Chapter 20. Electrochemistry

Common Student Misconceptions

- Students often have trouble balancing redox equations.

Lecture Outline

20.1 Oxidation-Reduction Reactions

- **Oxidation-reduction reactions** = chemical reactions in which the oxidation state of one or more substance changes (**redox reactions**).
  
  * Recall:
    * Oxidation involves loss of electrons (OIL).
    * Reduction involves gain of electrons (RIG).
  
- **Electrochemistry** = branch of chemistry that deals with relationships between electricity and chemical reactions.
  
- Consider the spontaneous reaction that occurs when Zn is added to HCl.
  
  \[
  \text{Zn}(s) + 2\text{H}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)
  \]
  
  - The oxidation numbers of Zn and H+ have changed.
  - The oxidation number of Zn has \(\uparrow\) from 0 to +2.
  - The oxidation number of H has \(\downarrow\) from +1 to 0.
  - \(\Rightarrow\) Zn is oxidized to \(\text{Zn}^{2+}\) while H+ is reduced to H2.
  
  - H+ causes Zn to be oxidized.
  - H+ is the **oxidizing agent** or oxidant. Examples of good oxidizing agents: H2O2, MnO4-1, Cr2O72-, Ce4+, O3, and the halogens.
  
  - Zn causes H+ to be reduced.
  - Zn is the **reducing agent** or reductant. Examples of good reducing agents: alkali and alkaline earth metals.
  
  - **Note:** the reducing agent is oxidized and the oxidizing agent is reduced.

Sample Exercise 20.1 (p. 779)

The nickel-cadmium (nicad) battery, a rechargeable “dry cell” used in battery-operated devices, uses the following redox reaction to generate electricity:

\[
\text{Cd}(s) + \text{NiO}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Cd(OH)}_2(s) + \text{Ni(OH)}_2(s)
\]

Identify the substances that are oxidized and reduced, and indicate which are oxidizing agents and which are reducing agents.
Practice Exercise 20.1

Identify the oxidizing and reducing agents in the following oxidation-reduction equation:

\[ 2 \text{H}_2\text{O}(l) + \text{Al}(s) + \text{MnO}_4^-(aq) \rightarrow \text{Al(OH)}_4^-(aq) + \text{MnO}_2(s) \]

20.2 Balancing Oxidation-Reduction Equations

- Conservation of mass: The amount of each element present at the beginning of the reaction must be present at the end.
- Conservation of charge: Electrons are not lost in a chemical reaction.

Half-Reactions

- Half-reactions are a convenient way of separating oxidation and reduction reactions.

\[ \text{Sn}^{2+}(aq) + 2\text{Fe}^{3+}(aq) \rightarrow \text{Sn}^{4+}(aq) + 2\text{Fe}^{2+}(aq) \]

Oxidation half-reaction: \( \text{Sn}^{2+}(aq) \rightarrow \text{Sn}^{4+}(aq) + 2e^- \) (electrons are a product)

Reduction half-reaction: \( 2\text{Fe}^{3+}(aq) + 2e^- \rightarrow 2\text{Fe}^{2+}(aq) \) (electrons are a reactant)

Practice:

Write half-reactions for a reaction between Cu\(^{2+}\) and Zn metal.

Overall:

Oxidation:

Reduction:

Balancing Equations by the Method of Half-Reactions

- Consider the titration of an acidic solution of Na\(_2\)C\(_2\)O\(_4\) (sodium oxalate, colorless) with KMnO\(_4\) (deep purple).
  - MnO\(_4^-\) is reduced to Mn\(^{2+}\) (pale pink) while the C\(_2\)O\(_4^{2-}\) is oxidized to CO\(_2\).
  - The equivalence point is indicated by the presence of a pale pink color.
  - If more KMnO\(_4\) is added, the solution turns purple due to the excess KMnO\(_4\).
• What is the balanced chemical equation for this reaction?

• We can determine this using the method of half-reactions:

a) Write the overall unbalanced reaction.

b) (i) Identify oxidized and reduced substances

(ii) Write down the two incomplete half reactions.
\[
\begin{align*}
\text{MnO}_4^- (aq) & \rightarrow \text{Mn}^{2+} (aq) \\
\text{C}_2\text{O}_4^{2-} (aq) & \rightarrow \text{CO}_2 (g)
\end{align*}
\]

c) Balance each half reaction:

(i) First, balance elements other than H and O.
\[
\begin{align*}
\text{MnO}_4^- (aq) & \rightarrow \text{Mn}^{2+} (aq) \\
\text{C}_2\text{O}_4^{2-} (aq) & \rightarrow 2\text{CO}_2 (g)
\end{align*}
\]

(ii) Then balance O atoms by adding water on side deficient in O atoms.
\[
\begin{align*}
\text{MnO}_4^- (aq) & \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O}(l) \\
\text{C}_2\text{O}_4^{2-} (aq) & \rightarrow 2\text{CO}_2 (g)
\end{align*}
\]

(iii) Then balance H by adding H\(^+\) for acidic solutions (or OH\(^-\) for alkaline solutions).
\[
\begin{align*}
8\text{H}^+ (aq) + \text{MnO}_4^- (aq) & \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O}(l) \\
\text{C}_2\text{O}_4^{2-} (aq) & \rightarrow 2\text{CO}_2 (g)
\end{align*}
\]

(iv) Finish by balancing charge by adding electrons.
   • This is an easy place to make an error!
   • For the permanganate half-reaction, note that there is a charge of 7\(^+\) on the left and 2\(^+\) on the right.
     \[
     5e^- + 8\text{H}^+ (aq) + \text{MnO}_4^- (aq) \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O}(l)
     \]
   • In the oxalate half-reaction, there is a 2\(^-\) charge on the left and a 0 charge on the right, so we need to add two electrons to the products:
     \[
     \text{C}_2\text{O}_4^{2-} (aq) \rightarrow 2\text{CO}_2 (g) + 2e^-
     \]

d) Multiply each half-reaction by the appropriate factors so that the number of electrons gained equals electrons lost.

• To balance the 5 electrons for permanganate and 2 electrons for oxalate, we need 10 electrons for both.

• Multiplying gives:
\[
\begin{align*}
10e^- & + 16\text{H}^+ (aq) + 2\text{MnO}_4^- (aq) \rightarrow 2\text{Mn}^{2+} (aq) + 8\text{H}_2\text{O}(l) \\
5\text{C}_2\text{O}_4^{2-} (aq) & \rightarrow 10\text{CO}_2 (g) + 10e^-
\end{align*}
\]

e) Now add the reactions and simplify.
\[
16\text{H}^+ (aq) + 2\text{MnO}_4^- (aq) + 5\text{C}_2\text{O}_4^{2-} (aq) \rightarrow 2\text{Mn}^{2+} (aq) + 8\text{H}_2\text{O}(l) + 10\text{CO}_2 (g)
\]

• The equation is now balanced!

• Note that all of the electrons have cancelled out!
Sample Exercise 20.2 (p. 782)

Complete and balance the following equation by the method of half-reactions:

\[
\text{Cr}_2\text{O}_7^{2-} (\text{aq}) + \text{Cl}^- (\text{aq}) \rightarrow \text{Cr}^{3+} (\text{aq}) + \text{Cl}_2(\text{g})
\]

Practice Exercise 20.2

Complete and balance the following oxidation-reduction equations using the method of half-reactions. Both reactions occur in acidic solution.

a) \( \text{Cu}_{(s)} + \text{NO}_3^- (\text{aq}) \rightarrow \text{Cu}^{2+} (\text{aq}) + \text{NO}_2(\text{g}) \)

b) \( \text{Mn}^{2+} (\text{aq}) + \text{NaBiO}_3(\text{s}) \rightarrow \text{Bi}^{3+} (\text{aq}) + \text{MnO}_4^- (\text{aq}) \)
Balancing Equations for Reactions Occurring in Basic Solution

- The same method as above is used, but OH\(^-\) is added to “neutralize” the H\(^+\) used.

- The equation must again be simplified by canceling like terms on both sides of the equation.

Sample Exercise 20.3 (p. 783)

Complete and balance the following equation:

\[ \text{CN}^-_{(aq)} + \text{MnO}_4^-_{(aq)} \rightarrow \text{CNO}^-_{(aq)} + \text{MnO}_2_{(s)} \] (basic solution)

Practice Exercise 20.3

Complete and balance the following equations for oxidation-reduction reactions that occur in basic solution:

a) \[ \text{NO}_2^-_{(aq)} + \text{Al}_{(s)} \rightarrow \text{NH}_3_{(aq)} + \text{Al(OH)}_4^-_{(aq)} \]

b) \[ \text{Cr(OH)}_3_{(s)} + \text{ClO}^-_{(aq)} \rightarrow \text{CrO}_4^{2-}_{(aq)} + \text{Cl}_2_{(g)} \]
20.3 Voltaic (Galvanic) Cells

- generates electrical energy from a spontaneous redox reaction
- can be used to do work IF the half reactions are kept separate
- electron transfer occurs via an external circuit
- must provide a conductor for transfer of electrons plus a salt bridge to keep the separate half-reactions electrically neutral
- anode is where oxidation takes place (electrons are released, so it is the negative electrode)
- electrons move from the anode to the cathode (where reduction takes place – electrons are attracted to the “positive” electrode)

If a strip of Zn is placed in a solution of CuSO₄, Cu is deposited on the Zn and the Zn dissolves by forming Zn²⁺.

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

- Zn is spontaneously oxidized to Zn²⁺ by Cu²⁺.
- The Cu²⁺ is spontaneously reduced to Cu⁰ by Zn.
- The entire process is spontaneous.

\[ \text{Anodic half-reaction: } \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \]
\[ \text{Cathodic half-reaction: } \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \]

- e.g. CuNO₃(aq) with a Cu electrode (cathode) and ZnNO₃(aq) with a Zn electrode (anode)

This voltaic cells consists of:
- An oxidation half-reaction: Zn(s) \rightarrow Zn²⁺(aq) + 2e⁻
  - Oxidation takes place at the anode.
- A reduction half-reaction: Cu²⁺(aq) + 2e⁻ \rightarrow Cu(s)
  - Reduction takes place at the cathode.
- A salt bridge (used to complete the electrical circuit).
  - Cations move from anode to cathode.
  - Anions move from cathode to anode.
• The two solid metals are the electrodes (cathode and anode).

• As oxidation occurs, Zn is converted to Zn$^{2+}$ and 2e$^-$.  
  • The electrons flow towards the cathode where they are used in the reduction reaction.

• We expect the Zn electrode to lose mass and the Cu electrode to gain mass.

• Electrons flow from the anode to the cathode.  
  → the anode is negative and the cathode is positive.

• Electrons cannot flow through the solution; they have to be transported through an external wire.

• Anions and cations move through a porous barrier or salt bridge.

• Cations move into the cathodic compartment to neutralize the excess negatively charged ions (Cathode: Cu$^{2+}$ + 2e$^-$ → Cu, so the counter ion of Cu is in excess).

• Anions move into the anodic compartment to neutralize the excess Zn$^{2+}$ ions formed by oxidation.

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**Sample Exercise 20.4 (p. 786)**
The following oxidation-reduction reaction is spontaneous:
$$Cr_2O_7^{2-} (aq) + 14 H^+ (aq) + 6 I^- (aq) \rightarrow 2 Cr^{3+} (aq) + 3 I_2(s) + 7 H_2O(l)$$

A solution containing K$_2$Cr$_2$O$_7$ and H$_2$SO$_4$ is poured into one beaker, and a solution of KI is poured into another. A salt bridge is used to join the beakers. A metallic conductor that will not react with either solution (such as platinum foil) is suspended in each solution, and the two conductors are connected with wires through a voltmeter or some other device to detect an electric current. The resultant voltaic cell generates an electric current. Indicate the reaction occurring at the anode, the reaction at the cathode, the direction of electron and ion migrations, and the signs of the electrodes.
Practice Exercise 20.4
The two half-reactions in a voltaic cell are
\[ \text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \]
\[ \text{ClO}_3^- (\text{aq}) + 6 \text{H}^+(\text{aq}) + 6 \text{e}^- \rightarrow \text{Cl}^{-}(\text{aq}) + 3 \text{H}_2\text{O}(l) \]

a) Indicate which reaction occurs at the anode and which at the cathode.
b) Which electrode is consumed in the cell reaction?
c) Which electrode is positive?

A Molecular View of the Electrode Process

• “Rules” of voltaic cells:
  • At the anode electrons are products.
    • Oxidation occurs at the anode.
  • At the cathode electrons are reagents.
    • Reduction occurs at the cathode.
  • The flow of electrons from anode to cathode requires an external wire.
    • The transfer of ions through a salt bridge maintains overall charge balance for the two compartments.
Figure 20.8  On the left hand side, the anode, the Zn is oxidized, releasing 2 electrons which migrate through the wire to the cathode (Cu electrode). At the cathode the Cu$^{2+}$ in solution is reduced and deposited onto the Cu electrode. The counter anion moves from the Cu compartment to the Zn compartment to balance the newly-produced Zn$^{2+}$ ions in the Zn compartment. Zn$^{2+}$ ions move into the Cu compartment to balance the excess anions leftover after the Cu$^{2+}$ is reduced.

20.4 Cell EMF

- The flow of electrons from anode to cathode is spontaneous, but what is the “driving force”?

- Electrons flow from anode to cathode because the cathode has a **lower electrical potential energy** than the anode.
  - Potential difference = difference in electrical potential.
  - The potential difference is measured in volts.
  - One volt (V) = the potential difference required to impart one joule (J) of energy to a charge of one coulomb (C):
    \[ 1V = 1 \frac{J}{C} \]

- **Electromotive force (emf)** = the force required to push electrons through the external circuit.
  - **Cell potential**: \( E_{\text{cell}} \) = emf of a cell.
    - \( E_{\text{cell}} \) = the cell voltage.
    - \( E_{\text{cell}} \) is > 0 for a spontaneous reaction.
  - For 1M solutions or 1 atm pressure for gases at 25°C (standard conditions), the **standard emf (standard cell potential)** is called \( E^{\circ}_{\text{cell}} \).
    - e.g. for the reaction: \( \text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s) \)
      - \( E^{\circ}_{\text{cell}} = +1.10\, \text{V} \)
Standard Reduction (Half-Cell) Potentials

- We can conveniently tabulate electrochemical data.

- **Standard reduction potentials**, $E_{\text{red}}^o$ are measured relative to the **standard hydrogen electrode** (SHE).

- The emf of a cell can be calculated from standard reduction potentials:
  \[ E_{\text{cell}}^o = E_{\text{red(cathode)}}^o - E_{\text{red(anode)}}^o \]

- We use the following half-reaction as our standard:
  \[ 2H^+(aq, \text{1 M}) + 2e^- \rightarrow H_2(g, \text{1 atm}) \quad E_{\text{cell}}^o = 0 \text{V}. \]

  - This electrode is called a **standard hydrogen electrode** (SHE).
  - The SHE is **assigned** a standard reduction potential of zero.
See your AP Chem packet for a more complete list of standard reduction potentials

- Example: Consider the half-reaction: \( \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \)
  - We can measure \( E^\circ_{\text{cell}} \) relative to the SHE (cathode):
    - \( = \) a Pt electrode in a tube placed in 1 \( M \) \( H^+ \) solution.
    - \( H_2 \) is bubbled through the tube.
    \[
    E^\circ_{\text{cell}} = E^\circ_{\text{red}(\text{cathode})} - E^\circ_{\text{red}(\text{anode})}
    \]
    \[
    0.76 \text{ V} = 0 \text{ V} - E^\circ_{\text{red}(\text{anode})}
    \]
    \[
    \Rightarrow E^\circ_{\text{red}(\text{anode})} = -0.76 \text{ V}.
    \]
  - Standard reduction potentials must be written as reduction reactions:
    \[
    \text{Zn}^{2+}(aq, 1M) + 2e^- \rightarrow \text{Zn}(s) \quad E^\circ_{\text{red}} = -0.76 \text{ V}.
    \]
  - Since \( E^\circ_{\text{red}} = -0.76 \text{ V} \) we conclude that the reduction of \( \text{Zn}^{2+} \) in the presence of the SHE is not spontaneous.
    - However, the oxidation of \( \text{Zn} \) with the SHE is spontaneous.
• The standard reduction potential is an **intensive property**.
  
  → Changing the stoichiometric coefficient does **not** affect $E_{\text{red}}^\circ$.

\[
2\text{Zn}^{2+} (aq) + 4e^- \rightarrow 2\text{Zn(s)} \quad E_{\text{red}}^\circ = -0.76 \text{ V}
\]

• Reactions with $E_{\text{red}}^\circ > 0$ are spontaneous reductions relative to the SHE.

• Reactions with $E_{\text{red}}^\circ < 0$ are spontaneous oxidations relative to the SHE.

• The larger the difference between $E_{\text{red}}^\circ$ values, the larger $E_{\text{cell}}^\circ$.

• The more **positive** the value of $E_{\text{red}}^\circ$, the **greater the driving force** for reduction.

**Sample Exercise 20.5 (p. 792)**

For the Zn-Cu$^{2+}$ voltaic cell shown in Figure 20.5, we have

\[
\text{Zn(s)} + \text{Cu}^{2+} (aq, 1\text{M}) \rightarrow \text{Zn}^{2+} (aq, 1\text{M}) + \text{Cu(s)} \quad E_{\text{cell}}^\circ = 1.10 \text{ V}
\]

Given that the standard reduction potential of Zn$^{2+}$ is $-0.76 \text{ V}$, calculate the $E_{\text{red}}^\circ$ for the reduction of Cu$^{2+}$ to Cu.

\[
\text{Cu}^{2+} (aq, 1\text{M}) + 2e^- \rightarrow \text{Cu(s)}
\]

(0.34 V)

**Practice Exercise 20.5**

A voltaic cell is based on the following half-reactions:

\[
\begin{align*}
\text{In}^+ (aq) & \rightarrow \text{In}^{3+} (aq) + 2e^- \\
\text{Br}_2(l) + 2e^- & \rightarrow 2\text{Br}^- (aq)
\end{align*}
\]

The standard emf for this cell is 1.46 V. Using the data in Table 20.1 or your AP Chem packet, calculate $E_{\text{red}}^\circ$ for the reduction of In$^{3+}$ to In$^+$.

(-0.40 V)
Sample Exercise 20.6 (p. 792)

Using the standard reduction potentials listed in Table 20.1 or your AP Chem packet, calculate the standard emf for the voltaic cell described in Sample Exercise 20.4, which is based on the following reaction:

\[
\text{Cr}_2\text{O}_7^{2-}_{\text{(aq)}} + 14 \text{H}^+_{\text{(aq)}} + 6 \text{I}^-_{\text{(aq)}} \rightarrow 2 \text{Cr}^{3+}_{\text{(aq)}} + 3 \text{I}_2(s) + 7 \text{H}_2\text{O(l)}
\]

(0.79 V)

Practice Exercise 20.6

Using the data in Table 20.1 or your AP Chem packet, calculate the standard emf for a cell that employs the following overall cell reaction:

\[
2 \text{Al(s)} + 3 \text{I}_2(s) \rightarrow 2 \text{Al}^{3+}_{\text{(aq)}} + 6 \text{I}^-_{\text{(aq)}}
\]

(+2.20 V)
Sample Exercise 20.7 (p. 793)

A voltaic cell is based on the following two standard half-reactions:

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

By using the data in Appendix E or your AP Chem packet, determine

a) the half-reactions that occur at the cathode and the anode, and

b) the standard cell potential (0.267 V)

Practice Exercise 20.7

A voltaic cell is based on a Co\(^{2+}\)/Co half-cell and an AgCl/Ag half-cell.

a) What reaction occurs at the anode?

b) What is the standard cell potential? (0.499 V)
Oxidizing and Reducing Agents

- Consider a table of standard reduction potentials.
- We can use this table to determine the relative strengths of reducing (and oxidizing) agents.
  - The more positive the $E_{\text{red}}^\circ$ the stronger the oxidizing agent (written in the table as a reactant).
  - The more negative the $E_{\text{red}}^\circ$ the stronger the reducing agent (written as a product in the table).
- We can use this to predict if one reactant can spontaneously oxidize another.
  - e.g.
    - F$_2$ can oxidize H$_2$ or Li.
    - Ni$^{2+}$ can oxidize Al(s).
- We can use this table to predict if one reactant can spontaneously reduce another.
  - e.g.
    - Li can reduce F$_2$. 

![Diagram showing oxidizing and reducing agents](image)
Sample Exercise 20.8 (p. 795)
Using Table 20.1 or your AP Chem packet, rank the following ions in order of increasing strength as oxidizing agents: \( \text{NO}_3^- \), \( \text{Ag}^+ \), \( \text{Cr}_2\text{O}_7^{2-} \).

Practice Exercise 20.8
Using Table 20.1 or your AP Chem packet, rank the following species from the strongest to the weakest reducing agent: \( \Gamma^- \), \( \text{Fe} \), \( \text{Al} \).

20.5 Spontaneity of Redox Reactions

- For any electrochemical process \( E^\circ = E^\circ_{\text{red(oxidation process)}} - E^\circ_{\text{red(reduction process)}} \).
  - A positive \( E^\circ \) indicates a spontaneous process (galvanic cell).
  - A negative \( E^\circ \) indicates a nonspontaneous process.

Sample Exercise 20.9 (p. 796)
Using standard reduction potentials (Table 20.1 or AP Chem packet), determine whether the following reactions are spontaneous under standard conditions:

a) \( \text{Cu} + 2 \text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2 \)

b) \( \text{Cl}_2 + 2 \Gamma^- \rightarrow 2 \text{Cl}^- + \text{I}_2 \)

Practice Exercise 20.9
Using standard reduction potentials (Appendix E or AP Chem packet), determine whether the following reactions are spontaneous under standard conditions:

a) \( \text{I}_2 + 5 \text{Cu}^{2+} + 6 \text{H}_2\text{O} \rightarrow 2 \text{IO}_3^- + 5 \text{Cu} + 12 \text{H}^+ \)

b) \( \text{Hg}^{2+} + 2 \Gamma^- \rightarrow \text{Hg} + \text{I}_2 \)

c) \( \text{H}_2\text{SO}_3 + 2 \text{Mn} + 4 \text{H}^+ \rightarrow \text{S} + 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O} \)
The above equation is used to understand the activity series of metals.

Consider the reaction of nickel with silver ion:

\[ \text{Ni}(s) + 2\text{Ag}^+(aq) \rightarrow \text{Ni}^{2+}(aq) + 2\text{Ag}(s) \]

The standard cell potential is:

\[ E^\circ_{\text{cell}} = E^\circ_{\text{red(Ag}^+/\text{Ag})} - E^\circ_{\text{red(Ni}^{2+}/\text{Ni})} \]

\[ = (0.80 \text{ V}) - (-0.28 \text{ V}) \]

\[ = 1.08 \text{ V} \]

This value indicates that the reaction is spontaneous.

**EMF and Free-Energy Change**

- We can show that:

\[ \Delta G = -nFE \]

Where \( \Delta G \) is the change in free energy, \( n \) is the number of moles of electrons transferred, \( F \) is *Faraday's constant* and \( E \) is the emf of the cell.

- We define a *faraday* (\( F \)) as:

\[ 1F = 96,500 \frac{C}{\text{mol e}^-} = 96,500 \frac{J}{(\text{V})(\text{mol e}^-)} \]

- Since \( n \) and \( F \) are positive, if \( \Delta G < 0 \) then \( E > 0 \), and the reaction will be spontaneous.

**Sample Exercise 20.10 (p. 798)**

a) Use the standard reduction potentials listed in Table 20.1 or your AP Chem packet to calculate the standard free-energy change, \( \Delta G^\circ \), for the following reaction:

\[ 4 \text{Ag}(s) + \frac{1}{2} \text{O}_2(g) + 4 \text{H}^+(aq) \rightarrow 4 \text{Ag}^{+}(aq) + 2 \text{H}_2\text{O}(l) \]

(\( \Delta G^\circ = -170 \text{ kJ/mol} \))

b) Suppose the reaction in part (a) were written as

\[ 2 \text{Ag}(s) + \frac{1}{2} \text{O}_2(g) + 2 \text{H}^+(aq) \rightarrow 2 \text{Ag}^{+}(aq) + \text{H}_2\text{O}(l) \]

What are the values of \( E^\circ \) and \( \Delta G^\circ \) when the reaction is written in this way?

(\( E^\circ = +0.43 \text{ V}, \Delta G^\circ = -83 \text{ kJ/mol} \))
Practice Exercise 20.10

Consider the following reaction:

\[3 \text{Ni}^{2+}_{(aq)} + 2 \text{Cr(OH)}_3_{(s)} + 10 \text{OH}^-_{(aq)} \rightarrow 3 \text{Ni}_{(s)} + 2 \text{CrO}_4^{2-}_{(aq)} + 8 \text{H}_2\text{O}(l)\]

a) What is the value of \(n\) for this reaction? (6)

b) Use the data in Appendix E or your AP Chem packet to calculate \(\Delta G^o\) for this reaction. (+87 kJ/mol)

20.6 Effect of Concentration on Cell EMF

- A voltaic cell is functional until \(E = 0\) at which point equilibrium has been reached.
  - The cell is then “dead.”
  - The point at which \(E = 0\) is determined by the concentrations of the species involved in the redox reaction.

The Nernst Equation

- We can calculate the cell potential under nonstandard conditions.
- Recall that:
  \[\Delta G = \Delta G^o + RT \ln Q\]
- We can substitute in our expression for the free energy change:
  \[-nFE = -nFE^o + RT \ln Q\]
- Rearranging, we get the Nernst equation:
  \[E = E^o - \frac{RT}{nF} \ln Q\]
  or
  \[E = E^o - \frac{2.303RT}{nF} \log Q\]
  - Note the change from natural logarithm to log base 10.
  - The Nernst equation can be simplified by collecting all the constants together and using a temperature of 298 K:
    \[E = E^o - \frac{0.0592}{n} \log Q\]
- Example: If we have the reaction:
  \[\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)\]
- If \([\text{Cu}^{2+}] = 5.0 \, M\) and \([\text{Zn}^{2+}] = 0.050M:\
  \[E_{cell} = 1.10V - \frac{0.0592}{2} \log \frac{0.050}{5.0} = 1.16V\]
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Sample Exercise 20.11 (p. 800)

Calculate the emf at 298 K generated by the cell described in Sample Exercise 20.4 when \([\text{Cr}_2\text{O}_7^{2-}] = 2.0 \, \text{M}, \) 
\([\text{H}^+] = 1.0 \, \text{M}, \) \([\Gamma^-] = 1.0 \, \text{M}, \) and \([\text{Cr}^{3+}] = 1.0 \times 10^{-5} \, \text{M}. \)

\[
\text{Cr}_2\text{O}_7^{2-} \text{(aq)} + 14 \text{H}^+ \text{(aq)} + 6 \Gamma^- \text{(aq)} \rightarrow 2 \text{Cr}^{3+} \text{(aq)} + 3 \text{I}_2(s) + 7 \text{H}_2\text{O}(l)
\]

\((E = +0.89 \, \text{V})\)

Practice Exercise 20.11

Calculate the emf generated by the cell described in the practice exercise accompanying Sample Exercise 20.6 when \([\text{Al}^{3+}] = 4.0 \times 10^{-3} \, \text{M} \) and \([\Gamma^-] = 0.010 \, \text{M}. \)

\((E = +2.36 \, \text{V})\)

Sample Exercise 20.12 (p. 800)

If the voltage of a Zn-H⁺ cell (like that in Figure 20.11) is 0.45 V at 25°C when \([\text{Zn}^{2+}] = 1.0 \, \text{M} \) and \(P_{\text{H}_2} = 1.0 \, \text{atm} \), what is the concentration of H⁺?

\([\text{H}^+] = 5.8 \times 10^{-6} \, \text{M}\)


**Practice Exercise 20.12**

What is the pH of the solution in the cathode compartment of the cell pictured in Figure 20.11 when $P_{H_2} = 1.0$ atm, $[Zn^{2+}]$ in the anode compartment is 0.10 M, and cell emf is 0.542 V?

$pH = 4.19$

---

**Concentration Cells**

- A **concentration cell** is one whose emf is generated solely because of a concentration difference.

- Example: Consider a cell with two compartments, each with a Ni(s) electrode but with difference concentrations of $Ni^{2+}(aq)$.
  - One cell has $[Ni^{2+}] = 1.0$ M and the other has $[Ni^{2+}] = 0.001$ M.
  - The standard cell potential is zero.
  - But this cell is operating under nonstandard conditions!
  - The driving force is the difference in $Ni^{2+}$ concentrations.
    - Anode (dilute $Ni^{2+}$): $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
    - Cathode (concentrated $Ni^{2+}$): $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

- Using the Nernst equation we can calculate a cell potential of $+0.0888$ V for this concentration cell.

---

![Concentration Cells Diagram](image-url)
Sample Exercise 20.13 (p. 802)

A voltaic cell is constructed with two hydrogen electrodes. Electrode 1 has $P_{H_2} = 1.00 \text{ atm}$ and an unknown concentration of $H^+_{(aq)}$. Electrode 2 is a standard hydrogen electrode ($[H^+] = 1.00 \text{ M, } P_{H_2} = 1.00 \text{ atm}$). At 298 K the measured cell voltage is 0.211 V, and the electrical current is observed to flow from electrode 1 through the external circuit to electrode 2. Calculate $[H^+]$ for the solution at electrode 1. What is its pH?

(pH = 3.57)

Practice Exercise 20.13

A concentration cell is constructed with two Zn(s)-Zn$^{2+}_{(aq)}$ half-cells. The first half-cell has $[Zn^{2+}] = 1.35 \text{ M}$, and the second half-cell has $[Zn^{2+}] = 3.75 \times 10^{-4} \text{ M}$.

a) Which half-cell is the anode of the cell?

b) What is the emf of the cell? (0.105 V)
Cell EMF and Chemical Equilibrium

- A system is at equilibrium when $\Delta G = 0$.
- From the Nernst equation, at equilibrium and 298 K ($E = 0$ V and $Q = K_{eq}$)

\[
0 = E^\circ - \frac{0.0592}{n} \log K_{eq}
\]

\[
\log K_{eq} = \frac{nE^\circ}{0.0592}
\]

- Thus, if we know the cell emf, we can calculate the equilibrium constant.

Sample Exercise 20.14 (p. 805)

Using standard reduction potentials from Appendix E or your AP Chem packet, calculate the equilibrium constant for the oxidation of Fe$^{2+}$ by O$_2$ in acidic solution.

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

($K_{eq} = 1. \times 10^{31}$)

Practice Exercise 20.14

Using standard reduction potentials from Appendix E or your AP Chem packet, calculate the equilibrium constant at 25°C for the reaction

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

($K_{eq} = 1.2 \times 10^{-10}$)
20.7 Batteries
• A battery is a portable, self-contained electrochemical power source consisting of one or more voltaic cells.

Lead-Acid Battery
• A 12-V car battery consists of 6 cathode/anode pairs each producing 2 V.
• Cathode: PbO$_2$ on a metal grid in sulfuric acid:
  \[ \text{PbO}_2(s) + \text{HSO}_4^-(aq) + 3\text{H}^+(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \]
• Anode: Pb:
  \[ \text{Pb}(s) + \text{HSO}_4^-(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^- \]

• The overall electrochemical reaction is
  \[ \text{PbO}_2(s) + \text{Pb}(s) + 2\text{HSO}_4^-(aq) + 2\text{H}^+(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \]

The cell potential for this reaction is:
\[
E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red (cathode)}} - E^{\circ}_{\text{red (anode)}}
= (+1.685 \text{ V}) - (-0.356 \text{ V})
= +2.041 \text{ V}.
\]

• Wood or glass-fiber spacers are used to prevent the electrodes from touching.
• An advantage of these cells is that they can be recharged.
  • An external source of energy is used to reverse the process.
Alkaline Battery

- The most common nonrechargeable battery is the alkaline battery.
- Powdered zinc metal is immobilized in a gel in contact with a concentrated solution of KOH.
- Thus these batteries are \textit{alkaline}.
- The reaction at the anode is:
  \[
  \text{Zn} (s) \rightarrow \text{Zn}^{2+} (aq) + 2e^{-}
  \]
- The reaction at the cathode is the reduction of MnO\(_2\):
  \[
  2\text{MnO}_2(s) + 2\text{H}_2\text{O}(l) + 2e^{-} \rightarrow 2\text{MnO(OH)}(s) + 2\text{OH}^{-}(aq)
  \]
- The cell potential of these batteries = 1.55 V at room temperature.

Nickel–Cadmium, Nickel–Metal–Hydride, and Lithium–Ion Batteries

- A common rechargeable battery is the nickel–cadmium (NiCad) battery.
- The reaction at the cathode is:
  \[
  2\text{NiO(OH)}(s) + 2\text{H}_2\text{O}(l) + 2e^{-} \rightarrow 2\text{Ni(OH)}_2(s) + 2\text{OH}^{-}(aq)
  \]
- The reaction at the anode is:
  \[
  \text{Cd}(s) + 2\text{OH}^{-}(aq) \rightarrow \text{Cd(OH)}_2(s) + 2e^{-}
  \]
- The cell potential of this battery is about 1.30 V at room temperature.
- Cadmium is a toxic heavy metal.
  - There are environmental concerns to be addressed with respect to disposal of such batteries.

- Other rechargeable batteries have been developed.
  - NiMH batteries (nickel–metal–hydride).
  - Li–ion batteries (lithium–ion batteries).

Fuel Cells

- Direct production of electricity from fuels occurs in a \textbf{fuel} cell.
- Cathode: reduction of oxygen:
  \[
  2\text{H}_2\text{O}(l) + \text{O}_2(g) + 4e^{-} \rightarrow 4\text{OH}^{-}(aq)
  \]
- Anode:
  \[
  2\text{H}_2(g) + 4\text{OH}^{-}(aq) \rightarrow 4\text{H}_2\text{O}(l) + 4e^{-}
  \]
20.8 Corrosion

- An example of an undesirable redox reaction is the corrosion of metals.
- Metal is attacked by a substance in the environment and converted to an unwanted compound.

**Corrosion of Iron**

- Consider the rusting of iron:
  - Since $E_{\text{red}}(\text{Fe}^{2+}) < E_{\text{red}}(\text{O}_2)$, iron can be oxidized by oxygen.
  - Cathode: $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$ \hspace{1em} $E_{\text{red}} = 1.23 \text{ V}$.  
  - Anode: $\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^-$ \hspace{1em} $E_{\text{red}} = -0.44 \text{ V}$.  

- Dissolved oxygen in water usually causes the oxidation of iron.
- The $\text{Fe}^{2+}$ initially formed can be further oxidized to $\text{Fe}^{3+}$, which forms rust, $\text{Fe}_2\text{O}_3\cdot x\text{H}_2\text{O}(s)$.
- Oxidation occurs at the site with the greatest concentration of $\text{O}_2$.
- Other factors to consider are the pH, presence of salts, stress on the iron, and contact with other metals.

**Preventing the Corrosion of Iron**

- Corrosion can be prevented by coating the iron with paint or another metal.
  - This prevents oxygen and water from reacting at the surface of the iron.
  - Galvanized iron is coated with a thin layer of zinc.
- Zinc protects the iron since $\text{Zn}$ is the anode and $\text{Fe}$ the cathode:
  \[
  \begin{align*}
  \text{Zn}^{2+}(aq) + 2e^- & \rightarrow \text{Zn}(s) \hspace{1em} E_{\text{red}} = -0.76 \text{ V} \\
  \text{Fe}^{2+}(aq) + 2e^- & \rightarrow \text{Fe}(s) \hspace{1em} E_{\text{red}} = -0.44 \text{ V}
  \end{align*}
  \]
  - The standard reduction potentials indicate that $\text{Zn}$ is easier to oxidize than $\text{Fe}$.
  - This process is **cathodic protection** (the *sacrificial anode* is destroyed).
• We can use something similar to protect underground pipelines.

• Often, Mg is used as a sacrificial anode:
  \[
  \begin{align*}
  \text{Mg}^{2+}(aq) + 2e^- &\rightarrow \text{Mg}(s) & E_{\text{red}}^0 &= -2.37 \text{ V} \\
  \text{Fe}^{2+}(aq) + 2e^- &\rightarrow \text{Fe}(s) & E_{\text{red}}^0 &= -0.44 \text{ V}
  \end{align*}
  \]

Sample Exercise 20.15 (p. 812)

Predict the nature of the corrosion that would take place if an iron gutter were nailed to a house using aluminum nails.

Practice Exercise 20.15

Based on the standard reduction potentials in Table 20.1 or your AP Chem packet, which of the following metals could provide cathodic protection to iron: Al, Cu, Ni, Zn?
20.9 Electrolysis

- **Electrolysis reactions** are nonspontaneous reactions that require an external current in order to force the reaction to proceed.

- In voltaic and electrolytic cells, reduction occurs at the cathode, and oxidation occurs at the anode.
  - However, in electrolytic cells, electrons are forced to flow from the anode to the cathode.
  - In electrolytic cells the anode is positive and the cathode is negative.
  - In voltaic cells the anode is negative and the cathode is positive.

Electrolysis of Aqueous Solutions

- Example, decomposition of molten NaCl.
  - Cathode: \(2\text{Na}^+(l) + 2e^- \rightarrow 2\text{Na}(l)\)
  - Anode: \(2\text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2e^-\).
  - Industrially, electrolysis is used to produce metals like Al.

- Electrolysis of high-melting ionic substances requires very high temperatures.

- Do we get the same products if we electrolyze an aqueous solution of the salt?

- Water complicates the issue!

- Example: Consider the electrolysis of NaF(aq):

  \[
  \begin{align*}
  \text{Na}^- (aq) + e^- &\rightarrow \text{Na}(s) \quad E^\circ_{\text{red}} = -2.71 \text{ V} \\
  2\text{H}_2\text{O}(l) + 2e^- &\rightarrow \text{H}_2(g) + 2\text{OH}^- (aq) \quad E^\circ_{\text{red}} = -0.83 \text{ V}
  \end{align*}
  \]

  - Thus water is more easily reduced than the sodium ion.

  \[
  \begin{align*}
  2\text{F}^- (aq) &\rightarrow \text{F}_2(g) + 2e^- \quad E^\circ_{\text{red}} = +2.87 \text{ V} \\
  2\text{H}_2\text{O}(l) &\rightarrow \text{O}_2(g) + 4\text{H}^+ (aq) + 4e^- \quad E^\circ_{\text{red}} = +1.23 \text{ V}
  \end{align*}
  \]

  - Thus it is easier to oxidize water than the fluoride ion.
Sample Exercise 20.16 (p. 814)

Electrolysis of AgF(aq) in an acidic solution leads to the formation of silver metal and oxygen gas.

a) Write the half-reaction that occurs at each electrode.

b) Calculate the minimum external emf required for this process under standard conditions.
   (-0.43 V)

Practice Exercise 20.16

The electrolysis of CuCl2(aq) produces Cu(s) and Cl2(g). What is the minimum external emf needed to drive this electrolysis under standard conditions?

(+1.02 V)
Electrolysis with Active Electrodes

- Active electrodes: electrodes that take part in electrolysis.
  - Example: electroplating.

- Consider an active Ni electrode and another metallic electrode (steel) placed in an aqueous solution of NiSO₄:
  - Anode: \( \text{Ni}(s) \rightarrow \text{Ni}^{2+}(aq) + 2e^- \)
  - Cathode: \( \text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s) \).

- Ni plates on the inert electrode.

- Electroplating is important in protecting objects from corrosion.

Quantitative Aspects of Electrolysis

- We want to know how much material we obtain with electrolysis.

- Consider the reduction of Cu⁺ to Cu.
  \[ \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \]

- Two mol of electrons will plate 1 mol of Cu.

- The charge of one mol of electrons is 96,500 C (1 F).
  - A coulomb is the amount of charge passing a point in one second when the current is one ampere.

- The amount of Cu can be calculated from the current \( I \) and time \( t \) required to plate.
  \[ Q = I \times t \]
Sample Exercise 20.17 (p. 817)

Calculate the number of grams of aluminum produced in 1.00 hr by the electrolysis of molten AlCl₃ if the electrical current is 10.0 A.

(3.36 g Al)

Practice Exercise 20.17

a) The half-reaction for formation of magnesium metal upon electrolysis of molten MgCl₂ is

\[ \text{Mg}^{2+} + 2e^- \rightarrow \text{Mg} \]

Calculate the mass of magnesium formed upon passage of a current of 60.0 A for a period of 4.00 x 10³ s.

(30.2 g Mg)

b) How many seconds would be required to produce 50.0 g of Mg from MgCl₂ if the current is 100.0 A?

(3.97 x 10³ s)
Electrical Work

- Free energy is a measure of the maximum amount of useful work that can be obtained from a system.
  - We know: \( \Delta G = w_{\text{max}} \)
  - And: \( \Delta G = -nFE \)
  - Thus: \( w_{\text{max}} = -nFE \)
- If \( E_{\text{cell}} \) is positive, \( w_{\text{max}} \) will be negative.
  - Work is done by the system on the surroundings.
- The emf can be thought of as being a measure of the driving force for a redox process.
  - In an electrolytic cell an external source of energy is required to force the reaction to proceed.
    \( w = nFE_{\text{external}} \)
  - In order to drive the nonspontaneous reaction the external emf must be greater than \( E_{\text{cell}} \).
  - From physics: Work is measured in units of watts:
    \( 1 \text{ W} = 1 \text{ J/s} \)
  - Electric utilities use units of kilowatt-hours:
    \[
    1 \text{ kWh} = (1000 \text{ W})(1 \text{ hour}) = \left( \frac{3600 \text{ s}}{1 \text{ hour}} \right) \left( \frac{1 \text{ J/s}}{1 \text{ W}} \right) = 3.6 \times 10^6 \text{ J}
    \]

Sample Exercise 20.18 (p. 818)

Calculate the number of kilowatt-hours of electricity required to produce \( 1.0 \times 10^3 \) kg of aluminum by electrolysis of \( \text{Al}^{3+} \) if the applied emf is 4.50 V.

(1.34 x 10^4 kWh)

Practice Exercise 20.18

Calculate the number of kilowatt-hours of electricity required to produce 1.00 kg of Mg by electrolysis of molten \( \text{MgCl}_2 \) if the applied emf is 5.00 V. Assume that the process is 100% efficient.

(11.0 kWh)
Sample Integrative Exercise 20 (p. 819)

The $K_{sp}$ at 298 K for iron (II) fluoride is $2.4 \times 10^{-6}$.

a) Write a half-reaction that gives the likely products of the two-electron reduction of $\text{FeF}_2(s)$ in water.

b) Use the $K_{sp}$ value and the standard reduction potential of $\text{Fe}^{2+}\text{(aq)}$ to calculate the standard reduction potential for the half-reaction in part (a). (-0.606 V)

c) Rationalize the difference in the reduction potential for the half-reaction in part (a) with that for $\text{Fe}^{2+}\text{(aq)}$. 