Chapter 18

Electrochemistry

Hill, Petrucci, McCreary & Perry 4th Ed.
Oxidation Reduction Reactions

• Oxidation = Loss of *electrons* from a chemical species = Increase in *Oxidation State*.  
  \[ \text{Na} \rightarrow \text{Na}^+ + 1 \text{ electron}^- \]
  a "+1" oxidation state

• Reduction = Gain of *electrons* by a chemical species = Decrease in *Oxidation State*.  
  \[ \text{Cl}_2 + 2 \text{ electrons}^- \rightarrow 2 \text{ Cl}^- \]
  a "-1" oxidation state
Balancing RedOx Equations

The “Oxidation Number” Method

\[ \text{I}_2 + \text{HNO}_3 \rightarrow 2 \text{HIO}_3 + \text{NO}_2 \]

- a 5 electron loss per iodine
- a 1 electron gain per nitrogen

Can you balance this equation?

You must balance the electron transfer and the atoms.

This reaction occurs in aqueous acidic solution.
Balancing RedOx Equations

The “Oxidation Number” Method

The atoms which change oxidation state are balanced first!
The Nitrogen change must occur 10 times to change one Iodine Molecule:

\[ \text{I}_2 + 10 \text{HNO}_3 \rightarrow 2 \text{HIO}_3 + 10 \text{NO}_2 \]

Now we must balance the atoms which do not change oxidation state!

\[ \text{I}_2 + 10 \text{HNO}_3 \rightarrow 2 \text{HIO}_3 + 10 \text{NO}_2 + 4 \text{H}_2\text{O} \]

Being in acidic aqueous solution means we have lots of H\(^+\) and H\(_2\)O to balance hydrogens and oxygens!
“Rules” for Oxidation Number Method

1. Assign Oxidation Numbers.

2. Initially Balance atoms that change oxidation state.

3. Determine the electron transfer for like atoms.

4. Alter coefficients (only!) so electron transfer balances for the entire equation.

5. Balance Hydrogen and Oxygen and other atoms or ions which do not change oxidation state.
Balancing RedOx Equations

“Half-Reaction” Method

\[
\begin{align*}
\text{Zn} & \quad + \quad \text{NO}_3^- & \quad \rightarrow & \quad \text{Zn}^{2+} & \quad + & \quad \text{NH}_4^+ \\
0 & \quad + & \quad 5 & \quad +2 & \quad -3
\end{align*}
\]

a 2 electron loss per Zn
an 8 electron gain per nitrogen

Balance this reaction by first dividing the reaction into an oxidation half-reaction and a reduction half-reaction.

Using coefficients only, balance all atoms, using H$_2$O and H$^+/\text{OH}^-$ to balance H & O, balance charge using electrons in the oxidation half-reaction.

Balance all atoms and charge in the reduction half-reaction the same way.

Multiply each balanced half-reaction by coefficients which cause the electrons to cancel, add the half-reactions together finally reducing any species occurring on both sides of arrow.
“Half-Reaction” Method

a 2 electron loss per Zn

\[
\begin{align*}
\text{Zn} & \quad + \quad \text{NO}_3^- & \quad \rightarrow & \quad \text{Zn}^{2+} & \quad + & \quad \text{NH}_4^+ \\
0 & \quad +5 & \quad +2 & \quad -3
\end{align*}
\]

an 8 electron gain per nitrogen

Balance this reaction by first dividing the reaction into an oxidation half-reaction and a reduction half-reaction.

**Oxidation:**

\[
\begin{align*}
\text{Zn} & \quad \rightarrow & \quad \text{Zn}^{2+} & \quad + & \quad 2 \text{ e}^- \\
\end{align*}
\]

**Reduction:**

\[
\begin{align*}
\text{NO}_3^- & \quad + \quad 8 \text{ e}^- & \quad + & \quad 10 \text{ H}^+ & \quad \rightarrow & \quad \text{NH}_4^+ & \quad + & \quad 3 \text{ H}_2\text{O}
\end{align*}
\]

Using coefficients only, balance all atoms, using \(\text{H}_2\text{O}\) and \(\text{H}^+ / \text{OH}^-\) to balance H & O, balance charge using electrons in the oxidation half-reaction /the reduction half-reaction.

Multiply each half-reaction by coefficients to cancel electrons, add the half-reactions together, reduce species occurring on both sides

\[
\begin{align*}
4 \text{ Zn} & \quad + \quad \text{NO}_3^- & \quad + \quad 10 \text{ H}^+ & \quad \rightarrow & \quad 4 \text{ Zn}^{2+} & \quad + & \quad \text{NH}_4^+ & \quad + & \quad 3 \text{ H}_2\text{O}
\end{align*}
\]
“Rules” for Half-Reaction Method

1. Assign Oxidation Numbers.

2. Separate into Oxidation and Reduction half-reactions.

3. Initially balance atoms that change oxidation state by changing only coefficients.

4. Balance any spectator ions.

“Rules” for Half-Reaction Method continued

6. Balance the charges on each half-reaction by using electrons.

7. Multiply half-reactions by whole numbers to balance the electron transfer.

8. Add the half-reactions together and cancel species occurring on both sides of the chemical equation.
Electrochemical Cells

An application of Oxidation/Reduction Reactions

Voltaic Cell – Produces electric current by means of a spontaneous RedOx reaction.

Electrolytic Cell – Uses an electric current to cause a non-spontaneous reaction to occur.
A Voltaic Cell

Zn + Cu$^{2+}$ → Zn$^{2+}$ + Cu

Oxidation Half-reaction: Zn → Zn$^{2+}$ + 2 e$^{-}$

Reduction Half-reaction: Cu$^{2+}$ + 2 e$^{-}$ → Cu

Anode Compartment

Cathode Compartment

current

salt bridge

Cu$^{2+}$

Zn$^{2+}$
Voltaic Cell Notation

ANODE || CATHODE

Anode Terminal || Anode Electrolyte || Cathode Electrolyte || Cathode Terminal

Zn || Zn\(^{2+}\) || Cu\(^{2+}\) || Cu

salt bridge
phase separator
Standard Hydrogen Electrode

Oxidation
\[
\text{ANODE} \quad \text{Pt} \quad \text{H}_2(\text{g}) \quad \text{H}^+(\text{aq}) \quad \text{Pt}
\]

\[
\text{CATHODE} \quad \text{Pt} \quad \text{H}^+(\text{aq}) \quad \text{H}_2(\text{g}) \quad \text{Pt}
\]

Half Reaction \quad E_{\text{red}}^0 = 0
\[
\text{H}_2(\text{g}) \rightarrow 2 \text{H}^+(\text{aq}) + 2\text{e}^- \quad \text{2 H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})
\]

Reduction
Standard Reduction Potentials
Cathode Potentials

Table 18.1 p 762:  \( emf \) in Volts vs SHE

Table Layout: Red. Half-Reactions vs SHE

Strongest Oxidizing Agents at Top

Strongest Reducing Agents at Bottom

For any pair of couples (half-reactions) the Anodes will always be lower in the table in the text.
Reduction Half-Reaction - Acidic Solution - E°, volt

\[
\begin{align*}
H_2O_2(aq) + 2 H^+(aq) + 2 e^- & \rightarrow 2 H_2O(l) & +1.763 \\
Cl_2(g) + 2 e^- & \rightarrow 2 Cl^-(aq) & +1.358 \\
O_2(g) + 4 H^+(aq) + 4 e^- & \rightarrow 2 H_2O(l) & +1.229 \\
Ag^+(aq) + e^- & \rightarrow Ag(s) & +0.800 \\
I_2(s) + 2 e^- & \rightarrow 2 I^-(aq) & +0.535 \\
Cu^{2+}(aq) + 2 e^- & \rightarrow Cu(s) & +0.340 \\
2 H^+(aq) + 2 e^- & \rightarrow H_2(g) & 0 \\
Pb^{2+}(aq) + 2 e^- & \rightarrow Pb(s) & -0.125 \\
Sn^{2+}(aq) + 2 e^- & \rightarrow Sn(s) & -0.137 \\
Zn^{2+}(aq) + 2 e^- & \rightarrow Zn(s) & -0.763 \\
Al^{3+}(aq) + 3 e^- & \rightarrow Al(s) & -1.676 \\
Mg^{2+}(aq) + 2 e^- & \rightarrow Mg(s) & -2.356 \\
Na^+(aq) + e^- & \rightarrow Na(s) & -2.713 \\
Li^+(aq) + e^- & \rightarrow Li(s) & -3.040
\end{align*}
\]
Cell Potentials

$$E^\circ_{\text{cell}} = E^\circ_{\text{red cathode}} - E^\circ_{\text{red anode}}$$

Higher in Table Lower in Table

The Anode Reaction is the Reverse of the reaction in the Table.

The Anode potential is opposite in sign of that tabulated, hence the subtraction.

$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn}(s) \quad E^\circ_{\text{red}} = E^\circ_{\text{cathode}} = -0.76 \text{ V}$

$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2e^- \quad E^\circ_{\text{ox}} = E^\circ_{\text{anode}} = +0.76 \text{ V}$
Half-Reactions are commonly represented by Reaction “Couples”

Half Reaction $\rightarrow$ Abbreviated "Couple"

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$    $Zn^{2+}_{(aq)}/Zn_{(s)}$

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$    $Zn_{(s)}/Zn^{2+}_{(aq)}$

The species Oxidized or Reduced are shown in the couples in the same order they occur in the reaction.
Reduction Half-Reaction - Acidic Solution – Couple

\[ \text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l}) \quad \text{H}_2\text{O}_2(\text{aq})/ \text{H}_2\text{O}(\text{l}) \]
\[ \text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq}) \quad \text{Cl}_2(\text{g})/ \text{Cl}^-(\text{aq}) \]
\[ \text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{I}) \quad \text{O}_2(\text{g})/ \text{H}_2\text{O}(\text{I}) \]
\[ \text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) \quad \text{Ag}^+(\text{aq})/ \text{Ag}(\text{s}) \]
\[ \text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq}) \quad \text{I}_2(\text{s})/ \text{I}^-(\text{aq}) \]
\[ \text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s}) \quad \text{Cu}^{2+}(\text{aq})/ \text{Cu}(\text{s}) \]
\[ 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) \quad \text{H}^+(\text{aq})/ \text{H}_2(\text{g}) \]
\[ \text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pb}(\text{s}) \quad \text{Pb}^{2+}(\text{aq})/ \text{Pb}(\text{s}) \]
\[ \text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s}) \quad \text{Sn}^{2+}(\text{aq})/ \text{Sn}(\text{s}) \]
\[ \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s}) \quad \text{Zn}^{2+}(\text{aq})/ \text{Zn}(\text{s}) \]
\[ \text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s}) \quad \text{Al}^{3+}(\text{aq})/ \text{Al}(\text{s}) \]
\[ \text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s}) \quad \text{Mg}^{2+}(\text{aq})/ \text{Mg}(\text{s}) \]
\[ \text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s}) \quad \text{Na}^+(\text{aq})/ \text{Na}(\text{s}) \]
\[ \text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s}) \quad \text{Li}^+(\text{aq})/ \text{Li}(\text{s}) \]
Gibb’s Free Energy & Cell Potential

\[ \Delta G^\circ = -n \, F \, E_\text{cell}^\circ \]

- A positive \( E_\text{cell} \)
  - Spontaneous
  - \( \Delta G \) is negative

- A negative \( E_\text{cell} \)
  - Non-spontaneous
  - \( \Delta G \) is positive

- \( n \) = # electrons transferred
- \( F \) = Faraday Constant
  - \( = 96,500 \text{ Coulombs/mole} \)
  - "charge of a mole of electrons"
  - "one Faraday of charge"
Cell Potentials & the Equilibrium Constant

$$\Delta G^\circ = -nF \cdot E_{cell}^\circ = -RT \ln K$$

Rearranging:

$$E_{cell}^\circ = \frac{RT}{nF} \ln K$$

Nernst Equation:

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln Q$$

An $E_{cell} < \left|\frac{0.104 \text{ V}}{n}\right|$ will give an equilibrium mixture: $\Delta G^\circ < \pm 10 \text{ kJ}$

For

$$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$$

$$Q = \frac{[\text{product}]}{[\text{reactant}]} = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$
Calculating Cell Potentials

Calculate the cell potential and write the cell notation and net chemical equation for the half reactions below.

\[
\begin{align*}
    \text{I}_2(\text{s}) + 2 \text{ e}^- & \rightarrow 2 \text{ I}^-_{(\text{aq})} & +0.535 \\
    \text{Sn}^{2+}_{(\text{aq})} + 2 \text{ e}^- & \rightarrow \text{Sn}_{(\text{s})} & -0.137
\end{align*}
\]
Calculating a Cell Potential - Process Specified

Given the following reaction, determine the cell potential and whether the reaction is spontaneous. Write the cell notation for the reaction as written.

\[ \text{Sn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Sn}^{2+}(aq) + \text{Cu}(s) \]
Electrolysis of Molten Salts

A molten salt is the simplest case.

\[ \text{NaCl}_{(s)} \xrightarrow{\text{melting}} \text{Na}^{+}_{(l)} + \text{Cl}^{-}_{(l)} \]

\[ 2 \text{Na}^{+}_{(l)} + 2 \text{Cl}^{-}_{(l)} \xrightarrow{\text{electrolysis}} 2 \text{Na}_{(l)} + \text{Cl}_2(g) \]

**Anode:**

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

2 mol 1 mol 2 Faradays

**Cathode:**

\[ \text{Na}^{+}_{(l)} + \text{e}^- \rightarrow \text{Na}_{(l)} \]

1 mol 1 Faraday 1 mol

1 mole electrons = 1 Faraday Charge = 96,500 Coulombs

1 ampere = 1 Coulomb/second

The amount of material produced depends directly on the amount of current passed through the cell.
Some Salts can be Electrolysed in Water

CuBr$_2$(aq) : $\text{Cu}^{2+}$(aq) + 2 Br$^-$ (aq) $\rightarrow$ Cu(s) + Br$_2$(l)

Anode Rxn: 2 Br$^-$ (aq) $\rightarrow$ Br$_2$(l) + 2 e$^-$  - ($E_{\text{red}} = 1.07$ V)

Cathode Rxn: $\text{Cu}^{2+}$(aq) + 2 e$^-$ $\rightarrow$ Cu(s)  $E_{\text{red}} = 0.34$ V

$E_{\text{cell}} = -0.73$ V

An applied voltage > 0.73 V will cause:
the reduction of Copper ion to Copper metal  .
and the oxidation of Bromide ion to Bromine. .
How much copper metal can be plated by a current of 5.0 amperes in 1 hour?

You will need to calculate the number of Faradays delivered by this current and relate that to the numbers of moles of copper.