Electrochemistry

Oxidation-Reduction Reactions

• In Chapter 4 we introduced the half-reaction method for balancing simple oxidation-reduction reactions.
  – Oxidation-reduction reactions always involve a transfer of electrons from one species to another.
  – Recall that the species losing electrons is oxidized, while the species gaining electrons is reduced.

Oxidation-Reduction Reactions

• Describing Oxidation-Reduction Reactions
  – An oxidizing agent is a species that oxidizes another species; it is itself reduced.
  – A reducing agent is a species that reduces another species; it is itself oxidized.

\[
\text{Fe}^{2+}_{(aq)} + \text{Cu}^{+}_{(s)} \rightarrow \text{Fe}^{3+}_{(aq)} + \text{Cu}^{2+}_{(s)}
\]
Balancing Oxidation-Reduction Equations in Acid Solution

1. Assign oxidation numbers
2. Determine half reactions
3. Complete and balance each half-reaction
   a. Balance all atoms except O and H
   b. Balance O atoms by adding H2O’s to one side
   c. Balance H atoms by adding H+ to one side
   d. Balance electric charges by adding e- to the more positive side
4. Combine each half reaction to obtain the final balanced oxidation reduction equation (Multiply by appropriate factors and cancel species appearing on both sides of equation

Balancing Oxidation-Reduction Equations in Basic Solution

1. Assign oxidation numbers
2. Determine half reactions
3. Complete and balance each half-reaction
   a. Balance all atoms except O and H
   b. Balance O atoms by adding H2O’s to one side
   c. Balance H atoms by adding H+ to one side
   d. Balance electric charges by adding e- to the more positive side
4. Note the number of H+ ions in the equation. Add this number of OH- ions to both sides of the equation.
5. Simplify the equation by noting that H+ and OH- react to form H2O. Cancel waters that occur on both sides of the equation and reduce the equation to simplest terms.
6. Combine each half reaction to obtain the final balanced oxidation reduction equation (Multiply by appropriate factors and cancel species appearing on both sides of equation
Balance in acid solution:
\[ \text{Mn}^{2+} + \text{BiO}_3^- \rightarrow \text{MnO}_4^- + \text{Bi}^{3+} \]

Balance in Basic solution:
\[ \text{S}^2^- + \text{I}_2 \rightarrow \text{SO}_4^{2-} + \text{I}^- \]

Oxidation-Reduction Reactions

- In this chapter we will show how a cell is constructed to **physically separate** an oxidation-reduction reaction into two **half-reactions**.
  - The force with which electrons travel from the oxidation half-reaction to the reduction half-reaction is measured as **voltage**.

Electrochemistry

- An **electrochemical cell** is a system consisting of electrodes that dip into an electrolyte in which a chemical reaction either uses or generates an electric current.
  - A **voltaic**, or **galvanic**, cell is an electrochemical cell in which a **spontaneous** reaction generates an electric current.
  - An **electrolytic cell** is an electrochemical cell in which an electric current drives an otherwise **nonspontaneous** reaction.
  - In this chapter we will discuss the basic principles behind these cells and explore some of their commercial uses.
Voltaic Cells

• A voltaic cell consists of two half-cells that are electrically connected. [See Video: Galvanic Voltaic Cells]
  – Each half-cell is a portion of the electrochemical cell in which a half-reaction takes place. [See Animation: Electrochemical Half-Reactions in a Galvanic Cell]
  – A simple half-cell can be made from a metal strip dipped into a solution of its metal ion.
  – For example, the zinc-zinc ion half cell consists of a zinc strip dipped into a solution of a zinc salt.

Voltaic Cells

• A voltaic cell consists of two half-cells that are electrically connected.
  – Another simple half-cell consists of a copper strip dipped into a solution of a copper salt.
  – In a voltaic cell, two half-cells are connected in such a way that electrons flow from one metal electrode to the other through an external circuit.
  – Figure 20.2 illustrates an atomic view of a zinc/copper voltaic cell.

Figure 20.2: Atomic view of voltaic cell.
Voltaic Cells

- As long as there is an external circuit, electrons **can flow** through it from one electrode to the other.
  - Because zinc has a greater tendency to lose electrons than copper, zinc atoms in the zinc electrode lose electrons to form zinc ions.
  - The electrons flow through the external circuit to the copper electrode where copper ions gain the electrons to become copper metal.

Voltaic Cells

- The two half-cells **must also be connected internally** to allow ions to flow between them.
  - Without this internal connection, too much positive charge builds up in the zinc half-cell (and too much negative charge in the copper half-cell) causing the reaction to stop.
  - Figure 20.3A and 20.3B show the two half-cells of a voltaic cell connected by **salt bridge**.

Figure 20.3: Two electrodes are connected by an external circuit.
Voltaic Cells

- A *salt bridge* is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell.
  - The salt bridge allows the flow of ions but *prevents the mixing of the different solutions that would allow direct reaction* of the cell reactants.
  - Figure 20.3C shows an actual setup of the zinc-copper cell.

Voltaic Cells

- The two half-cell reactions, as noted earlier, are:
  - Zn(s) → Zn^{2+}(aq) + 2e^- (oxidation half-reaction)
  - Cu^{2+}(aq) + 2e^- → Cu(s) (reduction half-reaction)
  - The first reaction, in which electrons are lost, is the *oxidation half-reaction*.
  - The electrode at which oxidation occurs is the *anode*.
  - The second reaction, in which electrons are gained, is the *reduction half-reaction*.
  - The electrode at which reduction occurs is the *cathode*.
Voltaic Cells

• Note that the sum of the two half-reactions

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

is the net reaction that occurs in the voltaic cell; it is called the cell reaction

- Note that electrons are given up at the anode and thus flow from it to the cathode where reduction occurs.
- The anode in a voltaic cell has a negative sign because electrons flow from it. [See Figure 20.4 and Animation: Anode Reaction]
- The cathode in a voltaic cell has a positive sign [See Animation: Cathode Reaction]

Notation for Voltaic Cells

• It is convenient to have a shorthand way of designating particular voltaic cells.

- The cell consisting of the zinc-zinc ion half-cell and the copper-copper ion half-cell, is written

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

- The anode (oxidation half-cell) is written on the right. The cathode (reduction half-cell) is written on the left.
The cell terminals are at the extreme ends in the cell notation.

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

A single vertical bar indicates a phase boundary, such as between a solid terminal and the electrode solution.

Notation for Voltaic Cells

- When the half-reaction involves a gas, an inert material such as platinum serves as a terminal and an electrode surface on which the reaction occurs.
  - Figure 20.5 shows a hydrogen electrode; hydrogen bubbles over a platinum plate immersed in an acidic solution.
  - The cathode half-reaction is
    \[
    2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)
    \]

- The notation for the hydrogen electrode, written as a cathode, is
  \[
  \text{H}^+(aq) \mid \text{H}_2(g) \mid \text{Pt}
  \]
  - To write such an electrode as an anode, you simply reverse the notation.

  \[
  \text{Pt} \mid \text{H}_2(g) \mid \text{H}^+(aq)
  \]
  - In the cell notation, these are written in parentheses. For example,

\[
\text{Zn}(s) \mid \text{Zn}^{2+}(1.0 \text{ M}) \parallel \text{H}^+(aq) \mid \text{H}_2(1.0 \text{ atm}) \parallel \text{Pt}
\]
A Problem To Consider

- Give the overall cell reaction for the voltaic cell

\[ \text{Cd(s)} | \text{Cd}^{2+} (1.0 \text{ M}) || \text{H}^+(aq) | \text{H}_2 (1.0 \text{ atm}) | \text{Pt} \]

- The half-cell reactions are

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

\[ \text{Cd(s)} + 2\text{H}^+(aq) \rightarrow \text{Cd}^{2+}(aq) + \text{H}_2(g) \]

Electromotive Force

- The movement of electrons is analogous to the pumping of water from one point to another.
  - Water moves from a point of high pressure to a point of lower pressure. Thus, a pressure difference is required.
  - The work expended in moving the water through a pipe depends on the volume of water and the pressure difference.
- An electric charge moves from a point of high electrical potential (high electrical pressure) to one of lower electrical potential.
- The work expended in moving the electrical charge through a conductor depends on the amount of charge and the potential difference.
Electromotive Force

- **Potential difference** is the difference in electric potential (electrical pressure) between two points.
  - You measure this quantity in volts.
  - The **volt**, \( V \), is the SI unit of potential difference equivalent to 1 joule of energy per coulomb of charge.
  
  \[
  1 \text{ volt} = \frac{1 \text{ J}}{\text{C}}
  \]

Electromotive Force

- The **Faraday constant**, \( F \), is the magnitude of charge on one mole of electrons; it equals 96,500 coulombs (9.65 \times 10^4 C).
  - In moving 1 mol of electrons through a circuit, the numerical value of the **work done by a voltaic cell** is the product of the Faraday constant (\( F \)) times the potential difference between the electrodes.

  \[
  \text{work (J)} = -F(\text{coulombs}) \times \text{volts (J/coulomb)}
  \]

Electromotive Force

- In the normal operation of a voltaic cell, the potential difference (**voltage**) across the electrodes is **less than than the maximum** possible voltage of the cell.
  - The actual flow of electrons reduces the electrical pressure.
  - Thus, a cell voltage has its maximum value when **no current flows**.
Electromotive Force

- The maximum potential difference between the electrodes of a voltaic cell is referred to as the electromotive force (emf) of the cell, or $E_{\text{cell}}$.
  - It can be measured by an electronic digital voltmeter (Figure 20.6), which draws negligible current.

Work Exercise 20.6 Look at Problems 20.51-54

Electromotive Force

- We can now write an expression for the maximum work attainable by a voltaic cell.
  - Let $n$ be the number of (mol) electrons transferred in the overall cell reaction.
  - The maximum work for molar amounts of reactants is
    $$ w_{\text{max}} = -nFE_{\text{cell}} $$

Work Exercise 20.6 Look at Problems 20.51-54
A Problem To Consider

• The emf of the electrochemical cell below is 0.650 V. Calculate the maximum electrical work of this cell when 0.500 g H₂ is consumed.

\[
\text{Hg}_2^{2+}(aq) + \text{H}_2(g) \rightleftharpoons 2\text{Hg}(l) + 2\text{H}^+(aq)
\]

- The half-reactions are

\[
\begin{align*}
\text{Hg}_2^{2+}(aq) + 2e^- & \rightleftharpoons 2\text{Hg}(l) \\
\text{H}_2(g) & \rightleftharpoons 2\text{H}^+(aq) + 2e^-
\end{align*}
\]

- \( n = 2 \), and the maximum work for the reaction is written as

\[
W_{\text{max}} = -nFE_{\text{cell}}
\]

\[
W_{\text{max}} = -2 \times (9.65 \times 10^4 \text{C}) \times (0.650 \text{ V})
\]

For 0.500 g H₂, the maximum work is

\[
0.500 \text{ g H}_2 \times 1 \text{ mol H}_2 \times \frac{1.25 \times 10^5 \text{ J}}{2 \text{ mol H}_2} = -3.09 \times 10^4 \text{ J}
\]

Standard Cell emf's and Standard Electrode Potentials

• A cell emf is a measure of the driving force of the cell reaction.

- The reaction at the anode has a definite oxidation potential, while the reaction at the cathode has a definite reduction potential.

- Thus, the overall cell emf is a combination of these two potentials.

\[
E_{\text{cell}} = \text{oxidation potential} + \text{reduction potential}
\]
A reduction potential is a measure of the tendency to gain electrons in the reduction half-reaction.

You can look at the oxidation half-reaction as the reverse of a corresponding reduction reaction.

The oxidation potential for an oxidation half-reaction is the negative of the reduction potential for the reverse reaction.

Standard Cell emf’s and Standard Electrode Potentials

- By convention, the Table of Standard Electrode Potentials (Table 20.1) are tabulated as reduction potentials.

- Consider the zinc-copper cell described earlier.

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

- The two half-reactions are

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

- The zinc half-reaction is an oxidation.

- If you write \( E_{Zn} \) for the reduction potential of zinc, then \( -E_{Zn} \) is the oxidation potential of zinc.

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

- The copper half-reaction is a reduction.

- Write \( E_{Cu} \) for the electrode potential.

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

- For this cell, the cell emf is the sum of the reduction potential for the copper half-cell and the oxidation potential for the zinc half-cell.
\[ E_{\text{cell}} = E_{\text{Cu}} + (-E_{\text{Zn}}) \]
\[ E_{\text{cell}} = E_{\text{Cu}} - E_{\text{Zn}} \]

- Note that the cell emf is the difference between the two electrode potentials.
- In general, \( E_{\text{cell}} \) is obtained by subtracting the anode potential from the cathode potential.
  \[ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \]
- The electrode potential is an intensive property whose value is independent of the amount of species in the reaction.

Thus, the electrode potential for the half-reaction

\[ 2\text{Cu}^{2+}(aq) + 4e^- \rightarrow 2\text{Cu}(s) \]

is the same as for

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

Tabulating Standard Electrode Potentials

- The standard emf, \( E^\circ_{\text{cell}} \), is the emf of a cell operating under standard conditions of concentration (1 M), pressure (1 atm), and temperature (25°C).
- Note that individual electrode potentials require that we choose a reference electrode.
- You arbitrarily assign this reference electrode a potential of zero and obtain the potentials of the other electrodes by measuring the emf’s.
By convention, the reference chosen for comparing electrode potentials is the standard hydrogen electrode. (See Figure 20.5)

Standard electrode potentials are measured relative to this hydrogen reference.

Tabulating Standard Electrode Potentials

- The standard electrode potential, $E^\circ$, is the electrode potential when concentrations of solutes are 1 M, gas pressures are 1 atm, and the temperature is 25°C. (Table 20.1)
  - For example, when you measure the emf of a cell composed of a zinc electrode connected to a hydrogen electrode, you obtain 0.76 V.
  - Since zinc acts as the anode (oxidation) in this cell, its reduction potential is listed as −0.76 V.

Strengths of Oxidizing and Reducing Agents

- Standard electrode potentials are useful in determining the strengths of oxidizing and reducing agents under standard-state conditions.
  - A reduction half-reaction has the general form
    \[
    \text{oxidized species} + n \text{e}^- \rightarrow \text{reduced species}
    \]
    - The oxidized species acts as an oxidizing agent.
  - Consequently, the strongest oxidizing agents in a table of standard electrode potentials are the oxidized species corresponding to the half-reactions with the largest (most positive) $E^\circ$ values. (For example $F_2(g)$)
An oxidation half-reaction has the general form
\[ \text{reduced species} \rightarrow \text{oxidized species} + n\text{e}^- \]

- The reduced species acts as a reducing agent.

- Consequently, the strongest reducing agents in a table of standard electrode potentials are the reduced species corresponding to the half-reactions with the smallest (most negative) \( E^\circ \) values. (for example, Li(s))

Calculating Cell emf’s from Standard Potentials

- The emf of a voltaic cell constructed from standard electrodes is easily calculated using a table of electrode potentials.
  - Consider a cell constructed of the following two half-reactions.
  
  \[
  \text{Cd}^{2+}(aq) + 2e^- \rightarrow \text{Cd}(s); \quad E^\circ = -0.40 \text{ V} \\
  \text{Ag}^+(aq) + 1e^- \rightarrow \text{Ag}(s); \quad E^\circ = 0.80 \text{ V}
  \]

  - You will need to reverse one of these reactions to obtain the oxidation part of the cell reaction.

  \[
  \text{Cd}^{2+}(aq) + 2e^- \rightarrow \text{Cd}(s); \quad E^\circ = -0.40 \text{ V} \\
  \text{Ag}^+(aq) + 1e^- \rightarrow \text{Ag}(s); \quad E^\circ = 0.80 \text{ V}
  \]

- This will be Cd, because has the more negative electrode potential.

  \[
  \text{Cd}^{2+}(aq) + 2e^- \rightarrow \text{Cd}(s); \quad E^\circ = -0.40 \text{ V} \\
  \text{Ag}^+(aq) + 1e^- \rightarrow \text{Ag}(s); \quad E^\circ = 0.80 \text{ V}
  \]

  - Therefore, you reverse the half-reaction and change the sign of the half-cell potential.

  \[
  \text{Cd}(s) \rightarrow \text{Cd}^{2+}(aq) + 2e^-; \quad E^\circ = 0.40 \text{ V} \\
  \text{Ag}^+(aq) + 1e^- \rightarrow \text{Ag}(s); \quad E^\circ = 0.80 \text{ V}
  \]

  - We must double the silver half-reaction so that when the reactions are added, the electrons cancel.
Cd(s) → Cd^{2+}(aq) + 2e\(^-\); \(E^\circ = 0.40\) V

\(\text{Ag}^+(aq) + \text{e}^- → \text{Ag}(s); \ E^\circ = 0.80\) V

• This does not affect the half-cell potentials, which do not depend on the amount of substance.

\(\text{Cd(s)} → \text{Cd}^{2+}(aq) + 2\text{e}^-; \ E^\circ = 0.40\) V

\(\text{Ag}^+(aq) + 2\text{e}^- → \text{Ag}(s); \ E^\circ = 0.80\) V

• Now we can add the two half-reactions to obtain the overall cell reaction and cell emf.

\(\text{Cd(s)} → \text{Cd}^{2+}(aq) + 2\text{e}^-; \ E^\circ = 0.40\) V

\(2\text{Ag}^+(aq) + 2\text{e}^- → 2\text{Ag}(s); \ E^\circ = 0.80\) V

Now we can add the two half-reactions to obtain the overall cell reaction and cell emf.

\(\text{Cd(s)} → \text{Cd}^{2+}(aq) + 2\text{e}^-; \ E^\circ = 0.40\) V

\(2\text{Ag}^+(aq) + 2\text{e}^- → 2\text{Ag}(s); \ E^\circ = 0.80\) V

\(\text{Cd(s)} + 2\text{Ag}^+(aq) → \text{Cd}^{2+}(aq) + 2\text{Ag}(s); \ E^\circ_{\text{cell}} = 1.20\) V

• The corresponding cell notation would be

\(\text{Cd(s)} | \text{Cd}^{2+}(1M) || \text{Ag}^+(1M) | \text{Ag(s)}\)

Do Exercise 20.7 See Problems 20.55-58

Note that the emf of the cell equals the standard electrode potential of the cathode minus the standard electrode potential of the anode.

\(E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}\)

• Calculate the standard emf for the following voltaic cell at 25°C using standard electrode potentials. What is the overall reaction?

\(\text{Al(s)} | \text{Al}^{3+}(aq) || \text{Fe}^{2+}(aq) | \text{Fe(s)}\)
The reduction half-reactions and standard potentials are

\[ \text{Al}^{3+}(aq) + 3e^- \rightarrow \text{Al}(s); \quad E^o = -1.66 \text{ V} \]

\[ \text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s); \quad E^o = -0.41 \text{ V} \]

\[ \text{Al}(s) \mid \text{Al}^{3+}(aq) \parallel \text{Fe}^{2+}(aq) \parallel \text{Fe}(s) \]

You reverse the first half-reaction and its half-cell potential to obtain

\[ \text{Al}(s) \rightarrow \text{Al}^{3+}(aq) + 3e^-; \quad E^o = 1.66 \text{ V} \]

\[ \text{Fe}^{3+}(aq) + 2e^- \rightarrow \text{Fe}(s); \quad E^o = -0.41 \text{ V} \]

To obtain the overall reaction we must balance the electrons.

\[ 2\text{Al}(s) \rightarrow 2\text{Al}^{3+}(aq) + 6e^-; \quad E^o = 1.66 \text{ V} \]

\[ 3\text{Fe}^{2+}(aq) + 6e^- \rightarrow 3\text{Fe}(s); \quad E^o = -0.41 \text{ V} \]

Now we add the reactions to get the overall cell reaction and cell emf.

\[ 2\text{Al}(s) \rightarrow 2\text{Al}^{3+}(aq) + 6e^-; \quad E^o = 1.66 \text{ V} \]

\[ 3\text{Fe}^{2+}(aq) + 6e^- \rightarrow 3\text{Fe}(s); \quad E^o = -0.41 \text{ V} \]

\[ 2\text{Al}(s) + 3\text{Fe}^{2+}(aq) \rightarrow 2\text{Al}^{3+}(aq) + 3\text{Fe}(s); \quad E^o = 1.25 \text{ V} \]

How do you determine the direction of spontaneity?

Look at example 20.7 and do example 20.8

See problems 20.59 and 20.60
Equilibrium Constants from emf’s

- Some of the most important results from electrochemistry are the relationships among $E^{\circ}_{\text{cell}}$, free energy, and equilibrium constant.
  - In Chapter 19 we saw that $\Delta G$ equals the maximum useful work of a reaction.
  - For a voltaic cell, $\text{work} = -nFE^\circ$, so when reactants are in their standard states
    \[ \Delta G^\circ = -nFE^\circ \]
  - The measurement of cell emf’s gives you yet another way of calculating equilibrium constants.

- Combining the previous equation, $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ with the equation $\Delta G^\circ = -RT\ln K$, we get
  \[ nFE^\circ_{\text{cell}} = RT\ln K \]
  - Or, rearranging, we get
    \[ E^\circ_{\text{cell}} = \frac{2.303RT}{nF} \log K \]
  - Substituting values for the constants $R$ and $F$ at 25°C gives the equation
    \[ E^\circ_{\text{cell}} = \frac{0.0592}{n} \log K \]
    (values in volts at 25°C)

Look at Examples 20.9 and 20.10

Do Exercises 20.10 and 20.11

Look at problems 20.67-72
A Problem To Consider

- The standard emf for the following cell is 1.10 V.

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

Calculate the equilibrium constant \( K_c \) for the reaction

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

- Note that \( n=2 \). Substituting into the equation relating \( E_{\text{cell}} \) and \( K \) gives

\[
1.10 \text{ V} = \frac{0.0592}{2} \log K
\]

- Solving for \( \log K \), you find

\[
\log K = 37.2
\]

- Now take the antilog of both sides:

\[
K_c = \text{anti log}(37.2) = 1.6 \times 10^{37}
\]

- The number of significant figures in the answer equals the number of decimal places in 37.2 (one). Thus

\[
K_c = 2 \times 10^{37}
\]
Dependence of emf on Concentration

- Recall that the free energy change, \( \Delta G \), is related to the standard free energy change, \( \Delta G^\circ \), by the following equation.

\[
\Delta G = \Delta G^\circ + RT \ln Q
\]

- Here \( Q \) is the thermodynamic reaction quotient.

- If we substitute \( \Delta G = -nFE_{\text{cell}} \) and \( \Delta G = -nFE_{\text{cell}}^\circ \) into this equation, we get

\[
-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q
\]

Dependence of emf on Concentration

- The result rearranges to give the Nernst equation, an equation relating the cell emf to its standard emf and the reaction quotient.

\[
E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log Q
\]

- Substituting values for \( R \) and \( F \) at 25 °C, we get

\[
E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q
\]

(values in volts at 25 °C)

Dependence of emf on Concentration

- The result rearranges to give the Nernst equation, an equation relating the cell emf to its standard emf and the reaction quotient.

- The Nernst equation illustrates why cell emf decreases as the cell reaction proceeds.

- As reactant concentrations decrease and product concentrations increase, \( Q \) increases, thus increasing \( \log Q \) which in turn decreases the cell emf.
A Problem To Consider

• What is the emf of the following voltaic cell at 25°C?

\[
\text{Zn(s)} | \text{Zn}^{2+} (1 \times 10^{-5} \text{M}) || \text{Cu}^{2+} (0.100 \text{M}) | \text{Cu(s)}
\]

The standard emf of the cell is 1.10 V.

– The cell reaction is

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

– The number of electrons transferred is 2; hence \( n = 2 \). The reaction quotient is

\[
Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1.00 \times 10^{-5}}{0.100} = 1.00 \times 10^{-4}
\]

– The standard emf is 1.10 V, so the Nernst equation becomes

\[
E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log Q
\]

\[
E_{\text{cell}} = 1.10 \text{ V} - \frac{0.0592}{2} \log (1.00 \times 10^{-4})
\]

\[
E_{\text{cell}} = 1.10 \text{ V} - (-0.12) = 1.22 \text{ V}
\]

– The cell emf is 1.22 V.

Do Exercise 20.13

Some Commercial Voltaic Cells

• The Leclanché dry cell, or zinc-carbon dry cell, is a voltaic cell with a zinc can as the anode and a graphite rod in the center surrounded by a paste of manganese dioxide, ammonium and zinc chlorides, and carbon black, as the cathode.

– The electrode reactions are

\[
\text{anode: } \text{Zn(s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2e^- \\
\text{cathode: } 2\text{NH}_4^+ (\text{aq}) + 2\text{MnO}_2(s) + 2e^- \rightarrow \text{Mn}_2\text{O}_3(s) + \text{H}_2\text{O(l)} + 2\text{NH}_3(\text{aq})
\]

*see Figure 20.9*
The alkaline dry cell, is similar to the Leclanché cell, but it has potassium hydroxide in place of ammonium chloride.

- The electrode reactions are:
  - Anode: \( \text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \)
  - Cathode: \( \text{MnO}_2(\text{s}) + \text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^- (\text{aq}) \)

(see Figure 20.10)
Some Commercial Voltaic Cells

• The **lithium-iodine battery** is a solid state battery in which the anode is lithium metal and the cathode is an I₂ complex.
  - The solid state electrodes are separated by a thin crystalline layer of lithium iodide.
  - Although it produces a low current, it is very reliable and is used to power pacemakers.

(see Figure 20.11)

---

Figure 20.11:
Solid-State Lithium-Iodine Battery

---

Some Commercial Voltaic Cells

• The **lead storage cell** (a rechargeable cell) consists of electrodes of lead alloy grids; one electrode is packed with a spongy lead to form the anode, and the other electrode is packed with lead dioxide to form the cathode.
  - The electrode reactions are

  \[
  \text{Pb}(s) + \text{HSO}_4^-(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^- \quad \text{anode}
  \]
  \[
  \text{PbO}_2(s) + 2\text{H}^+(aq) + \text{HSO}_4^-(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \quad \text{cathode}
  \]

(see Figure 20.12)
Some Commercial Voltaic Cells

- The **nickel-cadmium cell (nicad cell)** consists of an anode of cadmium and a cathode of hydrated nickel oxide on nickel; the electrolyte is potassium hydroxide.
  - The electrode reactions are
    
    $\text{Cd}(s) + 2\text{OH}^-(aq) \rightarrow \text{Cd(OH)}_2(s) + 2e^-$  \hspace{1cm} \text{anode}
    
    $\text{NiOOH}(s) + \text{H}_2\text{O}(l) + e^- \rightarrow \text{Ni(OH)}_2(s) + \text{OH}^-(aq)$  \hspace{1cm} \text{cathode}

(see Figure 20.14)
Some Commercial Voltaic Cells

- A fuel cell is essentially a battery, but differs by operating with a continuous supply of energetic reactants, or fuel.

  - For a hydrogen-oxygen fuel cell, the electrode reactions are

    \[
    \begin{align*}
    2\text{H}_2(\text{g}) + 4\text{OH}^-\text{(aq)} &\rightarrow \text{H}_2\text{O}(\text{l}) + 4\text{e}^- & \text{anode} \\
    \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- &\rightarrow 4\text{OH}^-\text{(aq)} & \text{cathode}
    \end{align*}
    \]

(see Figure 20.15)

Figure 20.15: Hydrogen-Oxygen Fuel Cell

To do:
Research how a fuel cell works and what different types exist.

Figure 20.16: The Electrochemical Process Involved in the Rusting of Iron

Water drop
Figure 20.17: Cathodic Protection of Buried Steel Pipe

- Magnesium rod
- Steel pipe
- Moist soil
- \( \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \)
- \( \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \)

Figure 20.18: A Demonstration of Cathodic Protection

- Unprotected nail
- \( \text{Fe}^{2+} + \text{Ferricyanide} \rightarrow \)
Electrolytic Cells

- An electrolytic cell is an electrochemical cell in which an electric current drives an otherwise nonspontaneous reaction. (See Video: Electrolysis of Water)
  - The process of producing a chemical change in an electrolytic cell is called electrolysis.
  - Many important substances, such as aluminum metal and chlorine gas are produced commercially by electrolysis.

Figure 20.19: Electrolysis of Molten Sodium Chloride

Electrolysis of Molten Salts

- A Downs cell is a commercial electrochemical cell used to obtain sodium metal by electrolysis of molten NaCl. (See Figure 20.20)
  - A number of other reactive metals are obtained by the electrolysis of a molten salt.
  - Lithium, magnesium, and calcium metals are all obtained by the electrolysis of the chlorides.

Do Exercise 20.15  See Problems 20.85-20.86
Figure 20.24: Purification of Copper by Electrolysis

Anode mud with gold and other metals

Figure 20.24: Purification of Copper by Electrolysis (cont’d)

Conceptual Problem 20.26 You have 1.0 M solutions of Al(NO₃)₃ and AgNO₃, along with Al and Ag electrodes to construct a voltaic cell. The salt bridge contains a saturated solution of KCl. Complete the picture below by:

a. writing the symbols of the elements and ions in the appropriate areas (both solutions and electrodes).
b. identifying the anode and cathode.
c. indicating the direction of electron flow through the external circuit.
d. indicating the cell end (assume standard conditions).
e. writing the appropriate half-reaction under each of the containers.
f. identifying the direction of ion flow in the salt bridge.
g. identifying the species undergoing oxidation and reduction.
h. writing the balanced overall reaction for the cell.
Stoichiometry of Electrolysis

- What is new in this type of stoichiometric problem is the measurement of numbers of electrons.
  - You do not weigh them as you do substances.
  - Rather, you measure the quantity of electric charge that has passed through a circuit.
  - To determine this we must know the current and the length of time it has been flowing.

Electric current is measured in amperes.

- An ampere (A) is the base SI unit of current equivalent to 1 coulomb/second.

- The quantity of electric charge passing through a circuit in a given amount of time is given by

\[
\text{Electric charge (coul)} = \text{electric current (coul/sec)} \times \text{time lapse (sec)}
\]

A Problem To Consider

- When an aqueous solution of potassium iodide is electrolyzed using platinum electrodes, the half-reactions are

\[
\begin{align*}
2\text{I}^-(aq) & \rightarrow \text{I}_2(aq) + 2e^- \\
2\text{H}_2\text{O}(l) + 2e^- & \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)
\end{align*}
\]

How many grams of iodine are produced when a current of 8.52 mA flows through the cell for 10.0 min?

- When the current flows for 6.00 x 10² s (10.0 min), the amount of charge is

\[
(8.52 \times 10^{-3} \text{ A}) \times (6.00 \times 10^2 \text{ s}) = 5.11 \text{ C}
\]
A Problem To Consider

- When an aqueous solution of potassium iodide is electrolyzed using platinum electrodes, the half-reactions are

  \[ 2I^- (aq) \rightarrow I_2 (aq) + 2e^- \]
  \[ 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^- (aq) \]

  How many grams of iodine are produced when a current of 8.52 mA flows through the cell for 10.0 min?

  - Note that two moles of electrons are equivalent to one mole of \( I_2 \). Hence,

  \[ 5.11 \times 10^{-4} \text{ C} \times \frac{1 \text{ mol } e^-}{9.65 \times 10^{-4} \text{ C}} \times \frac{1 \text{ mol } I_2}{2 \text{ mol } e^-} \times \frac{254 \text{ g } I_2}{1 \text{ mol } I_2} = 6.73 \times 10^{-3} \text{ g } I_2 \]

Do Example 20.16

See Problems 20.87 – 20.88

Do Example 20.18

See Problems 20.91-20.92
Operational Skills

• Balancing oxidation-reduction reactions
• Sketching and labeling a voltaic cell
• Writing the cell reaction from the cell notation
• Calculating the quantity of work from a given amount of cell reactant
• Determining the relative strengths of oxidizing and reducing agents
• Determining the direction of spontaneity from electrode potentials
• Calculating the emf from standard potentials

Operational Skills

• Calculating the free-energy change from electrode potentials
• Calculating the cell emf from free-energy change
• Calculating the equilibrium constant from cell emf
• Calculating the cell emf for nonstandard conditions
• Predicting the half-reactions in an aqueous electrolysis
• Relating the amounts of product and charge in an electrolysis

End of Chapter 20