This error alone will result in the calculated hypochlorous acid concentration to be off by more than ±30%. Any drift in the reference electrode or the ORP analyzer will only add to this error.
3. Any change in the ORP with temperature is not compensated, further increasing the error in the calculated concentration of hypochlorous acid.

ORP is not suitable for measuring exact concentrations of a substance. Virtually all ORP half-reactions involve more than one component, and the vast majority have pH dependence. Additionally, the logarithmic dependence of ORP on concentration multiplies any errors in the measured millivolts. That being said, many customers use ORP as an indirect method to concentration measurements. For instance, customers may determine that an ORP value between 650–750 mV is sufficient for disinfection of their process water. And customers will set their Free chlorine pump to a certain speed to ensure that the ORP is between 650–750 mV. It is important to note that customers should perform experiments to confirm a suitable ORP range, as process waters can vary in their COD content.

Monitoring ORP Reactions

Monitoring ORP reactions is the best application of ORP measurements. When an oxidation-reduction reaction goes to completion, there is usually a large change in the ORP. The typical purpose of using ORP is to ensure that an ORP reaction has gone to completion, i.e., the substance of interest has been completely reduced or completely oxidized.

A titration curve for a simple oxidation-reduction reaction is shown in Graph 1 for the reaction between an oxidant and reductant with standard potentials of +1,000 mV and -1,000 mV, respectively:

The ORP of the oxidation-reduction reaction in Graph 1 can be outlined as follows:

1. *The ORP is due to the oxidant or reductant that is in excess.*
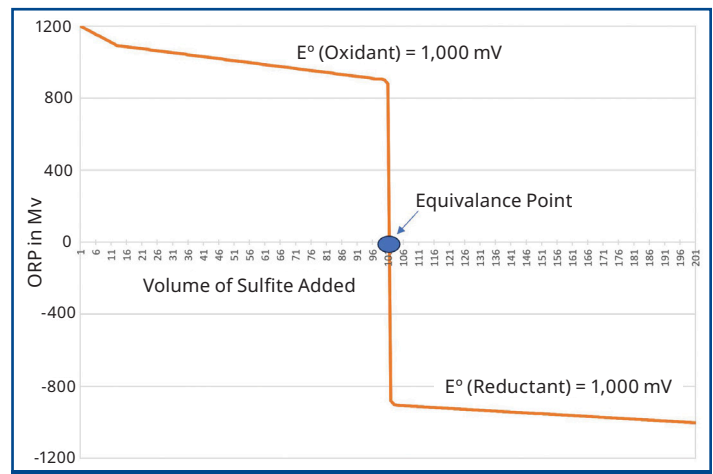
Graph 1 *ORP oxidation-reduction reaction*

In Graph 1, the presence of the oxidant or oxidizer on the left hand side of the curve produces positive ORP values, while the presence of the reductant or reducer on the right hand side of the curve produces negative ORP values.

2. The *equivalence point* is the point where the oxidation-reduction reaction has gone to completion. Near this point there is a large change in the ORP. For a reaction such as this, with no pH dependence assumed, the equivalence point (E_{EP}) can be calculated from the standard potentials for the half reactions of the oxidant and reductant ($E°_{ox}$ and $E°_{re}$), and the number of electrons in their respective half-reactions (n_{ox} and n_{re}):

Equation 9:

$$E_{EP} = \frac{n_{ox}E°_{ox} + n_{re}E°_{re}}{n_{ox} + n_{re}}$$

3. The ORP change near the equivalence point is quite large–1,600 mV.
4. After the equivalence point, the ORP continues to drop slowly and levels out as more reductant is added. The proper area of control would be well below the equivalence point.

As previously mentioned, many ORP reactions are pH dependent. Graph 2 shows the pH dependence of the ORP reaction between hypochlorous acid and sodium sulfite.
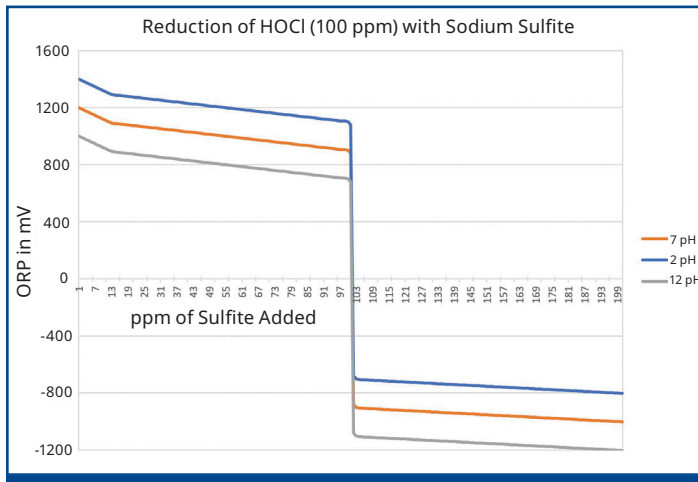
Graph 2 *ORP oxidation-reduction reaction*

The titration curves for each pH are offset, but retain the same basic form.

The equivalence point for a pH dependent reaction can be calculated from a formula similar to the one already given, which includes the pH and the coefficients for hydrogen ion (H+) in the half-reactions for the oxidant and reductant (a_{ox} and a_{re}):

Equation 10:

$$E_{EP} = \frac{n_{ox}E^{\circ}_{ox} + n_{re}E^{\circ}_{re}}{n_{ox} + n_{re}} + \frac{a_{ox}pH + a_{re}pH}{n_{ox} + n_{re}} \cdot (59.16)$$

Both of the examples of ORP titration curves demonstrate utility of ORP measurement for endpoint detection of oxidation-reduction reactions.

Common ORP Applications

Applications that use ORP for monitoring and controlling oxidation-reduction reactions include cyanide destruction, dechlorination, chromate reduction, hypochlorite bleach production, and chlorine and chlorine dioxide scrubber monitoring.

Concentration measurement with ORP, as was described, is problematic, but ORP can be used in some cases for leak detection to detect the presence of an oxidant or reductant.

Finally, ORP is measured, in some instances, for the control of biological growth. The principle behind these applications is that a minimum ORP value will successfully destroy microorganisms. This approach has been used in the chlorination of swimming pools and cooling towers. It should be noted that both of these applications also include pH control.

How to Approach ORP Applications

Regardless of the nature of the application under consideration, the steps to follow are the same:

1. Look up the two half-reaction(s) of the redox couple(s) involved in the application in a handbook of chemistry or other reference.
2. Note all of the chemical substances involved in the half-reaction and their concentration range in the application under consideration.
3. Substituting their minimum and maximum concentrations into the Nernst equation can provide the contribution of each substance to the overall ORP.
4. If an oxidation-reduction reaction is being monitored or controlled, the equivalence point can be calculated over the pH range of the process.

Following the above steps will allow a good estimate of the ORP behavior of the application, which can then be compared with the goals of the application.

Summary

The oxidation reduction potential of a solution is a measure of the oxidizing or reducing power of the solution. Every overall oxidation or reduction reaction can be characterized by two half-reactions. The ORP of the solution depends upon the logarithm of the concentration of the components participating in the half-reaction. The ORP can be calculated using the Nernst equation. ORP is not a good method for measuring concentration due to its logarithmic dependence on concentration and its dependence on multiple solution components. The best use of an ORP measurement is in monitoring and controlling oxidation-reduction reactions.

The Emerson Solution

Accurate ORP measurement requires a reliable ORP sensor and transmitter. The Rosemount™ 3500P ORP Sensor features a rebuildable double junction reference cell that allows for wide application flexibility by using different reference electrolyte solutions. The resulting ORP sensors last longer, respond faster and drift less, minimizing maintenance and lowering the total cost of ownership.

The Rosemount 1058 Dual-Channel Transmitter supports continuous measurement of liquid analysis inputs from one or two sensors. Each sensor channel is independently configurable to support a wide selection of digital or analog liquid analysis sensors including ORP sensors. The transmitter features a large color LCD screen with intuitive menus and alpha-numeric keypad enable easy configuration and calibration.

Rosemount 3500P ORP Sensor

Rosemount 1058 Dual-Channel Transmitter

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