Electrochemistry is the study of the relationships between electricity and chemical reactions.

- It includes the study of both spontaneous and nonspontaneous processes.
Redox reactions: assigning oxidation numbers

Oxidation numbers help keep track of what species loses electrons and what species gains them.

- An element is oxidized when the oxidation number increases
- An element is reduced when the oxidation number decreases
- An oxidizing agent causes another element to be oxidized
- A reducing agent causes another element to be reduced.

Assigning oxidation numbers (sect. 4.4)

1. Elemental form, each atom has ox. # = 0.
   \[ \text{Zn} \quad \text{O}_2 \quad \text{O}_3 \quad \text{I}_2 \quad \text{S}_8 \quad \text{P}_4 \]
2. Simple ions, = charge on ion. -1 for \( \text{Cl}^- \), +2 for \( \text{Mg}^{2+} \)
3. The ox. # of F is ALWAYS -1 with all other elements.
   \[ \text{FeF}_3 \quad \text{PF}_5 \quad \text{SF}_6 \quad \text{OF}_2 \]
4. The ox. # of O is normally -2 (except in the peroxide ion, which has an oxidation number of −1) and the ox. # of H is +1 (except with metals).
   - O is -2 in \( \text{NO} \) and \( \text{H} \) is +1 in \( \text{CH}_4 \)
   - O is -1 in \( \text{Na}_2\text{O}_2 \) and \( \text{H} \) is -1 in \( \text{CaH}_2 \)
5. Algebraic sum of oxidation numbers
   - = 0 for a neutral compound
   - = overall charge for an ion
Examples

Assign the oxidation numbers to each element in each of the following compounds:

SiBr₄

K₃PO₄

Cu(NO₃)₃

Example

Label the species that undergo oxidation and reduction. Identify the oxidizing agent and reducing agent.

Cd(s) + NiO₂(s) + 2H₂O(l) → Cd(OH)₂(s) + Ni(OH)₂(s)
Example

Label the species that undergo oxidation and reduction. Also identify the oxidizing agent and reducing agent.

\[
\text{Cu(s)} + 2\text{AgNO}_3(aq) \rightarrow \text{Cu(NO}_3)_2(aq) + 2\text{Ag(s)}
\]

<table>
<thead>
<tr>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
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<tbody>
<tr>
<td>Cu(s)</td>
<td>Cu(NO}_3)_2(aq)</td>
</tr>
<tr>
<td>0</td>
<td>+2</td>
</tr>
<tr>
<td>+1</td>
<td>+5</td>
</tr>
<tr>
<td>+5</td>
<td>+2</td>
</tr>
<tr>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Oxidizing agent: Ag in AgNO₃; Reducing agent: Cu

Electron transfer reactions

Essential features:
- one reactant is oxidized
- one reactant is reduced
- the oxidizing agent is reduced
- the reducing agent is oxidized
- an element is oxidized if its ox # increases; it is reduced if its ox # decreases.
- the extent of oxidation and reduction must balance

All redox reactions must be balanced for both mass and charge.
**Steps for balancing equations**
by the method of half-reactions

1. Assign oxidation states.
2. Divide the equation into two half-reactions.
3. Balance each half-reaction as follows:
   a. Balance elements other than O and H
   b. Balance O by adding H\textsubscript{2}O
   c. Balance H by adding H\textsuperscript{+}
   d. Balance charge by adding e\textsuperscript{-} to the more positive side
4. Multiply by factors so that e\textsuperscript{-} lost = e\textsuperscript{-} gained
5. Add and cancel (check mass & check charge).
6. If in a basic solution, add OH\textsuperscript{-} to neutralize.
7. Check balance of atoms and charge.

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**Balancing redox reactions:**
using half-reactions

Cu (s) + AgNO\textsubscript{3} (aq) → Cu(NO\textsubscript{3})\textsubscript{2} (aq) + Ag (s)
The spectator ion (NO\textsubscript{3}\textsuperscript{-}) is unimportant to the net equation, so let’s examine the unbalanced net equation.

Cu (s) + Ag\textsuperscript{+} (aq) → Cu\textsuperscript{2+} (aq) + Ag (s)
There are two halves of the reaction: the oxidation half and the reduction half.

Cu (s) → Cu\textsuperscript{2+} (aq) + 2 e\textsuperscript{-}
Ag\textsuperscript{+} (aq) + e\textsuperscript{-} → Ag (s)
Balance the charges and masses, multiply 2\textsuperscript{nd} rxn. by 2.

Cu (s) → Cu\textsuperscript{2+} (aq) + 2 e\textsuperscript{-}
2 Ag\textsuperscript{+} (aq) + 2 e\textsuperscript{-} → 2 Ag (s)
Cu (s) + 2 Ag\textsuperscript{+} (aq) → Cu\textsuperscript{2+} (aq) + 2 Ag (s)
Sometimes it’s necessary to add H\textsubscript{2}O and either H\textsuperscript{+} or OH\textsuperscript{-}. 
Consider the reaction between MnO$_4^-$ and C$_2$O$_4^{2-}$:

MnO$_4^-$ (aq) + C$_2$O$_4^{2-}$ (aq) $\rightarrow$ Mn$^{2+}$ (aq) + CO$_2$ (g)

First, we assign oxidation numbers.

MnO$_4^-$ + C$_2$O$_4^{2-}$ $\rightarrow$ Mn$^{2+}$ + CO$_2$

Since the manganese goes from +7 to +2, it is reduced.

Since the carbon goes from +3 to +4, it is oxidized.

Oxidation Half-Reaction

C$_2$O$_4^{2-}$ $\rightarrow$ CO$_2$

To balance the carbon, we add a coefficient of 2:

C$_2$O$_4^{2-}$ $\rightarrow$ 2 CO$_2$

The oxygen is now balanced as well. To balance the charge, add 2 electrons to the right side.

C$_2$O$_4^{2-}$ $\rightarrow$ 2 CO$_2$ + 2 e$^-$

Reduction Half-Reaction

MnO$_4^-$ $\rightarrow$ Mn$^{2+}$

To balance the oxygen, add 4 waters to the right side.

MnO$_4^-$ $\rightarrow$ Mn$^{2+}$ + 4 H$_2$O

To balance the hydrogen, we add 8 H$^+$ to the left side.

8 H$^+$ + MnO$_4^-$ $\rightarrow$ Mn$^{2+}$ + 4 H$_2$O

To balance the charge, we add 5 e$^-$ to the left side.

5 e$^-$ + 8 H$^+$ + MnO$_4^-$ $\rightarrow$ Mn$^{2+}$ + 4 H$_2$O
Combining the Half-Reactions

Now we evaluate the two half-reactions together:

\[
\begin{align*}
C_2O_4^{2-} & \rightarrow 2 \text{CO}_2 + 2 \text{e}^- \\
5 \text{e}^- + 8 \text{H}^+ + \text{MnO}_4^- & \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}
\end{align*}
\]

To attain the same number of electrons on each side, multiply the first reaction by 5 and the second by 2.

\[
\begin{align*}
5 C_2O_4^{2-} & \rightarrow 10 \text{CO}_2 + 10 \text{e}^- \\
10 \text{e}^- + 16 \text{H}^+ + 2 \text{MnO}_4^- & \rightarrow 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}
\end{align*}
\]

Add these together:

\[
\begin{align*}
16 \text{H}^+ + 2 \text{MnO}_4^- + 5 C_2O_4^{2-} & \rightarrow 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O} + 10 \text{CO}_2 + 10 \text{e}^-
\end{align*}
\]

Example

Iodide will react with permanganate ions to form iodine and manganese (IV) oxide. Write the balanced net ionic equation if the reaction occurs in an acidic solution.

\[
\begin{align*}
6 \text{I}^- (\text{aq}) + 2 \text{MnO}_4^- (\text{aq}) + 8 \text{H}^+ (\text{aq}) & \rightarrow 3 \text{I}_2 (\text{aq}) + 2 \text{MnO}_2 (\text{aq}) + 4 \text{H}_2\text{O} (\text{l})
\end{align*}
\]
Example

Do the previous example in a basic solution. Iodide will react with permanganate ions to form iodine and manganese (IV) oxide.

If a reaction occurs in basic solution, one can balance it as if it occurred in acid. Once the equation is balanced, add OH\(^{-}\) to each side to “neutralize” the H\(^{+}\) in the equation and create water in its place. If this produces water on both sides, you might have to subtract water from each side.

Two types of electrical cells

**Voltaic/galvanic cell**
- spontaneous chemical reaction that produces electrical energy

**Electrolytic cell**
- electrical energy is used for a nonspontaneous chemical reaction
Voltaic cells

In spontaneous oxidation-reduction (redox) reactions, electrons are transferred and energy is released.

We can use that energy to do work if we make the electrons flow through an external device.

The oxidation occurs at the anode. The reduction occurs at the cathode.

A salt bridge, a U-shaped tube that contains a salt/agar solution, is used to keep the charges balanced.
Voltaic Cells

• In the cell, electrons leave the anode and flow through the wire to the cathode.
• As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment.
• As the electrons reach the cathode, cations in the cathode are attracted to the now negative cathode.
• The electrons are taken by the cation, and the neutral metal is deposited on the cathode.

Electromotive force (emf)

Water spontaneously flows one way in a waterfall.

Likewise, electrons only spontaneously flow one way in a redox reaction — from higher to lower potential energy.
Electromotive force (emf)

The potential difference between the anode and cathode in a cell is called the electromotive force (emf).

It is also called the cell potential ($E_{\text{cell}}$). Cell potential is measured in volts (V) and it is often called the cell voltage.

$$1 \text{ V} = 1 \frac{\text{J}}{\text{C}}$$

Standard cell potentials

The cell potential at standard conditions can be found through this equation:

$$E_{\text{cell}}^\circ = E_{\text{red}}^\circ (\text{cathode}) - E_{\text{red}}^\circ (\text{anode})$$

Cell potential is based on the potential energy per unit of charge, it is an intensive property.
Standard Hydrogen Electrode

\[ 2 \text{H}^+ (aq, 1\text{M}) + 2 \text{e}^- \rightarrow \text{H}_2 (g, 1\text{atm}) \]

By definition, the reduction potential for hydrogen is 0.00 V:

Using a SHE

\[ \text{Zn(s)} \rightarrow \text{Zn}^{2+} (aq) + 2 \text{e}^- \]

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

For the oxidation in this cell, 
\[ E_{\text{red}}^0 = -0.76 \text{ V} \]
For the reduction, 
\[ E_{\text{red}}^0 = +0.34 \text{ V} \]

\[ E_{\text{cell}}^0 = E_{\text{red}}^0 (\text{cathode}) - E_{\text{red}}^0 (\text{anode}) \]
\[ = +0.34 \text{ V} - (-0.76 \text{ V}) = +1.10 \text{ V} \]

**Standard reduction potentials**

<table>
<thead>
<tr>
<th>Reduction Half-Reaction</th>
<th>( E^0 ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{I}_2(s) + 2e^- \rightarrow 2\text{I}^- )</td>
<td>+1.06</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} )</td>
<td>+0.34</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} )</td>
<td>-0.76</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2\text{O}^- + 2e^- \rightarrow \text{H}_2\text{O}_2\text{O}^- )</td>
<td>-0.83</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 3e^- \rightarrow \text{Al} )</td>
<td>-1.66</td>
</tr>
<tr>
<td>( \text{Na}^+ + e^- \rightarrow \text{Na} )</td>
<td>-2.71</td>
</tr>
<tr>
<td>( \text{Li}^+ + e^- \rightarrow \text{Li} )</td>
<td>-3.05</td>
</tr>
<tr>
<td>( \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} )</td>
<td>+1.51</td>
</tr>
<tr>
<td>( \text{Br}_2 + 2e^- \rightarrow 2\text{Br}^- )</td>
<td>+0.96</td>
</tr>
<tr>
<td>( \text{Ag}^{+} + e^- \rightarrow \text{Ag} )</td>
<td>+0.80</td>
</tr>
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<td>( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} )</td>
<td>+0.77</td>
</tr>
<tr>
<td>( \text{O}_3(\text{aq}) + 4\text{H}^+ + 3e^- \rightarrow \text{NO}^- + 2\text{H}_2\text{O} )</td>
<td>+1.23</td>
</tr>
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<td>+0.40</td>
</tr>
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<td>( \text{MnO}_2(\text{aq}) + 2\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} )</td>
<td>-0.59</td>
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</table>
Standard reduction potentials

Substances at the top of the list have a strong tendency to be reduced and therefore are strong oxidizing agents.

- Most positive reduction potentials

Substances at the bottom of the list are weak oxidizing agents, strongest reducing agents.

- Most negative reduction potentials

Oxidizing and reducing agents

The greater the difference between the two, the greater the voltage of the cell.

\[ E^{\circ}_{\text{cell}} > 0 \quad \text{product favored} \]
\[ E^{\circ}_{\text{cell}} < 0 \quad \text{reactant favored} \]

\[ E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} \text{ (cathode)} - E^{\circ}_{\text{red}} \text{ (anode)} \]

\[ E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} \text{ (reduction)} - E^{\circ}_{\text{red}} \text{ (oxidation)} \]
Example

Write the overall reaction for the voltaic cell, use cell notation to describe the voltaic cell, and calculate the standard EMF for a voltaic cell containing cadmium and silver electrodes.

\[
\begin{align*}
Ag^+ (aq) + e^- &\rightarrow Ag (s) \quad E_{\text{red}}^o = +0.799 \text{ V} \\
Cd^{2+} (aq) + 2 e^- &\rightarrow Cd (s) \quad E_{\text{red}}^o = -0.40 \text{ V}
\end{align*}
\]

Standard reduction potentials

1. All potentials are for reduction reactions.
2. The more positive \( E^o \), the better the oxidizing ability.
3. The more negative \( E^o \), the more likely the reverse (oxidation) reaction will occur.
4. When the reaction is reversed, the sign changes.
5. Reaction of the upper left with the lower right is product favored.
6. The sign of the half-reaction potential is in reference to the SHE \( \left( H_2 (g, 1 \text{ bar})/H^+ (aq, 1 \text{ M}) \right) \) standard cell.
7. Potentials depend on the nature of reactants and products and NOT on the amounts.
Free Energy

$\Delta G$ for a redox reaction:

$$\Delta G = -nFE$$

Under standard conditions, $\Delta G^\circ = -nFE^\circ$

where $n$ is the number of moles of electrons transferred, and $F$ is the Faraday constant.

1 $F = 96,485 \text{ C/mol} = 96,485 \text{ J/V-mol}$

Example

Calculate $\Delta G^\circ$ for

$$2 \text{ Cr(s) + 3 Pb}^{2+}(aq) \rightarrow 2 \text{ Cr}^{3+}(aq) + 3 \text{ Pb(s)}$$

from Appendix E:

$$\text{Cr}^{3+}(aq) + 3 \text{ e}^- \rightarrow \text{Cr} (s) \quad E^\circ = -0.74 \text{ V}$$

$$\text{Pb}^{2+}(aq) + 2 \text{ e}^- \rightarrow \text{Pb} (s) \quad E^\circ = -0.13 \text{ V}$$
Nernst Equation
\[ \Delta G = \Delta G^\circ + RT \ln Q \]
This means
\[ -nFE = -nFE^\circ + RT \ln Q \]
Dividing both sides by \(-nF\), obtain the Nernst equation:
\[ E = E^\circ - \frac{RT}{nF} \ln Q \]

\[ E = E^\circ - \frac{2.303 \, RT}{n \, F} \log Q \]

at 25 °C
\[ E = E^\circ - \frac{0.0592 \, log Q}{n} \]

Example
Calculate the emf for the following cell at 25 °C.
\[ \text{Cr (s)} \mid \text{Cr}^{3+} (\text{aq, 1.00 M}) \parallel \text{Pb}^{2+} (\text{aq, 0.010 M}) \parallel \text{Pb (s)} \]
Example

Calculate the emf for the following reaction at 25 °C.

$$4 \text{Fe}^{2+}(aq) + \text{O}_2(g) + 4\text{H}^+(aq) \rightarrow 4 \text{Fe}^{3+}(aq) + 2\text{H}_2\text{O}(l)$$

a) Under standard conditions
b) When $[\text{Fe}^{2+}] = 1.3 \text{ M}$, $[\text{Fe}^{3+}] = 0.010 \text{ M}$, $P_{\text{O}_2} = 0.50 \text{ atm}$, and the pH in the cathode half-cell is 3.50.

Concentration cells

A cell may be created that has the same substance at both electrodes.

- $E^\circ_{\text{cell}}$ would be 0, but Q would not be.
- $E$ will not be 0 as long as the concentrations are different.
Applications

Batteries: a portable, self-contained electrochemical power source that consists of one or more voltaic cells.

- Batteries can be **primary** cells (cannot be recharged when “dead”—the reaction is complete) or **secondary** cells (rechargeable).
- Prevention of corrosion (“rust-proofing”)
- Electrolysis

- Lead–acid battery: reactants and products are solids, so $Q$ is 1 and the potential is independent of concentrations; however, made with lead and sulfuric acid (hazards).
- Alkaline battery: most common primary battery.
- Ni–Cd and Ni–metal hydride batteries: lightweight, rechargeable; Cd is toxic and heavy, so hydrides are replacing it.
- Lithium-ion batteries: rechargeable, light; produce more voltage than Ni-based batteries.
Fuel Cells

- Combustion of fuel is one way to drive an electrical generator to convert to mechanical to electrical energy.
- Conversion is only 40% efficient, with the remainder lost as heat.
- Direct conversion of chemical to electrical energy is expected to be more efficient and is the basis for fuel cells.
- Fuel cells are NOT batteries; the source of energy must be continuously provided.
Hydrogen fuel cells

Adsorbing \( \text{H}_2 \) onto a metal or metal alloy.

**Cathode:** \[ \text{O}_2(g) + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(l) \]

**Anode:** \[ 2 \text{H}_2(g) \rightarrow 4 \text{H}^+ + 4 \text{e}^- \]

**Overall:** \[ \text{O}_2(g) + 2 \text{H}_2(g) \rightarrow 2 \text{H}_2\text{O}(l) \]

Corrosion

Corrosion is an oxidation process.

- The common term is rusting.

1. Fe oxidized at anode region of metal
2. \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \)
3. \( \text{Fe}^{2+} \) oxidized to \( \text{Fe}^{3+} \), rust (\( \text{Fe}_2\text{O}_3 \)) forms.
4. \( \text{O}_2 \) reduced at cathode region
5. \( \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O} \)
6. Or \( \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \)
7. Electrons from Fe oxidation migrate to region acting as cathode.
Corrosion Prevention

- **Cathodic protection**: occurs because zinc coating is more easily oxidized than iron, so zinc is sacrificed to keep the iron from rusting.

- **Sacrificial anode**: is attached to the pipe to prevent corrosion of underground pipes. The anode is oxidized before the pipe.

Electrolytic cells

- **Electrolysis** involves the use of an external source of electrical energy to drive nonspontaneous chemical reactions.
Electrolytic cell

Electrolytic cell with an active metal electrode.

**Stoichiometry of Electrolysis**

\[ Q = It = nF \]

Current (C/s) \times \text{time (s)} = \text{charge (C)}

where 1 A = 1 C/s, \( t \) = time, \( n \) = moles of electrons that travel through conductor, and \( F \) is Faraday's constant.

\[ F = \frac{96,485 \text{ C}}{\text{mole e}^-} \]

**Example:**

Gold can be plated out of a solution containing \( \text{Au}^{3+} \) according to the following half-reaction:

\[ \text{Au}^{3+}(aq) + 3e^- \rightarrow \text{Au}(s) \]

What mass of gold (in grams) can be plated by the flow of 0.5 A of current for 5 minutes?