Oxidation - Reduction Theory

Oxidation-Reduction - REDOX

A chemical reaction where there is a net change in the oxidation number of one or more species.

Both an oxidation and a reduction must occur during the reaction.

Oxidizing agent

The species that gains electrons during the reaction:

Causes an oxidation.
It is reduced.

\[ A_{\text{ox}} + n \, e^- = A_{\text{red}} \]
\[ Fe^{3+} + e^- = Fe^{2+} \]

Reducing agent

The species that loses electrons during the reaction:

Causes a reduction.
It is oxidized.

\[ B_{\text{red}} = B_{\text{ox}} + n \, e^- \]
\[ Zn^0_{(s)} = Zn^{2+} + 2 \, e^- \]

Overall reaction

Both an oxidation and a reduction must occur in a reaction. The oxidizing agent accepts one or more electrons from the reducing agent.

\[ A_{\text{ox}} + B_{\text{red}} = A_{\text{red}} + B_{\text{ox}} \]
\[ 2 \, Fe^{3+} + Zn^0_{(s)} = 2 \, Fe^{2+} + Zn^{2+} \]

Half reactions

A common approach for listing species that undergo REDOX is by using half-reactions.

For \[ 2 \, Fe^{3+} + Zn^0_{(s)} = 2 \, Fe^{2+} + Zn^{2+} \]
\[ Fe^{3+} + e^- = Fe^{2+} \quad \text{(reduction)} \]
\[ Zn^0_{(s)} = Zn^{2+} + 2e^- \quad \text{(oxidation)} \]

You'll find this approach useful for a number of reasons.

Half reactions

Tables are available which list half reactions as either oxidations or reductions.

Will provide

- Standard E° values to help predict reactions and equilibria.
- Other species that participate in the reaction.
- Show the relative ability to gain or loss electrons.
### Standard reduction potentials

<table>
<thead>
<tr>
<th>Half reaction</th>
<th>(E^0, \text{V})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_2 + 2H^+ + e^- = 2 HF)</td>
<td>3.06</td>
</tr>
<tr>
<td>(Ce^{4+} + e^- = Ce^{3+}) (in 1N HCl)</td>
<td>1.28</td>
</tr>
<tr>
<td>(O_2 + 4H^+ + 4e^- = 2 H_2O)</td>
<td>1.229</td>
</tr>
<tr>
<td>(Ag^+ + e^- = Ag)</td>
<td>0.800</td>
</tr>
<tr>
<td>(2H^+ + 2e^- = H_2)</td>
<td>0.000</td>
</tr>
<tr>
<td>(Fe^{2+} + 2e^- = Fe)</td>
<td>-0.440</td>
</tr>
<tr>
<td>(Zn^{2+} + 2e^- = Zn)</td>
<td>-0.763</td>
</tr>
<tr>
<td>(Al^{3+} + 3e^- = Al)</td>
<td>-1.66</td>
</tr>
<tr>
<td>(Li^+ + e^- = Li)</td>
<td>-3.04</td>
</tr>
</tbody>
</table>

### Half reactions

Having a half-reaction table also makes producing a balanced chemical reaction very easy.

**Example**

Determine the balanced equation for the reaction of \(Fe^{2+}\) with \(Cr_2O_7^{2-}\) in an acidic solution.

### Half reactions

From the standard reduction potentials, we can obtain the following:

\[Fe^{3+} + e^- = Fe^{2+}\]
\[Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O\]

- We know that one of the half reactions must be reversed since an oxidation and a reduction must both occur.
- Based on the question, we know that it is the iron half reaction that must be an oxidation.

\[Fe^{2+} = Fe^{3+} + e^-\]
\[Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O\]

Now all we need to do is make sure that the electrons are the same on both sides.

This requires that we multiply the Fe half reaction by six so:

\[6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ = 6Fe^{3+} + 2Cr^{3+} + 7H_2O\]

(balanced equation)

### REDOX reactions

There are two general ways to conduct an oxidation-reduction reaction

**Mixing oxidant and reductant together**

\[Cu^{2+} + Zn_{(s)} \rightleftharpoons Cu_{(s)} + Zn^{2+}\]

This approach does not allow for any control of our reaction.

### REDOX reactions

**Electrochemical cells**

Each half reaction is put in a separate ‘half cell’ which is connected electrically.

Permits better control over the system.
Electrochemical cells

Cu^{2+} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}

Electrons are transferred from one half-cell to the other using an external metal conductor.

Salt bridge

Allows ion migration in solution but prevents extensive mixing of electrolytes.

It can be a simple porous disk or a gel saturated with a non-interfering salt like KCl.

Cl^- \rightarrow KCl \rightarrow K^+

Cl^- is released to Zn side as Zn^{0} is converted to Zn^{2+}

K^+ is released to Cu side as Cu^{2+} is converted to Cu^{0}

For our example, we have zinc ion being produced.

This is an oxidation so:

- The electrode is the anode
- is positive (+).

Zn \rightarrow Zn^{2+} + 2e^-

For our other half cell, we have copper metal being produced.

This is a reduction so:

The electrode is the cathode
- is negative (-)

Cu^{2+} + 2e^- \rightarrow Cu

Types of electrochemical cells

Galvanic
- The ‘spontaneous’ reaction
- Produces electrical energy

Electrolytic
- Non-spontaneous reaction
- Required electrical energy to occur

For a reversible cell, galvanic reaction can occur spontaneously and then be reversed electrolytically - rechargeable batteries.
Not all reactions are reversible.

**Examples of non-reversible reactions**

If a gas is produced which escapes.

\[
2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 (g)
\]

If one or more of the species decomposes.

A measure of how willing a species is to gain or lose electrons.

**Standard potentials**

Potential of a cell acting as a cathode compared to the standard hydrogen electrode.

Values also require other standard conditions.

**Hydrogen electrode (SHE)**

The ultimate reference electrode.

\[
\text{H}_2 \text{ is constantly bubbled into a 1 M HCl solution}
\]

\[
\text{Pt / H}_2 (1 \text{atm}), 1\text{M H}^+ // \text{Pt black plate}
\]

\[
E^o = 0.000000 \text{ V}
\]

All other standard potentials are then reported relative to SHE.

Standard potentials are defined using specific concentrations.

- All dissolved species are at 1 M
- Slightly soluble species must be at saturation.
- Any gas is constantly introduced at 1 atm
- Any metal must be in electrical contact
- Any other solids must also be in contact with the conducting electrode.

The standard potential for \(\text{Cu}^{2+} + 2\text{e}^- = \text{Cu} (s)\) is +0.334V.

**This means that:**

If a sample of copper metal is placed in a 1 M Cu\(^{2+}\) solution, we'll measure a value if 0.334V if compared to:

\[
2 \text{H}^+ + 2 \text{e}^- = \text{H}_2 (g) \quad (1 \text{ M}) \quad (1 \text{ atm})
\]

One thing that we would like to know if the spontaneous direction for a reaction.

This requires that we determine the \(E_{\text{cell}}\).

Since our standard potentials \((E^o)\) are commonly listed as reductions, we'll base our definitions on that.

\[
E_{\text{cell}} = E_{\text{forward}} - E_{\text{reverse}}
\]

\[
E^o_{\text{cell}} = E^o_{\text{forward}} - E^o_{\text{reverse}}
\]
Cell potentials

You know that both an oxidation and a reduction must occur.
One of your half reactions must be reversed.
The spontaneous or galvanic direction for a reaction is the one where $E_{\text{cell}}$ is a positive value so.
The half reaction with the largest $E$ value will proceed as a reduction.
The other will be reversed - oxidation.

For our copper-zinc cell at standard conditions:

\[
\begin{align*}
\text{Cu}^{2+} + 2e^- & = \text{Cu}^0 & +0.334 \text{ V} \\
\text{Zn}^{2+} + 2e^- & = \text{Zn}^0 & -0.763 \text{ V}
\end{align*}
\]

\[E_{\text{cell}} = 1.097 \text{ V}\]

Galvanic reaction at standard conditions.

\[
\text{Cu}^{2+} + \text{Zn}^0 = \text{Cu}^0 + \text{Zn}^{2+}
\]

Schematic representations

Rather than attempt to draw out an entire cell, a type of shorthand can be used.

For our copper-zinc cell, it would be:

\[
\text{Zn} / \text{Zn}^{2+} (1\text{ M}) \ || \ \text{Cu}^{2+} (1\text{ M}) / \text{Cu}
\]
The anode is always on the left
// = boundaries
\| = salt bridge
Other conditions like concentration are listed just after each species.

Other examples

\[
\text{Pt, H}_2 (1\text{ atm}) / \text{H}^+ (1\text{ M})
\]

This is the SHE. Pt is used to maintain electrical contact so is listed. The pressure of \(\text{H}_2\) is given in atmospheres.

\[
\text{Pt, H}_2 (1\text{ atm}) / \text{HCl} (0.01\text{ M}) \|| \text{Ag}^+ (\text{sat}) / \text{Ag}
\]

A saturated silver solution (1.8x10^{-8}\text{M}) based on the $K_{\text{SP}}$ of AgCl and the [Cl⁻].

Calomel reference electrode

\textbf{Calomel electrode (SCE)}

A much more common reference electrode.

It much easier to work with - no gas.

\[
\text{Hg} / \text{Hg}_2\text{Cl}_2 (\text{sat}) \ || \ \text{KCl} \ || \ \text{KCl solution}
\]

KCl is used to maintain constant ionic strength.

\textbf{Calomel electrode}

Different KCl concentrations can be used.

- 0.1 M - least temperature sensitive
- Saturated - easier to make and maintain.

\[E = 0.244V\]

Using this electrode will alter our measured values since our reference is now 0.2444V not 0.0000V.
Calomel reference electrode

Since the calomel electrode has a value of 0.244V, all of our measurements will be offset by that amount.

For standard electrode potentials:
$$E_{\text{measured}} = E^0 - 0.244$$

<table>
<thead>
<tr>
<th>Half reaction</th>
<th>$E^0_{\text{SHE}}$</th>
<th>$E^0_{\text{SCE}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}^+ + e^- = \text{Ag}$</td>
<td>0.800</td>
<td>0.556</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2e^- = \text{Zn}$</td>
<td>-0.763</td>
<td>-1.007</td>
</tr>
</tbody>
</table>

Concentration dependency of E

$E^0$ values are based on standard conditions.
The $E$ value will vary if any of the concentrations vary from standard conditions.

This effect can be experimentally determined by measuring $E$ verses a standard (indicating) electrode.

Theoretically, the electrode potential can be determined by the **Nernst equation**.

The Nernst equation

For $A^a + ne^- = B^b$

$$E = E^0 + \frac{RT}{nF} \ln \frac{aA^a}{aB^b}$$

where:
- $E^0$ = standard electrode potential
- $R$ = gas constant - 8.314 J/mol
- $T$ = absolute temperature
- $F$ = Faraday’s constant - 96000 coul
- $n$ = number of electrons involved
- $a$ = activity

Concentration dependency of E

If we assume that concentration is proportional to activity and limit our work to 25°C, the equation becomes:

$$E = E^0 - \frac{0.0592}{n} \log \frac{[A]^a}{[B]^b}$$

Variations of $E$ are based on ratio of the concentrations.

This also includes a conversion from base $e$ to base 10 logs.

Concentration dependency of E

Example

Determine the potential of a Pt indicating electrode if dipped in a solution containing 0.1M Sn$^{4+}$ and 0.01M Sn$^{2+}$:

$$\text{Sn}^{4+} + 2e^- = \text{Sn}^{2+} \quad E^0 = 0.15V$$

$$E = E^0 - \frac{0.0592}{2} \log \frac{0.01 \text{ M}}{0.1 \text{ M}}$$

$$= 0.18 \text{ V}$$

Concentration dependency of E

Another example

Determine the potential of a Pt indicating electrode if placed in a solution containing 0.05 M Cr$_2$O$_7^{2-}$ and 1.5 M Cr$^{3+}$, if pH = 0.00 (as HCl).

$$\text{Cr}_2\text{O}_7^{2-} + 14 \text{ H}^+ + 6e^- = 2\text{Cr}^{3+} + 7 \text{ H}_2\text{O}$$

$$E^0 = 1.33 \text{ V}$$
Concentration dependency of E

$$E = E^0 - \frac{0.0592}{6} \log \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$= 1.33 \text{ V} - \frac{0.0592}{6} \log \frac{(1.5)^2}{(0.05)(1)^{14}}$$

$$= 1.00 \text{ V}$$

We can use variations in $E$ to determine the concentration of species in solution.
- potentiometric methods.

The most straightforward example is when an electrode is produced by placing a metal in contact with a solution of its ion.

$\text{Ag}^+ + e^- \quad = \quad \text{Ag}$
$\text{Cu}^{2+} + 2e^- \quad = \quad \text{Cu}$
$\text{Zn}^{2+} + 2e^- \quad = \quad \text{Zn}$

**Example**

A silver metal indicating electrode is dipped into a solution containing $\text{Ag}^+$. A value of $+0.692\text{V}$ is measured versus SHE.

Determine the concentration of $\text{Ag}^+$ in this solution.

$\text{Ag}^+ + e^- \quad = \quad \text{Ag}$

$E^0 = 0.800\text{V}$

$$E = E^0 - 0.0592 \log \frac{1}{[\text{Ag}^+]}$$

$0.692 = 0.800 + 0.0592 \log [\text{Ag}^+]$

$$\log[\text{Ag}^+] = \frac{-1.08}{0.0592}$$

$[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ M}$

Calculation of cell potentials

To determine the galvanic $E_{\text{cell}}$ at standard conditions using reduction potentials:

$$E_{\text{cell}} = E^0_{\text{forward}} - E^0_{\text{reverse}}$$

Where

$E^0_{\text{forward}}$ - half reaction with the largest or least negative $E^0$ value.

$E^0_{\text{reverse}}$ - half reaction with the smallest or most negative $E^0$ value.

At non-standard conditions, we don’t know which will proceed as a reduction until we calculate each $E$ value.

**Steps in determining the spontaneous direction and $E$ of a cell.**

- Calculate the $E$ for each half reaction
- The half reaction with the largest or least negative $E$ value will proceed as a reduction.
- Calculate $E_{\text{cell}} = E_{\text{forward}} - E_{\text{reverse}}$
Example
Determine the spontaneous direction and $E_{\text{cell}}$ for the following system.

\[
Pb / Pb^{2+} (0.01M) \ || \ Sn^{2+} (2.5M) / Sn
\]

**Half reaction**

\[
Pb^{2+} + 2e^- = Pb \quad -0.126 \text{ V} \\
Sn^{2+} + 2e^- = Sn \quad -0.136 \text{ V}
\]

**Note:** The above cell notation may or may not be correct.

Calculation of cell potentials

For lead:
\[
E = -0.126 - \frac{0.0592}{2} \log \frac{1}{0.01} = -0.185 \text{ V}
\]

For tin:
\[
E = -0.136 - \frac{0.0592}{2} \log \frac{1}{2.5} = -0.124 \text{ V}
\]

Under our conditions, tin will proceed as a reduction.

Calculation of cell potentials

\[
\begin{align*}
Sn^{2+} + 2e^- &= Sn \\
- (Pb^{2+} + 2e^- &= Pb) \\
Sn^{2+} + Pb &= Sn + Pb^{2+} \\
&= 0.061 \text{ V}
\end{align*}
\]

So determining the spontaneous $E_{\text{cell}}$ is really nothing more than doing two sets of calculations prior to the final calculation.

Cell potential and equilibrium

We now know that changing concentrations will change $E_{\text{cell}}$. $E$ is a measure of the equilibrium conditions of a REDOX reaction.

It can be used for determining direction and $E_{\text{cell}}$ at non-standard conditions.

Determining the equilibrium constant for an REDOX reaction.

Can be modified to include other equilibrium expressions.

Example
Determine the potential of a silver electrode in a saturated solution of AgCl.

\[
E = 0.800V - 0.0592 \log \frac{1}{[Ag^+]} 
\]

Unfortunately, we don't know $[Ag^+]$.

We do know that $K_{SP \ AgCl} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$
Cell potential and equilibrium

Since we're dealing with a saturated AgCl solution, we know that:

\[ [\text{Ag}^+] = [\text{Cl}^-] = K_{\text{SP}}^{1/2} \]

\[ E = 0.800 \text{V} - 0.0592 \log \frac{1}{K_{\text{SP}}^{1/2}} \]

= 0.511 V

If \([\text{Ag}^+] \neq [\text{Cl}^-]\), we could use the expression

\[ E = 0.800 \text{V} - 0.0592 \log \frac{[\text{Cl}^-]}{K_{\text{SP}}} \]

Equilibrium constants

We can develop equilibrium constants for REDOX based reactions based on the fact at equilibrium:

\[ E_{\text{cell}} = 0 = E_{\text{forward}} - E_{\text{reverse}} \]

or

\[ E_{\text{forward}} = E_{\text{reverse}} \]

Equilibrium constants

For the general equilibrium:

\[ n \text{A}_{\text{RED}} + m \text{B}_{\text{OX}} \rightleftharpoons n \text{A}_{\text{OX}} + m \text{B}_{\text{RED}} \]

we have two half reactions

\[ n \text{A}_{\text{OX}} + nm \text{e}^- = n \text{A}_{\text{RED}} \]
\[ m \text{B}_{\text{OX}} + nm \text{e}^- = m \text{B}_{\text{RED}} \]

\( nm - n \times m = \) lowest common denominator for the balanced reaction.

Equilibrium constants

At equilibrium \( E_A = E_B \) so:

\[ E_A^0 - \frac{0.0592}{nm} \log \frac{[\text{A}_{\text{RED}}]^n}{[\text{A}_{\text{OX}}]^n} = E_B^0 - \frac{0.0592}{nm} \log \frac{[\text{B}_{\text{RED}}]^m}{[\text{B}_{\text{OX}}]^m} \]

\[ E_B^0 - E_A^0 = \frac{0.0592}{nm} \log \frac{[\text{A}_{\text{OX}}]^n[\text{B}_{\text{RED}}]^m}{[\text{A}_{\text{RED}}]^n[\text{B}_{\text{OX}}]^m} \]

\[ \log K_{\text{EQ}} = \frac{nm(E_B^0 - E_A^0)}{0.0592} \]

\( A - \) species reduced

\( B - \) species oxidized

Equilibrium constants

Example

In an earlier example, we determined the galvanic direction for the reaction copper and zinc.

\[ \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0 \quad +0.334 \text{V} \]
\[ \text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}^0 \quad -0.763 \text{V} \]

\[ E_{\text{cell}} \quad 1.097 \text{V} \]

Galvanic reaction at standard conditions.

\[ \text{Cu}^{2+} + \text{Zn}^0 \rightarrow \text{Cu}^0 + \text{Zn}^{2+} \]

Equilibrium constants

The \( K \) for this reaction would be:

\[ \log K_{\text{EQ}} = \frac{2 \times 2 \times 1.097}{0.0592} \]

\[ K_{\text{EQ}} = 1.32 \times 10^{74} = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \]

Essentially, all copper(II) will be removed from solution.