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Education Series
ORP Theory

Introduction

Oxidation Reduction Potential (ORP) is, simply put, an indication of a solution's ability to oxidize or reduce another solution. It is a ratio of oxidized species to reduced species in a solution containing both. Some commonly used oxidizers include chlorine, ozone, bromine, sodium hypochlorite, and hydrogen peroxide. Examples of reductants include sodium bisulfite (also known as sodium metabisulfite) and sulfur dioxide. The terms "ORP" and "Redox" are both commonly used and are interchangeable.

Theory

Redox measurements and electrodes are, in certain regards, very similar to pH measurements and electrodes. Where a pH probe indicates acid/base levels by measuring the hydrogen ion activity, a redox probe indicates oxidizing/reducing cabability of a solution by measuring the electron activity.

From acid/base theory, we know that a solution containing a strong acid will also contain its conjugate weak base, and a solution containing a strong base will also contain its conjugate weak acid. Similarly, a solution containing a reducing agent will also contain a corresponding oxidizer.

Returning yet again to the pH analogy, an acid is defined as a substance able to donate a hydrogen ion, where a base is defined as a substance capable of accepting a hydrogen ion. Analogously, a reduction agent is a substance capable of donating an electron, where an oxidizing agent is capable of accepting an electron. Furthermore, there can be no oxidation without simultaneous reduction.

The indicator electrode measures electron activity, and to do this it must be both chemically inert and an electron conductor. Platinum is the most frequently used material for ORP electrodes, except in applications containing strong reducing solutions, such as alkaline cyanide solutions, where the catalytic properties of platinum cause hydrogen ions to be reduced at the electrode surface, forming the generation of stray potentials. In applications such as these, Gold is typically the material of choice.

Unlike pH and other ion-specific electrodes which are specific in nature, one must bear in mind that ORP electrodes merely measure the ratio of oxidized to reduced forms of all chemical species in solution, so some pre-knowledge of the sample must be known for the ORP reading to be meaningful.

ORP electrodes measure the redox potential according to the Nernst half-cell potential equation:

$$E = E^o + (2.3RT / nF) \times (\log [^aOx] / [^aRed])$$

Where:

- E = electrode potential measured
- E^o = a voltage specific to the system under analysis. Values of E^o are available in chemical handbooks for a particular reaction, such as $Fe^{+3} + e \rightarrow Fe^{+2}$.
- R = the universal gas constant
- T = Absolute Temperature (K)
- n = the number of electrons involved in the equilibrium between the oxidized and reduced species.

- F = the Faraday constant (96500 coulombs)
- [ ] = denotes activity of bracketed ions

Let us take a look at a mixture of solutions of ferrous chloride (Fe^{+2}) and ferric chloride (Fe^{+3}) where we place a combination ORP probe into the solution (a combination ORP probe has a reference electrode built into the same body as the ORP sensing electrode. The reference electrode provides a stable, constant voltage to which the unknown voltage read by the ORP sensing element is compared).

In such a solution, there is a tendency for ferrous ions to each lose an electron and therefor be oxidized to the ferric form, with the simultaneous tendency of ferric ions to each be reduced to the ferrous form. This creates a measureable voltage which is picked up by the ORP sensing electrode:

$$Fe^{+2} - 1e \longrightarrow Fe^{+3}$$

$$Fe^{+3} + 1e \longrightarrow Fe^{+2}$$
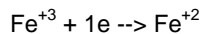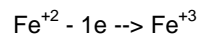
The following equation represents the output voltage produced by the ORP electrode when compared to that of the reference electrode. Thus, the voltage E is a measure of the ratio of activities of ferric ion and ferrous ion.

$$E = [E^o + (2.3RT/nF) \times (\log [Fe^{+3}]/[Fe^{+2}])] - E_{ref}$$

where E_{ref} is the half-cell potential of the reference electrode at 25^oC

pH Effects

A good example of the pH dependency of some ORP reactions is the reduction of the toxic hexavalent chrome, Cr^{+6}, in the form of $Cr_2O_7^{-2}$ to the nontoxic trivalent chrome Cr^{+3}:

$$Cr_2O_7^{-2} + 14H^+ + 6e = 2Cr^{+3} + 7H_2O$$
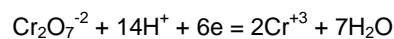
$$E^o = 1.33 \text{ V}$$

The Nernst equation for this reaction is:

$$E = E^o + (2.3RT/nF) \times \log ([Cr_2O_7^{-2}][H^+] / [(Cr^{+3})^2])$$

where n = +6 and the term (H^+) shows that the potential is dependent on solution pH. This can be rewritten as:

$$E = E^o - (14/6) \times ((2.3RT)(pH)/1F) + (2.3RT/6F) \times \log [Cr_2O_7^{-2}] / [(Cr^{+3})^2] - E_{ref}$$

While the pH is constant, the pH term can be lumped together with the E^o so that the variable potential is a true function of the ORP state of the chrome ions.

In some cases, the pH effect may be present on both the oxidation and reduction reactions, while in other cases, pH changes may only affect the potential of one reaction.

Temperature Effects

Temperature has 2 distinct effects on ORP measurements:

- Electrodes will have a different output potential at different temperatures for a given ratio of ionic activity.
- Ionic activity is affected, arising from temperature effects on dissocation, activity coefficients, and interactions between ions in solution.

In general, however, ORP measurements are not compensated for temperature effects due to the fact that:

- The isopotential point (the point of thermal independence) of ORP systems are specific only for that particular redox reaction (i.e. there is no "standard" isopoint for all ORP reactions).
- The chemistry of the redox reaction can be quite complex, especially if several ionic species involving varying numbers of electrons transferred (thus varying values for n within one equation) contribute to the reaction / oxidation reduction potential.
- Most ORP measurements are done at constant temperatures, such as in process measurement and control.

Conclusion

ORP measurements depends upon some pre-knowledge of the sample being measured and can only be made under the following conditions:

- There are two reacting substances present in solution: one being oxidized, while the other being simultaneously reduced.
- The speed of reaction, following the addition of one of the above substances, is sufficiently fast for adequate measurement and/or control.
- Contaminating substances capable of causing undesired side reactions of oxidation or reduction are controlled / held to a minimum.
- The pH of the solution is controlled if the reaction is pH dependent.