Application Data Sheet
ADS 43-014/rev.B
May 2008

FUNDAMENTALS OF ORP MEASUREMENT

WHAT IS ORP?

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

OXIDATION

Oxidation is the loss of electrons by an atom, molecule, or ion. It may or may not be accompanied by the addition of oxygen, which is the origin of the term. Familiar examples are iron rusting and wood burning.

When a substance has been oxidized, its oxidation state increases. Many substances can exist in a number of oxidation states. A good example is sulfur, which can exhibit oxidation states of -2 (H_2S); 0 (S); +4 (SO_2); and +6 (SO_4^{-2}). Substances with multiple oxidation states can be sequentially oxidized from one oxidation state to the next higher. Adjacent oxidation states of a particular substance are referred to as redox couples. In the case below, the redox couple is Fe^{+2}/Fe:

$$\underset{\text{iron}}{Fe} \quad = \quad \underset{\text{ferrous ion}}{Fe^{+2}} \quad + \quad \underset{\text{electrons}}{2e^{-}}$$

The chemical equation shown above is called the *half-reaction* for the oxidation, because, as will be seen, the electrons lost by the iron atom cannot exist in solution and have to be accepted by another substance in solution. So the complete reaction involving the oxidation of iron will have to include another substance, which will be reduced. 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 substance is reduced, its oxidation state is lowered. As was the case with oxidation, substances 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 below is the half-reaction for the reduction of chlorine:

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

The redox couple in the above case is Cl_2/Cl^- (chlorine/chloride).

Oxidation reactions are always accompanied by reduction reactions. The electrons lost in oxidation must have another substance as a destination, and the electrons gained in reduction reactions have to come from a source.

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

OXIDATION: $Fe = Fe^{+2} + 2e^{-}$
(Half- Reaction)

REDUCTION: $Cl_2 + 2e^{-} = 2Cl^{-}$
(Half- Reaction)

OVERALL REACTION: $Fe + Cl_2 \Rightarrow FeCl_2$

In the reaction above, 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 a substance is oxidized or reduced is given by the *standard potential* of its redox couple, symbolized by E°. The standard potentials of quite a number of redox couples are tabulated in reference books, along with their half-reactions. All are referenced to the redox couple for hydrogen ion/hydrogen (H^+/H_2), which is assigned a standard potential of 0 millivolts. The standard potential refers to half reaction written as a reduction. The negative of the tabulated standard potential gives the standard potential for the oxidation half-reaction. An example of these follows:

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OXIDANTS:		E° (mV)
$O_3 + 2H^+ + 2e^-$	$= O_2 + H_2O$	+2,007
$HOCl + H^+ + 2e^-$	$= Cl^- + H_2O$	+1,490
REDUCTANTS:		
$SO_4^{-2} + H_2O + 2e^-$	$= SO_3^{-2} + 2\ OH^-$	-930
$Na^+ + e^-$	$= Na$	-2,713

ORP IN SOLUTIONS

The standard potential for a half reaction is based on the assumption that the concentrations of all the chemical substances shown in the half reaction are at 1 molar concentration. In a process, however, the concentrations 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:

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

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

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

HALF-REACTION:

$HOCl + H^+ + 2e^- \Rightarrow Cl^- + H_2O$

$E° = 1{,}490$ mV

NERNST EQUATION (25°C)

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

Examining the hypochlorous acid/chloride equation shows some important properties of ORP:

1. *The ORP depends upon the concentrations of all the substances 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.
2. The ORP is a function of the *logarithm* of the concentration ratio.
3. The coefficient that multiplies this logarithm of concentration is equal to -59.16 mV, divided by the number of electrons in the half-reaction (n). 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 ±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, as is the case with pH. Therefore, *ORP measurements are almost never temperature compensated.*

When checking the influence of an individual substance in the half reaction, the Nernst equation can be partitioned into individual logarithms for each substance, and the contribution of that substance calculated over its expected concentration range.

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 electrode (platinum, sometimes gold), which, due to its low resistance, will give up electrons to an oxidant or accept electrons from a reductant. The ORP electrode will continue to accept or give up electrons until it develops a potential, due to the build up charge, which is equal to the ORP of the solution. The typical accuracy of an ORP measurement is ±5 mV.

Sometimes the exchange of electrons between the ORP electrode and certain chemical substances is hampered by a low rate of electron exchange (exchange current density). In these cases, ORP may respond more strongly to a second redox couple in the solution (like dissolved oxygen). This leads to measurement errors, and it is recommended that new ORP applications be checked out in the laboratory before going on-line.

THE REFERENCE ELECTRODE

The reference electrode used for ORP measurements is typically the same silver-silver chloride electrode used with pH measurements. In contrast with pH measurements, some offset in the reference is tolerable in ORP since, as will be seen, the mV changes measured in most ORP applications are large.

In certain specific applications (for example, bleach production), an ORP sensor may use a silver billet as a reference, or even a pH electrode.

THE APPLICATION OF ORP

Due to its dependence upon the concentrations of multiple chemical substances, the application of ORP for many has been a puzzling and often frustrating experience. When considering ORP for a particular application, it is necessary to know the half-reaction involved and the concentration range of all the substances appearing in the half-reaction. It is also necessary to use the Nernst equation to get an idea of the expected ORP behavior.

CONCENTRATION MEASUREMENT WITH ORP

ORP is often applied to a concentration measurement (chlorine in water for example) without a clear understanding of all the factors involved. When the equation for the ORP of a hypochlorous solution (in the previous section) is considered, the problems associated with a concentration measurement can be outlined:

1. The ORP depends upon chloride ion (Cl^-) and pH (H^+) as much as it does hypochlorous acid (chlorine in water). Any change in the chloride concentration or pH will affect the ORP. Therefore, to measure chlorine accurately, chloride ion and pH must be measured to a high accuracy or carefully controlled to constant values.
2. To calculate hypochlorous concentration from the measured millivolts, the measured millivolts will appear as the exponent of 10. The typical accuracy of an ORP measurement is ±5 mV. This error alone will result in the calculated hypochlorous acid concentration being 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 derived concentration.

In general, ORP is not a good technique to apply to concentration measurements. Virtually all ORP half-reactions involve more than one substance, and the vast majority have pH dependence. The logarithmic dependence of ORP on concentration multiplies any errors in the measured millivolts.

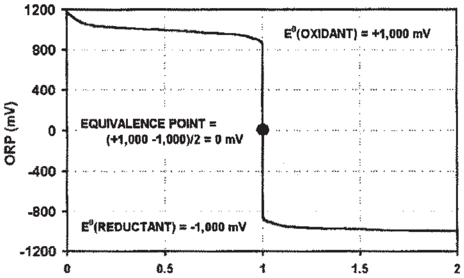
MONITORING ORP REACTIONS

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, which overwhelms the factors that make concentration measurements a problem. 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 below for the reaction between an oxidant and reductant with standard potentials of +1,000 mV and -1,000 mV, respectively (see Graph 1, below):

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

1. *The ORP is due to the redox couple of the reagent (oxidant or reductant) that is in excess.*



GRAPH 1

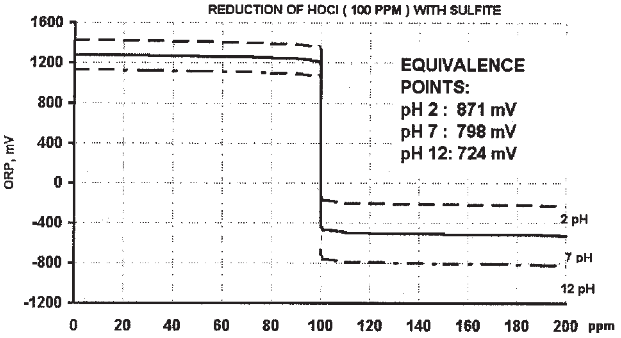
   In this case, the redox couple of the oxidant determines the left portion of the curve and the right portion by the redox couple of the reductant controls the left portion of the curve.

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}):

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

3. The ORP change near the equivalence point is quite large—1,600 mV. Only controlling the ORP to within ±100 mV would still ensure completion of the reaction.
4. Beyond the equivalence point, the ORP continues to drop, but once again levels out as more reductant is added. If control were attempted on this flat portion of the curve, it would be very easy to add excessive amounts of reductant. Hence, the proper area of control would be well below the equivalence point, but above the flat portion of the reductant portion of the curve, somewhere between -400 and -800 mV.

The behavior of the ORP accompanying an oxidation-reduction reaction will depend on pH if the ORP of the oxidant or reductant is pH dependent. The following titration curve (see Graph 2) shows the ORP of the reaction of hypochlorous acid and bisulfite ion. The half-reactions for both of the redox couples are pH dependent.



GRAPH 2

The titration curves for each pH are offset, but retain the same basic form. Even with a variation in pH of 2 to 12, controlling the ORP somewhere between 0 and +400 mV would ensure complete reduction of hypochlorous acid.

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}):

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

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

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 using bisulfite.

Concentration measurement with ORP, as was seen, 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 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 oxidation or reduction can be characterized by a half-reaction, which gives all of the chemical substances participating in the reaction. The ORP of the solution depends upon the logarithm of the concentrations of the substances 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.

INSTRUMENTATION

Model 1056 Analyzer

- MULTI-PARAMETER INSTRUMENT – single or dual input. Any combination of pH/ORP/ISE, Resistivity/Conductivity, Chlorine, Oxygen, Ozone, Turbidity, Flow.
- LARGE DISPLAY – easy-to-read process measurements.
- SEVEN LANGUAGES: English, French, German, Italian, Spanish, Portuguese, and Chinese.
- HART AND PROFIBUS DP Digital Communications

Model 3500 pH/ORP Sensors

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