Harnessing the Power in Nature

- The goal of scientific research is to understand nature.
- Once we understand the nature of something, we can then use it efficiently.
- The average U.S. household currently consumes 1000 kWh of electricity per month.
- Almost all of this electricity is generated at a remote power plant by either the combustion of fossil fuels or nuclear fission.

Electricity from Chemistry

- Many chemical reactions involve the transfer of electrons between atoms or ions.
  - Electron transfer reactions
    - All single displacement and combustion reactions
    - Some synthesis and decomposition reactions
  - The flow of electrons is associated with electricity.
  - Basic research into the nature of this relationship may, in the near future, lead to cheaper, more efficient ways of generating electricity.
  - Fuel cell

Oxidation–Reduction

- Reactions where electrons are transferred from one atom to another are called oxidation–reduction reactions.
  - Redox reactions for short
- Atoms that lose electrons are being oxidized; atoms that gain electrons are being reduced.

\[ 2 \text{Na(s)} + \text{Cl}_2(g) \rightarrow 2 \text{Na}^+ \text{Cl}^-(s) \]

\[ \text{Na} \rightarrow \text{Na}^+ + 1 \text{e}^- \text{ oxidation} \]

\[ \text{Cl}_2 + 2 \text{e}^- \rightarrow 2 \text{Cl}^- \text{ reduction} \]

Oxidation and Reduction

- **Oxidation** is the process that occurs when
  - the oxidation number of an element increases,
  - an element loses electrons,
  - a compound adds oxygen,
  - a compound loses hydrogen, or
  - a half-reaction has electrons as products.

- **Reduction** is the process that occurs when
  - the oxidation number of an element decreases,
  - an element gains electrons,
  - a compound loses oxygen,
  - a compound gains hydrogen, or
  - a half-reaction has electrons as reactants.

Half-Reactions

- We generally split the redox reaction into two separate half-reactions—a reaction just involving oxidation or reduction.
  - The oxidation half-reaction has electrons as products.
  - The reduction half-reaction has electrons as reactants.

\[ 3 \text{Cl}_2 + \text{I}^- + 3\text{H}_2\text{O} \rightarrow 6 \text{Cl}^- + \text{IO}_3^- + 6 \text{H}^+ \]

\[ \begin{array}{cccc}
\text{Oxidation:} \ & \text{I}^- & \rightarrow & \text{IO}_3^- + 6 \text{e}^- \\
\text{Reduction:} \ & \text{Cl}_2 & + & 2 \text{e}^- & \rightarrow & 2 \text{Cl}^- \\
\end{array} \]
Balancing Redox Reactions by the Half-Reaction Method

- In this method, the reaction is broken down into two half-reactions, one for oxidation and another for reduction.
- Each half-reaction includes electrons.
  - Electrons go on the product side of the oxidation half-reaction—loss of electrons.
  - Electrons go on the reactant side of the reduction half-reaction—gain of electrons.
- Each half-reaction is balanced for its atoms.
- Then the two half-reactions are adjusted so that the electrons lost and gained will be equal when combined.

Balancing Redox Reactions

1. **Assign oxidation states.**
   a) Determine the element oxidized and the element reduced.
2. **Write oxidation and reduction half-reactions, including electrons.**
   a) Oxidation electrons on right, and reduction electrons on left of the arrow.
3. **Balance half-reactions by mass.**
   a) First balance elements other than H and O.
   b) Add H_2O where O is needed.
   c) Add H^+ where H is needed.
   d) If the reaction is done in a base, neutralize H^+ with OH^-.
4. **Balance half-reactions by charge.**
   a) Balance charge by adjusting electrons.
5. **Balance electrons between half-reactions.**
6. **Add half-reactions.**
7. **Check by counting atoms and total charge.**

**Example 18.1 Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution**

Balance the redox equation:

\[ \text{Al}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Al}^{3+}(aq) + \text{Cu}(s) \]

**General Procedure**

1. **Assign oxidation states to all atoms and identify the substances being oxidized and reduced.**
   \[ \text{Al}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Al}^{3+}(aq) + \text{Cu}(s) \]
   - Reduction: \( \text{Al}^{3+}(aq) \rightarrow \text{Al}(s) \)
   - Oxidation: \( \text{Cu}^{2+}(aq) \rightarrow \text{Cu}(s) \)
2. **Separate the overall reaction into two half-reactions: one for oxidation and one for reduction.**
   - Balance all elements other than H and O.
   - Balance 0 by adding H_2O.
   - Balance H by adding H^+.
3. **Balance half-reactions by mass.**
   - Balance all elements other than H and O.
   - Balance O by adding H_2O.
   - Balance H by adding H^+.
4. **Balance half-reactions by charge.**
   - Make the sum of the charges on both sides of the equation equal by adding as many electrons as necessary.
5. **Balance electrons between half-reactions.**
   - Multiply one or both half-reactions by a small whole number.
6. **Add the two half-reactions together, canceling electrons and other species as necessary.**
7. **Verify that the reaction is balanced both with respect to mass and with respect to charge.**

**For Practice 18.1**

Balance the redox reaction in acidic solution:

\[ \text{Fe}^{2+}(aq) + \text{MnO}_4^-(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{Mn}^{2+}(aq) \]
All elements other than H and O are balanced so proceed to balance H and O.

Fe^2+ (aq) → Fe^3+ (aq)  
MnO_4^- (aq) → MnO_4^- (aq) + 4 H^+ (aq)

Step 4 Balance each half-reaction with respect to charge by adding electrons. (Make the sum of the charges on both sides of the equation equal by adding as many electrons as necessary.)

Fe^2+ (aq) → Fe^3+ (aq) + e^-  
5 e^- + 8 H^+ (aq) + MnO_4^- (aq) → MnO_4^- (aq) + 4 H_2 O

Step 5 Make the number of electrons in each half-reaction equal by multiplying one or both half-reactions by a small whole number:

5 [Fe^2+ (aq)] → [Fe^3+ (aq) + 5 e^-]
5 [e^-] → 5 [H^+ (aq) + MnO_4^- (aq)] → MnO_4^- (aq) + 4 H_2 O

Step 6 Add the two half-reactions together canceling electrons and other species as necessary:

5 Fe^2+ (aq) + 5 H^+ (aq) + 5 MnO_4^- (aq) → MnO_4^- (aq) + 4 H_2 O
5 Fe^2+ (aq) + 5 MnO_4^- (aq) → MnO_4^- (aq) + 4 H_2 O

Step 7 Verify that the reaction is balanced both with respect to mass and with respect to charge.
Verify that the reaction is balanced.

For Practice 18.3
Balance the following redox reaction occurring in basic solution.

\[ \text{ClO}_3^- (aq) + \text{OH}^- (aq) \rightarrow \text{ClO}_2^- (aq) + \text{Cl}^- (aq) \]

Example 18.4
Calculating Standard Potentials for Electrochemical Cells from Standard Electrode Potentials of the Half-Reactions

Use tabulated standard electrode potentials to calculate the standard cell potential for the following reaction occurring in an electrochemical cell at 25°C. (The equation is balanced.)

\[ \text{Al}(s) + \text{NO}_3^- (aq) + 4 \text{H}^+ (aq) \rightarrow \text{Al}^{3+} (aq) + \text{NO}_2(g) + 2 \text{H}_2\text{O}(l) \]

Solution

Begin by separating the reaction into oxidation and reduction half-reactions. (In this case, you can readily see that Al is oxidized. In cases where it is not so apparent, you may want to assign oxidation states to determine the correct half-reactions.)

Oxidation: \[ \text{Al}(s) \rightarrow \text{Al}^{3+} (aq) + 3e^- \]
Reduction: \[ \text{NO}_3^- (aq) + 4 \text{H}^+ (aq) + 3e^- \rightarrow \text{NO}_2(g) + 2 \text{H}_2\text{O}(l) \]

Electrical Current

- Electrons flow through a conductor in response to an electrical potential difference similar to water flowing downhill in response to a difference in gravitational potential energy.
- Electric current – the amount of electric charge that passes a point in a given period of time
  - Whether as electrons flowing through a wire, or ions flowing through a solution

Redox Reactions and Current

- Redox reactions involve the transfer of electrons from one substance to another.
- Therefore, redox reactions have the potential to generate an electric current.
- To use that current, we need to separate the place where oxidation is occurring from the place where reduction is occurring.
Electrochemistry

- **Electrochemistry** is the study of redox reactions that produce or require an electric current.
- The conversion between chemical energy and electrical energy is carried out in an electrochemical cell.
- Spontaneous redox reactions take place in a voltaic cell. Also known as galvanic cells.
- Nonspontaneous redox reactions can be made to occur in an electrolytic cell by the addition of electrical energy.

Electrochemical Cells

- Oxidation and reduction half-reactions are kept separate in half-cells.
- Electron flow through a wire along with ion flow through a solution constitutes an electric circuit.
- It requires a conductive solid electrode to allow the transfer of electrons. Through external circuit. Metal or graphite.
- Requires ion exchange between the two half-cells of the system. Electrolyte.

Electrodes

- **Anode**
  - Electrode where oxidation occurs
  - Anions attracted to it
  - Connected to positive end of battery in an electrolytic cell
  - Loses weight in electrolytic cell
- **Cathode**
  - Electrode where reduction occurs
  - Cations attracted to it
  - Connected to negative end of battery in an electrolytic cell
  - Gains weight in electrolytic cell
  - Electrode where plating takes place in electroplating

Voltaic Cell

The salt bridge is required to complete the circuit and maintain charge balance.

Current

- **Current** is the number of electrons that flow through the system per second.
  - Unit = ampere
- 1 A of current = 1 coulomb of charge flowing each second
  - 1 A = $6.242 \times 10^{18}$ electrons per second
- Electrode surface area dictates the number of electrons that can flow.
  - Larger batteries produce larger currents.

Voltage

- The difference in potential energy between the reactants and products is the **potential difference**.
  - Unit = volt
- 1 V = 1 J of energy per coulomb of charge
  - The voltage needed to drive electrons through the external circuit
- The amount of force pushing the electrons through the wire is called the **electromotive force, emf**.
Cell Potential

- The difference in potential energy between the anode and the cathode in a voltaic cell is called the **cell potential**.
- The cell potential depends on the relative ease with which the oxidizing agent is reduced at the cathode and the reducing agent is oxidized at the anode.
- The cell potential under standard conditions is called the **standard emf, \( E^\circ_{\text{cell}} \)**.
  - 25 °C, 1 atm for gases, 1 M concentration of solution
  - Sum of the cell potentials for the half-reactions

Cell Notation

- Shorthand description of a voltaic cell
- Electrode | electrolyte || electrolyte | electrode
- Oxidation half-cell on the left; reduction half-cell on the right
- Single | = phase barrier
  - If multiple electrolytes in same phase, a comma is used rather than |
  - Often use an **inert electrode**
- Double line || = salt bridge

Voltaic Cell

Anode = Zn(s)  
The anode is oxidized to Zn\(^{2+}\).

Cathode = Cu(s)  
Cu\(^{2+}\) ions are reduced at the cathode.

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

Electrodes

- Typically
  - The anode is made of the metal that is oxidized.
  - The cathode is made of the same metal as is produced by the reduction.
- If the redox reaction we are running involves the oxidation or reduction of an ion to a different oxidation state, or the oxidation or reduction of a gas, we may use an **inert electrode**.
  - An **inert electrode** is one that does not participate in the reaction, but just provides a surface for the transfer of electrons to take place on.

Electrochemical Cell Notation

Because the half-reaction involves reducing the Mn oxidation state from +7 to +2, we use an electrode that will provide a surface for the electron transfer without reacting with the MnO\(_4\)^{2-}.

Platinum works well because it is extremely nonreactive and conducts electricity.

Fe(s) | Fe\(^{2+}\)(aq) || MnO\(_4\)^{2-}(aq), Mn\(^{2+}\)(aq), H\(^{+}\)(aq) | Pt(s)

Cell Potential

- A half-reaction with a strong tendency to occur has a large positive half-cell potential.
- When two half-cells are connected, the electrons will flow so that the half-reaction with the stronger tendency will occur.
Which Way Will Electrons Flow?

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2 \text{e}^- & E^\circ &= +0.76 \\
\text{Cu}^{2+} + 2 \text{e}^- & \rightarrow \text{Cu} & E^\circ &= -0.34
\end{align*}
\]

Under standard conditions, zinc has a stronger tendency to oxidize than copper. Therefore, the electrons flow from zinc; making zinc the anode.

Standard Reduction Potential

- We cannot measure the absolute tendency of a half-reaction, we can only measure it relative to another half-reaction.
- We select as a standard half-reaction the reduction of \( \text{H}^+ \) to \( \text{H}_2 \) under standard conditions, which we assign a potential difference \( = 0 \) V.
  - Standard hydrogen electrode, SHE

Half-Cell Potentials

- SHE reduction potential is defined to be exactly 0 V.
- Standard reduction potentials compare the tendency for a particular reduction half-reaction to occur relative to the reduction of \( \text{H}^+ \) to \( \text{H}_2 \).
  - Under standard conditions
- Half-reactions with a stronger tendency toward reduction than the SHE have a positive value for \( E^\circ_{\text{red}} \).
- Half-reactions with a stronger tendency toward oxidation than the SHE have a negative value for \( E^\circ_{\text{red}} \).
- For an oxidation half-reaction, \( E^\circ_{\text{oxidation}} = - E^\circ_{\text{reduction}} \).
Example 18.4 Calculating Standard Potentials for Electrochemical Cells from Standard Electrode Potentials of the Half-Reactions

Look up the standard electrode potentials for each half-reaction in Table 18.1. Add the half-cell reactions together to obtain the overall redox equation. Calculate the standard cell potential by subtracting the electrode potential of the anode from the electrode potential of the cathode.

Example 18.4 Calculating Standard Potentials for Electrochemical Cells from Standard Electrode Potentials of the Half-Reactions

Continued

Example 18.5 Predicting Spontaneous Redox Reactions and Sketching Electrochemical Cells

Without calculating $E_{\text{cell}}$, predict whether each of the following redox reactions is spontaneous. If the reaction is spontaneous as written, make a sketch of the electrochemical cell in which the reaction could occur. If the reaction is not spontaneous as written, write an equation for the spontaneous direction in which the reaction would occur and sketch the electrochemical cell in the spontaneous reaction.

Solution

* a. $\text{Fe}(s) + \text{Mg}^2+(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Mg}(s)$
  - The reaction involves the reduction of $\text{Mg}^2+$ to $\text{Mg}$ and the oxidation of $\text{Fe}$.
  - $E^o_{\text{cell}} = E^o_{\text{red}} - E^o_{\text{ox}}$
  - $E^o_{\text{cell}} = 0.77 \text{ V} - (-2.71 \text{ V}) = 3.48 \text{ V}$

Calculating Cell Potentials under Standard Conditions

- $E^o_{\text{cell}} = E^o_{\text{oxidation}} + E^o_{\text{reduction}}$
- $E^o_{\text{cell}} = E^o_{\text{cathode}} - E^o_{\text{Anode}}$

- When adding $E^o$ values for the half-cells, do not multiply the half-cell $E^o$ values, even if you need to multiply the half-reactions to balance the equation.

Example 18.5 Predicting Spontaneous Redox Reactions and Sketching Electrochemical Cells

Continued

However, the magnesium half-reaction has the more negative electrode potential and therefore requires electrons more strongly and undergoes oxidation. The iron half-reaction has the more positive electrode potential and therefore attracts electrons more strongly and undergoes reduction. So the reaction as written is not spontaneous. (The reaction pairs the reduction of $\text{Mg}^2+$ with the reverse of a half-reaction above it in Table 18.1—such pairings are not spontaneous.)

However, the reverse reaction is spontaneous.

$\text{Mg}^{2+}(aq) + 2\text{e}^{-} \rightarrow \text{Mg}(s)$
Example 18.5 Predicting Spontaneous Redox Reactions and Sketching Electrochemical Cells

Continued

The corresponding electrochemical cell is shown in Figure 18.9.

![Mg/Fe²⁺ Electrochemical Cell](image)

b. Fe(s) + Pb²⁺(aq) → Fe²⁺(aq) + Pb(s)
   This reaction involves the reduction of Pb²⁺:
   \[ \text{Pb}^{2+} (aq) + 2e^- \rightarrow \text{Pb} (s) \]  
   \[ E^\circ = -0.13 \text{ V} \]
   and the oxidation of Fe:
   \[ \text{Fe} (s) \rightarrow \text{Fe}^{2+} (aq) + 2e^- \]  
   \[ E^\circ = -0.45 \text{ V} \]

Example 18.5 Predicting Spontaneous Redox Reactions and Sketching Electrochemical Cells

Continued

For Practice 18.5
Are the following redox reactions spontaneous under standard conditions?

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

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

Predicting Spontaneity of Redox Reactions

- A spontaneous reaction will take place when a reduction half-reaction is paired with an oxidation half-reaction lower on the table.
- If paired the other way, the reverse reaction is spontaneous.

\[ \text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu} (s) \quad E^\circ_{\text{red}} = +0.34 \text{ V} \]
\[ \text{Zn}^{2+} (aq) + 2e^- \rightarrow \text{Zn} (s) \quad E^\circ_{\text{red}} = -0.76 \text{ V} \]

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

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

Example 18.5 Predicting Spontaneous Redox Reactions and Sketching Electrochemical Cells

Continued

The tin half-reaction has the more negative electrode potential and therefore repels electrons and undergoes oxidation. The lead half-reaction has the more positive electrode potential and therefore attracts electrons and undergoes reduction. Therefore, the reaction is spontaneous as written. (The reaction pairs the reduction of Pb²⁺ with the reverse of a half-reaction below it in Table 18.1—such pairings are always spontaneous.) The corresponding electrochemical cell is shown in Figure 18.10.

![Fe/Pb²⁺ Electrochemical Cell](image)

Tendencies from the Table of Standard Reduction Potentials

- A redox reaction will be spontaneous when there is a strong tendency for the oxidizing agent to be reduced and the reducing agent to be oxidized.
  - Higher on the table of standard reduction potentials = stronger tendency for the reactant to be reduced
  - Lower on the table of standard reduction potentials = stronger tendency for the product to be oxidized

Predicting Whether a Metal Will Dissolve in an Acid

- Metals dissolve in acids.
  - If the reduction of the metal ion is easier than the reduction of H⁺(aq)
  - If their ion reduction reaction lies below H⁺ reduction on the table

- Almost all metals will dissolve in HNO₃.
  - Having N reduced rather than H
  - Au and Pt dissolve in HNO₃ + HCl

\[ \text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l) \]
For a spontaneous reaction
- one that proceeds in the forward direction with the chemicals in their standard states
  \( \Delta G^\circ < 1 \) (negative)
  \( E^\circ > 1 \) (positive)
  \( K > 1 \)

\[ \Delta G^\circ = -RT \ln K = -nFE^\circ \]
- \( n \) = the number of electrons
- \( F \) = Faraday’s constant = 96,485 C/mol

**Example 18.7 Relating \( E^\circ_{\text{cell}} \) and \( K \)**

**Solution**
Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Find \( E^\circ_{\text{cell}} \) by subtracting \( E^\circ_{\text{an}} \) from \( E^\circ_{\text{cat}} \).

\[ E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{an}} \]

The answer has no units, as expected for an equilibrium constant. The magnitude of the answer is small, indicating that the reaction lies far to the left at equilibrium, as expected for a reaction in which \( E^\circ_{\text{cell}} \) is negative.

For Practice 18.7
Use the tabulated electrode potentials to calculate \( K \) for the oxidation of iron by \( H^+ \) (at 25°C).

**Example 18.8 Calculating \( E^\circ_{\text{cell}} \) under Nonstandard Conditions**

Determine the cell potential for an electrochemical cell based on the following two half-reactions:

Oxidation

\[ \text{MnO}_2(s) + 2H^+(aq) \rightarrow Mn^{2+}(aq) + H_2O(l) \]

Reduction

\[ \text{Fe}(s) + 2H^+(aq) \rightarrow \text{Fe}^{2+}(aq) + 2H_2(g) \]

Calculate \( E^\circ_{\text{cell}} \), the voltage for the cell will be different when the ion concentrations are not 1 M.

**Cell Potential When Ion Concentrations Are Not 1 M**

- We know there is a relationship between the reaction quotient, \( Q \); the equilibrium constant, \( K \); and the free energy change, \( \Delta G^\circ \).
- Changing the concentrations of the reactants and products so they are not 1 M will affect the standard free energy change, \( \Delta G^\circ \).
- Because \( \Delta G^\circ \) determines the cell potential, \( E^\circ_{\text{cell}} \), the voltage for the cell will be different when the ion concentrations are not 1 M.
Example 18.8 Calculating $E_{\text{cell}}$ under Nonstandard Conditions

Determine the cell potential for an electrochemical cell based on the following two half-reactions:

Oxidation: $\text{Cr}^3+(aq) + 2\text{e}^- \rightarrow \text{Cr}^{2+}(aq)$

Reduction: $\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$

Sort

You are given the half-reactions for a redox reaction and the concentrations of the aqueous reactants and products. You are asked to find the cell potential.

Given:

Find:

$E_{\text{cell}}$

Strategize

Use the tabulated values of electrode potentials to calculate $E_{\text{cell}}$. Then use Equation 18.9 to calculate $E_{\text{cell}}$.

Conceptual Plan

Sort

Write the oxidation and reduction half-reactions, multiplying by the appropriate coefficients to cancel the electrons. Find the standard electrode potentials for each.

Solution

Calculate $E_{\text{cell}}$ from $E_{\text{cell}}$. The value of $n$ (the number of moles of electrons) corresponds to the number of electrons (6 in this case) canceled in the half-reactions. Determine $Q$ based on the overall balanced equation and the given concentrations of the reactants and products. (Note that pure liquid water, solid MnO$_2$, and solid copper are omitted from the expression for $Q$.)

Check

The answer has the correct units (V). The value of $E_{\text{cell}}$ is larger than $E_{\text{cell}}$, as expected based on Le Châtelier’s principle because one of the aqueous reactants has a concentration greater than standard conditions and the one aqueous product has a concentration less than standard conditions. Therefore, the reaction has a greater tendency to proceed toward products and has a greater cell potential.

For Practice 18.8

Determine the cell potential of an electrochemical cell based on the following two half-reactions:

Oxidation: $\text{N}_2\text{O}_5$(aq) + 2$\text{H}^+$(aq) + e$^- \rightarrow \text{NO}_3^-(aq) +$ 2$\text{H}_2\text{O}(l)$

Reduction: $\text{VO}_2^+$(aq) + 2$\text{H}^+$(aq) + e$^- \rightarrow \text{VO}^{2+}$(aq) + H$_2$O(l)

Concentration Cells

- It is possible to get a spontaneous reaction when the oxidation and reduction reactions are the same, as long as the electrolyte concentrations are different.
- The difference in energy is due to the entropic difference in the solutions.
  - The more concentrated solution has lower entropy than the less concentrated solution.
  - Electrons will flow from the electrode in the less concentrated solution to the electrode in the more concentrated solution.
    - Oxidation of the electrode in the less concentrated solution will increase the ion concentration in the solution; the less concentrated solution has the anode.
    - Reduction of the solution ions at the electrode in the more concentrated solution reduces the ion concentration; the more concentrated solution has the cathode.
When the cell concentrations are equal there is no difference in energy between the half-cells and no electrons flow.

When the cell concentrations are different, electrons flow from the side with the less concentrated solution (anode) to the side with the more concentrated solution (cathode).

Leclanché Acidic Dry Cell
- Electrolyte in paste form
  - ZnCl₂ + NH₄Cl
    - Or MgBr₂
- Anode = Zn (or Mg)
  \[ \text{Zn(s)} \rightarrow \text{Zn}^{2+}(aq) + 2 \text{e}^- \]
- Cathode = graphite rod
- MnO₂ is reduced.
  \[ 2 \text{MnO}_2(s) + 2 \text{NH}_4^+(aq) + 2 \text{H}_2\text{O}(l) + 2 \text{e}^- \rightarrow 2 \text{NH}_3\text{OH}(aq) + 2 \text{Mn(O)OH(s)} \]
- Cell voltage = 1.5 V
- Expensive, nonrechargeable, heavy, easily corroded

Alkaline Dry Cell
- Same basic cell as acidic dry cell, except electrolyte is alkaline KOH paste
- Anode = Zn (or Mg)
  \[ \text{Zn(s)} \rightarrow \text{Zn}^{2+}(aq) + 2 \text{e}^- \]
- Cathode = graphite or brass rod
- MnO₂ is reduced.
  \[ 2 \text{MnO}_2(s) + 2 \text{NH}_4^+(aq) + 2 \text{H}_2\text{O}(l) + 2 \text{e}^- \rightarrow 2 \text{NH}_3\text{OH}(aq) + 2 \text{Mn(O)OH(s)} \]
- Cell voltage = 1.54 V
- Longer shelf life than acidic dry cell and rechargeable, with little corrosion of zinc.

Lead Storage Battery
- Six cells in series
- Electrolyte = 30% H₂SO₄
- Anode = Pb
  \[ \text{Pb(s)} + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) + 2 \text{e}^- \]
- Cathode = Pb coated with PbO₂
- Pb₃O₄ is reduced.
  \[ \text{Pb}_3\text{O}_4(s) + 4 \text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2 \text{e}^- \rightarrow \text{PbSO}_4(s) + 2 \text{H}_2\text{O}(l) \]
- Cell voltage = 2.09 V
- Rechargeable, heavy

NiCad Battery
- Electrolyte is concentrated KOH solution
- Anode = Cd
  \[ \text{Cd(s)} + 2 \text{OH}^- (aq) \rightarrow \text{Cd(OH)}_2(s) + 2 \text{e}^- \quad E^0 = 0.81 \text{ V} \]
- Cathode = Ni coated with NiO₂
- NiO₂ is reduced.
  \[ \text{NiO}_2(s) + 2 \text{H}_2\text{O}(l) + 2 \text{e}^- \rightarrow \text{Ni(OH)}_2(s) + 2 \text{OH}^- \quad E^0 = 0.49 \text{ V} \]
- Cell voltage = 1.30 V
- Rechargeable, long life, light; however, recharging incorrectly can lead to battery breakdown
Ni-MH Battery

- Electrolyte is concentrated KOH solution
- Anode = metal alloy with dissolved hydrogen
  - Oxidation of H from H$_2$ to H$^+$
  $\text{M} \cdot \text{H}_2(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow \text{M}(\text{s}) + \text{H}_2\text{O}(\text{l}) + e^-$
  $E^\circ = 0.89 \text{ V}$
- Cathode = Ni coated with NiO$_2$
- NiO$_2$ is reduced.
  $\text{NiO}_2(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) + 2 e^- \rightarrow \text{Ni(OH)}_2(\text{s}) + 2\text{OH}^-$
  $E^\circ = 0.49 \text{ V}$
- Cell voltage = 1.30 V
- Rechargeable, long life, light, more environmentally friendly than NiCad, greater energy density than NiCad

Lithium Ion Battery

- Electrolyte is concentrated KOH solution
- Anode = graphite impregnated with Li ions
- Cathode = Li - transition metal oxide
  - Reduction of transition metal
- Work on Li ion migration from anode to cathode causing a corresponding migration of electrons from anode to cathode
- Rechargeable, long life, very light, more environmentally friendly, greater energy density

Fuel Cells

- Like batteries in which reactants are constantly being added
  - So it never runs down!
- Anode and cathode both Pt coated metal
- Electrolyte is OH$^-$ solution.
- Anode reaction
  $2 \text{H}_2 + 4\text{OH}^- \rightarrow 4 \text{H}_2\text{O}(\text{l}) + 4 e^-$
- Cathode reaction
  $\text{O}_2 + 4 \text{H}_2\text{O} + 4 e^- \rightarrow 4 \text{OH}^-$

Voltaic versus Electrolytic Cells

- In all electrochemical cells, oxidation occurs at the anode, reduction occurs at the cathode.
- In voltaic cells
  - Anode is the source of electrons and has a (−) charge.
  - Cathode draws electrons and has a (+) charge.
- In electrolytic cells
  - Electrons are drawn off the anode, so it must have a place to release the electrons—the positive terminal of the battery.
  - Electrons are forced toward the anode, so it must have a source of electrons—the negative terminal of the battery.
Electrolysis

• **Electrolysis** is the process of using electrical energy to break a compound apart.

• Electrolysis is done in an electrolytic cell.

• Electrolytic cells can be used to separate elements from their compounds.

Electrolysis

• In electrolysis we use electrical energy to overcome the energy barrier of a nonspontaneous reaction, allowing it to occur.

• The reaction that takes place is the opposite of the spontaneous process.

\[
2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \quad \text{electrolysis}
\]

• Some applications are (1) metal extraction from minerals and purification, (2) production of H\textsubscript{2} for fuel cells, and (3) metal plating.

Electrolytic Cells

• The electrical energy is supplied by a direct current power supply.
  – AC alternates the flow of electrons so the reaction won’t be able to proceed.

• Some electrolysis reactions require more voltage than \( E_{\text{cell}} \) predicts. This is called the overvoltage.

Electrolytic Cells

• The source of energy is a battery or DC power supply.

• The positive terminal of the source is attached to the anode.

• The negative terminal of the source is attached to the cathode.

• Electrolyte can be either an aqueous salt solution or a molten ionic salt.

• Cations in the electrolyte are attracted to the cathode and anions are attracted to the anode.

• Cations pick up electrons from the cathode and are reduced; anions release electrons to the anode and are oxidized.

Electrolysis of Pure Compounds

• The compound must be in molten (liquid) state.

• Electrodes are normally graphite.

• Cations are reduced at the cathode to metal element.

• Anions are oxidized at the anode to nonmetal element.

Electrolysis of Water

• The compound must be in molten (liquid) state.

• Electrodes are normally graphite.

• Cations are reduced at the cathode to metal element.

• Anions are oxidized at the anode to nonmetal element.
Electrolysis of NaCl

Electrolysis of a Molten Salt

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

Electroplating

In electroplating, the work piece is the cathode.

Cations are reduced at cathode and plate to the surface of the work piece.

The anode is made of the plate metal. The anode oxidizes and replaces the metal cations in the solution.

Mixtures of Ions

- When more than one cation is present, the cation that is easiest to reduce will be reduced first at the cathode.
  - Least negative or most positive \( E^\text{red}_{\text{cath}} \)
- When more than one anion is present, the anion that is easiest to oxidize will be oxidized first at the anode.
  - Least negative or most positive \( E^\text{ox}_{\text{anode}} \)

Electrolysis of Aqueous Solutions

- Possible cathode reactions
  - Reduction of cation to metal
  - Reduction of water to \( \text{H}_2 \)
    - \( 2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2 \text{OH}^- \) \( E^\circ = -0.83 \) V at stand. cond.
  - Possible anode reactions
    - Oxidation of anion to element
    - Oxidation of \( \text{H}_2\text{O} \) to \( \text{O}_2 \)
      - \( 2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4e^- + 4\text{H}^+ \) \( E^\circ = -1.23 \) V at stand. cond.
    - Oxidation of electrode
      - Particularly Cu
      - Graphite doesn’t oxidize
    - Half-reactions that lead to least negative \( E^\text{cell} \) will occur.
  - Unless overvoltage changes the conditions

Electrolysis of NaI \((aq)\) with Inert Electrodes

Possible reductions
\[ \text{Na}^+ + 1e^- \rightarrow \text{Na} \] \( E^\circ = -2.71 \) V
\[ 2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2 \text{OH}^- \] \( E^\circ = -0.41 \) V

Possible oxidations
\[ 2 \Gamma \rightarrow \Gamma_2 + 2e^- \] \( E^\circ = -0.54 \) V
\[ 2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4e^- + 4\text{H}^+ \] \( E^\circ = -0.82 \) V

Electrolysis of NaI \((aq)\) with Inert Electrodes

Possible reductions
\[ \text{Na}^+ + 1e^- \rightarrow \text{Na} \] \( E^\circ = -2.71 \) V
\[ 2 \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2 \text{OH}^- \] \( E^\circ = -0.41 \) V

Possible oxidations
\[ 2 \Gamma \rightarrow \Gamma_2 + 2e^- \] \( E^\circ = -0.54 \) V
\[ 2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4e^- + 4\text{H}^+ \] \( E^\circ = -0.82 \) V
Electrolysis of NaI\(_{(aq)}\) with Inert Electrodes

**Overall reaction**

\[
2 \text{I}^-\text{(aq)} + 2 \text{H}_2\text{O(l)} \rightarrow \text{I}_2\text{(aq)} + \text{H}_2\text{(g)} + 2 \text{OH}^-\text{(aq)}
\]

Stoichiometry of Electrolysis

- In an electrolytic cell, the amount of product made is related to the number of electrons transferred.
  - Essentially, the electrons are a reactant.
- The number of moles of electrons that flow through the electrolytic cell depends on the current and length of time.
  - 1 amp = 1 coulomb of charge/second
  - 1 mole of e\(^-\) = 96,485 coulombs of charge
  - Faraday’s constant

**Example 18.9 Predicting the Products of Electrolysis Reactions**

a. a mixture of molten AlBr\(_3\) and MgBr\(_2\)

b. an aqueous solution of LiI

**Solution**

a. In the electrolysis of a molten salt, the anion is oxidized and the cation is reduced. However, this mixture contains two cations. Start by writing the possible oxidation and reduction half-reactions that might occur.

Since Br\(^-\) is the only anion, write the equation for its oxidation, which occurs at the anode.

At the cathode, both the reduction of Al\(^{3+}\) and the reduction of Mg\(^{2+}\) are possible. The one that actually occurs is the one that occurs most easily. Since the reduction of Al\(^{3+}\) has a more positive electrode potential in aqueous solution, this ion is more easily reduced. Therefore, the reduction of Al\(^{3+}\) occurs at the cathode.

b. Since LiI is in an aqueous solution, two different oxidation half-reactions are possible at the anode, the oxidation of I\(^-\) and the oxidation of water. Write half-reactions for each, including the electrode potential. Remember to use the electrode potential of water under conditions in which [H\(^+\)] = 10\(^{-7}\) M. Since the oxidation of I\(^-\) has the more negative electrode potential, it will be the half-reaction to occur at the anode.

Similarly, write half-reactions for the two possible reduction half-reactions that might occur at the cathode, the reduction of Li\(^+\) and the reduction of water. Since the reduction of water has the more positive electrode potential (even when considering overvoltage, which would raise the necessary voltage by about 0.4–0.6 V), it will be the half-reaction to occur at the cathode.

**Example 18.10 Stoichiometry of Electrolysis**

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

\[
\text{Au}^{3+} + 3 e^- \rightarrow \text{Au}\
\]

What mass of gold (in grams) is plated by a 25-minute flow of 5.5 A current?

**Sort**

- You are given the half-reaction for the plating of gold, which shows the stoichiometric relationship between moles of electrons and moles of gold. You are also given the current and duration. You must find the mass of gold that will be deposited in that time.
- Given: 3 mol e\(^-\) = 1 mole Au
- 5.5 amps
- 25 minutes
- Find: g Au

**Strategy**

You need to find the amount of gold, which is related stoichiometrically to the number of electrons that flow through the cell. Begin with time in minutes and convert to seconds. Then, since current is a measure of charge per unit time, use the given current and the time to find the number of coulombs. You can then use Faraday’s constant to calculate the number of moles of electrons and the stoichiometry of the reaction to find the number of moles of gold. Finally, use the molar mass of gold to convert to mass of gold.
Example 18.10  Stoichiometry of Electrolysis

Continued

Conceptual Plan

Follow the conceptual plan to solve the problem, canceling units to arrive at the mass of gold.

Solution

Check

The answer has the correct units (g Au). The magnitude of the answer is reasonable if we consider that 10 amps of current for 1 hour is the equivalent of about 1/3 mol of electrons (check for yourself), which would produce 1/9 mol (or about 20 g) of gold.

Silver can be plated out of a solution containing Ag⁺ according to the half-reaction:

How much time (in minutes) would it take to plate 12 g of silver using a current of 3.0 A?

For Practice

18.10

Reduction of O₂

• O₂ is very easy to reduce in moist conditions.
  \[ O_2(g) + 2 H_2O(l) + 4 e^- \rightarrow 2 OH^-(aq) \quad E^{\circ} = 0.40 \text{ V} \]

• O₂ is even easier to reduce under acidic conditions.
  \[ O_2(g) + 4 H^+ + 4 e^- \rightarrow 2 H_2O(l) \quad E^{\circ} = 1.23 \text{ V} \]

• Because the reduction of most metal ions lies below O₂ on the table of standard reduction potentials, the oxidation of those metals by O₂ is spontaneous.

Corrosion

• Corrosion is the spontaneous oxidation of a metal by chemicals in the environment.
  – Mainly O₂
• Because many materials we use are active metals, corrosion can be a very big problem.
  – Metals are often used for their strength and malleability, but these properties are lost when the metal corrodes.
  – For many metals, the product of corrosion also does not adhere to the metal, and as it flakes off more metal can corrode.

Rusting

• At the anodic regions, Fe(s) is oxidized to Fe²⁺.
• The electrons travel through the metal to a cathodic region where O₂ is reduced.
  – In acidic solution from gases dissolved in the moisture
• The Fe²⁺ ions migrate through the moisture to the cathodic region where they are further oxidized to Fe³⁺, which combines with the oxygen and water to form rust.
  – Rust is hydrated iron(III) oxide, Fe₂O₃•nH₂O
  – The exact composition depends on the conditions.
  – Moisture must be present.
  – Water is a reactant.
  – It is required for ion flow between cathodic and anodic regions.
• Electrolytes promote rusting.
  – Enhances current flow
• Acids promote rusting.
  – Lowering pH will lower \( E^{\circ}_{\text{red}} \) of O₂.

Corrosion of Iron: Rusting

The Rusting of Iron

• Water is required for ion flow between cathodic and anodic regions.
Preventing Corrosion

• One way to reduce or slow corrosion is to coat the metal surface to keep it from contacting corrosive chemicals in the environment.
  – Paint
  – Some metals, such as Al, form an oxide that strongly attaches to the metal surface, preventing the rest from corroding.
• Another method to protect one metal is to attach it to a more reactive metal that is cheap.
  – Sacrificial electrode
  • Galvanized nails

Sacrificial Anode

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