Chapter 15

Redox Equilibria and Electrochemistry

"It is better to wear out than to rust out."

Bishop Richard Cumberland
1631-1718
Introduction

Life on this planet derives from the photosynthetic process by which plant cells trap and use solar energy. The deceptively simple photosynthetic equation

$$\text{H}_2\text{O} + \text{CO}_2 \xrightarrow{\text{light}} \text{carbohydrates} + \text{O}_2$$

occurs via a complex cascade of biochemical reactions. The critical events are a light-activated transfer of an electron to an acceptor in the chloroplast, a flow of electrons from water through an electron transport chain, and the resulting formation of carbohydrates from carbon dioxide. The key reactions that involve electron transfer are called redox reactions. In evolutionary terms the change from anaerobic life to aerobic (oxygen-using) life was an important step because it allowed a rich energy source to be used. The redox reactions of oxygen with glucose, mediated by the transport proteins myoglobin and hemoglobin, provide an efficient way of generating the energy for life processes.

Most of the energy used by our industrial society comes from the combustion of fossil fuels, such as gas, coal, and oil. Fossil fuels are the end products of millions of years of sun-trapping reaction by plants. The burning of fossil fuels is a redox process by which electrons are transferred from dioxygen to water and carbon dioxide. As you can see, the common thread in the production of useful energy by plant and animal life involves reactions that involve the gain and loss of electrons.

The study of electron transfer processes in natural and synthetic systems has become an extremely important subfield of chemistry and is called electrochemistry. The field of electrochemistry is broadening rapidly as research reveals the incredibly varied part played by redox reactions in such diverse disciplines as neurophysiology, meteorology, and geochemistry. Indeed, it is worth quoting an axiom of electrochemists — "There are only two kinds of reactions: redox and the rest!" In this series of experiments, you have the opportunity to explore the fundamentals of solution electrochemistry. The experiments have been designed such that the basic principles of redox equilibria can be investigated. You may then apply the principles to your own field of endeavor.
Background Chemistry

Chemical reactions that involve the movement of electrons between chemical species are called redox reactions (an abbreviation of reduction-oxidation reaction). Redox reactions can be identified, and the movement of electrons can be followed, by using a sort of formal "bookkeeping" of the number of electrons associated with atoms. This accounting of electrons involves assigning arbitrary oxidation numbers to individual atoms within a chemical species. Redox reactions are reactions in which there are changes in oxidation numbers. Every redox reaction can be divided into two half-reactions: one that involves a gain of electrons and one that involves a loss of electrons. The gain of electrons is called reduction and the loss of electrons is called oxidation.

Consider the following interesting chemical reaction in which a copper coin is dropped into a dilute solution of silver nitrate (AgNO₃). Beautiful, shining needles of metallic silver crystals grow slowly from the copper surface, especially if the solution is not disturbed. The solution also slowly changes from colorless to a pale blue color, indicating that Cu²⁺ ions are being produced. The overall chemical equation is

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

for which the net ionic equation is

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

This reaction is a redox reaction because the oxidation number of copper is changing from 0 to +2 (Cu(s) to Cu²⁺) and that of silver is changing from +1 to 0 (Ag⁺ to Ag(s)). The NO₃⁻ ion remains unchanged during the reaction and is called a spectator ion. The reaction can be divided into two half-reactions:

Reduction: \[ 2\text{Ag}^+ + 2e^- \rightleftharpoons 2\text{Ag(s)} \]

Oxidation: \[ \text{Cu(s)} \rightleftharpoons \text{Cu}^{2+} + 2e^- \]

which add together to give the redox reaction. Redox reactions in which the reactants are observed to react and produce products — i.e., proceed from left to right — are called spontaneous reactions. The reverse reaction,

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

will not occur and is said to be a nonspontaneous reaction. The energy given out in the spontaneous reaction in which the copper coin reduced Ag⁺ to silver crystals is lost as
heat to the solution. The redox reaction will eventually come to equilibrium, and no more heat will be given out.

Redox reactions in which electrons are completely lost by one species and completely accepted by another are very useful because the two half-reactions can often be physically separated. The electrons that are transferred may then be allowed to flow through external wires in a circuit and be made to do useful work. Electrochemistry is the study of redox reactions that either produce or utilize electrical energy (moving electrons and/or ions) in devices called electrochemical cells.

In the redox reaction

\[ \text{Cu}_{(s)} + 2\text{Ag}^+ \rightleftharpoons \text{Cu}^{2+} + 2\text{Ag}_{(s)} \]

the two half-reactions can actually be separated by placing the reactants in different compartments, partitioned by some type of porous medium that prevents mixing, but not ion flow. The compartments, called half-cells, each contain a metal electrode in contact with its own metal ion, as shown in Figure 15.1.

![An Electrochemical Cell Made up of Two Half-Cells](image)

An external connection between the two electrodes completes the circuit, and electrons will flow from the copper electrode through the external wire and meter and into the silver electrode. The copper electrode will dissolve, forming Cu$^{2+}$ ions in solution, and Ag$^{+}$ ions will pick up electrons at the surface of the silver electrode and be deposited as silver atoms. The electrode at which oxidation takes place (the copper electrode) is called the anode, and the electrode at which reduction takes place (the silver electrode) is called the cathode. The combination of the two half-cells is called an electrochemical cell.
In the electrochemical cell under discussion, it is a fact that oxidation,

\[ \text{Cu}_{(s)} \rightleftharpoons \text{Cu}^{2+} + 2e^- \]

occurs at the copper electrode (anode) and that reduction,

\[ 2\text{Ag}^+ + 2e^- \rightleftharpoons 2\text{Ag}_{(s)} \]

occurs at the silver electrode (cathode). The relative tendency of a particular species to give up or accept electrons is manifested as a measurable electrical force, or voltage (potential), between the two electrodes. This force may be considered as being the sum of two potentials called \textit{half-cell potentials} or \textit{single-electrode potentials}.

The tendency of a species to give up or accept electrons can only be compared relative to another species. In order to obtain consistent electrochemical data, it is necessary to compare all single electrodes to a standard reference electrode. The universal reference electrode, chosen by international agreement, is the \textit{standard hydrogen electrode} (SHE), which is shown in the diagram in Figure 15.2.

\[ \begin{align*}
\text{wire} & \rightarrow \text{meter} \\
\text{glass tube} & \\
\text{hydrogen gas at 1 atm pressure} & \\
\text{1M HCl solution} & \\
\text{finely divided Pt}_{(s)} & \\
\text{on a Pt}_{(s)} & \\
\text{electrode} & \\
\end{align*} \]

**Figure 15.2** A Standard Hydrogen Electrode

The half-reaction at the SHE,

\[ 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(g) \]

is arbitrarily written, for the moment, as a reduction.

An arbitrary assignment of \textit{zero} electrode potential (0.00 V) is given to the SHE, and all other electrode potentials are referred to it. It is now customary to report \textit{single} electrode potentials in tables, and it must be remembered that these single half-cell potentials are really measured in combination with a SHE at 0.00 V.
The single-electrode potential value is dependent on the concentration of the ion surrounding the electrode and on the temperature. Standard conditions of 1 M concentration and 298 K (25 °C) have been chosen, and by international agreement all standard electrode potentials are reported as standard reduction potentials (E°). Some examples follow.

\[
\begin{align*}
\text{Al}^{3+} + 3e^- & \rightleftharpoons \text{Al}_{(s)} & E^\circ &= -1.66 \text{ V} \\
\text{Cu}^{2+} + 2e^- & \rightleftharpoons \text{Cu}_{(s)} & E^\circ &= 0.34 \text{ V} \\
2\text{H}^+ + 2e^- & \rightleftharpoons \text{H}_2(\text{g}) & E^\circ &= 0.00 \text{ V} \\
\text{Ag}^+ + e^- & \rightleftharpoons \text{Ag}_{(s)} & E^\circ &= 0.80 \text{ V}
\end{align*}
\]

A useful way of thinking about these E° values is to remember that the more positive the E° value, the more that reaction goes to the right. The E° value for oxidation reactions is obtained simply by changing the sign of the appropriate reduction reaction, e.g.,

\[
\text{Cu}_{(s)} \rightleftharpoons \text{Cu}^{2+} + 2e^- \quad E^\circ = -0.34 \text{ V}
\]

One very important practical consideration in the measurement of cell potentials is that the cell reaction must be carried out under standard conditions. A simple wire connection between the two electrodes would allow the electrons to flow and the redox reaction to go to completion. In the process the concentrations of ions in each half-cell would change dramatically, and the cell voltage would drop to zero, its equilibrium value. Cell potential measurements are, therefore, usually made with instruments that have very high resistance in order to minimize the flow of electrons during the measurement.

Another important consideration is the electrical connection that must be made between the two half-cell solutions before the cell voltage measurement can be made. The connection is called a salt bridge. The salt bridge allows electrical neutrality to be maintained in each half-cell. In the voltage measurement, a few electrons must flow from the anode, through the meter, and into the cathode. Cations are generated in the anode half-cell solution, and to maintain a charge balance, anions flow from the salt bridge. Cations are consumed in the cathode half-cell, and to maintain charge balance, cations flow from the salt bridge. The net result is simply a flow of inert electrolyte from the salt bridge into the cell.

Standard reduction potential values refer, of course, to voltages measured under standard conditions. In the case of nonstandard conditions, the reduction potential value will be different from those reported at 1 M and 25 °C. The quantitative
relationship between cell potential and concentration (and temperature) is called the Nernst law:

\[ E = E^\circ - \frac{RT}{nF} \ln Q \]

where \( E^\circ \) is the standard potential, \( Q \) is the reaction quotient, \( F \) is the Faraday constant, \( n \) is the number of moles of electrons transferred in the cell reaction, \( R \) is the gas constant, and \( T \) is the absolute temperature. The Nernst law may be rewritten, after substituting for all constants and putting \( T = 298 \) K, as

\[ E = E^\circ - \frac{0.0592}{n} \log_{10} Q \]

The Nernst law is valid both for the potentials of half-reactions and for overall redox reactions. For a reaction that has come to equilibrium, the cell voltage must be zero, i.e.,

\[ E = 0 \quad \text{and} \quad Q = K \]

where \( K \) is the equilibrium constant for the reaction. At equilibrium the Nernst law becomes

\[ E = 0 = E^\circ - \frac{0.0592}{n} \log_{10} K \]

and, rearranging,

\[ \log_{10} K = \frac{nE^\circ}{0.0592} \]

The value of the equilibrium constant for a redox reaction (at 25°C) can be calculated using the above relationship.

An electrochemical cell in which a spontaneous redox reaction can occur is called a voltaic cell, or battery. Voltaic cells are useful energy storage devices in which a suitable redox system is packed into an appropriate container. The voltage produced by a voltaic cell is, of course, dependent upon the particular redox reaction used, the concentration of materials, and the design of the package. A battery in use is a device in which chemical energy is converted into flowing electrons in a redox reaction that eventually winds down to an equilibrium state. At equilibrium, the battery is dead and the cell voltage is zero.

An electrochemical cell in which a nonspontaneous redox reaction is made to occur by means of an external power source is called an electrolysis cell. Automobile batteries that are being recharged are examples of electrolysis cells. When a run-down, lead-acid automobile battery is recharged, an outside voltage source pushes the nonspontaneous reaction to completion. Electrolysis cells are used extensively in the
industrial production of a wide variety of useful chemicals such as chlorine, sodium hydroxide, aluminum, and in metal finishing and plating.

Unfortunately, spontaneous electrochemistry is not always a useful process. The corrosion of iron and steel is estimated to cost over 80 billion dollars a year in the United States. We see the results in automobiles and other consumer products, as well as in bridges, buildings, and in storage tanks. Many of the typical results of corrosion are best explained in terms of electrochemical mechanisms. Iron, which shows evidence of corrosion, is often found to have anodic areas at which

\[ \text{Fe}(s) \quad \Rightarrow \quad \text{Fe}^{2+} + 2e^- \]

and cathodic areas at which atmospheric dioxygen is reduced to \( \text{OH}^- \) ions:

\[ \text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \quad \Rightarrow \quad 4\text{OH}^- \]

Iron (II) hydroxide (Fe(OH)\(_2\)) precipitates as an insoluble solid and is subsequently oxidized to a loose, flaky deposit of hydrated iron oxide called rust. The rusting process is spontaneous under a wide variety of conditions. The major factors appear to be the presence of dioxygen, water, microimpurities, and dissimilar metals in contact with each other.
Pre-Laboratory Quiz

1. Give the name of one naturally occurring redox process.

2. What is the definition of oxidation? Reduction?

3. How many electrons are transferred in the following redox reaction:
   \[ \text{Cu}^{2+} + 2\text{Ag}_\text{(s)} \rightleftharpoons \text{Cu}_\text{(s)} + 2\text{Ag}^+ \]

4. Is the redox reaction in Question 3 spontaneous or nonspontaneous?

5. Draw a diagram of the universal reference electrode that has a standard reduction potential of 0.00 V.
6. Which is the best reducing agent, $\text{Al}_3^+$ or $\text{Ag}_3^-$?

7. Write out the Nernst law and explain each symbol.

8. Give a definition of an electrolysis cell.

9. Give the name of one product manufactured by electrolysis.

10. What is the electrolyte in an automobile battery?
Laboratory Experiments

Flowchart of the Experiments

Section A. Redox Reaction Investigations

Section B. A Small-Scale Electrochemical Cell

Section C. An Electrochemical Series from Cell Data

Section D. Electrographic Analysis of Metals

Section E. Nernst's Law and Potentiometric Redox Titrations

Part 1. The Ce$^{4+}$ - Fe$^{2+}$ Titration
Part 2. The Fe$^{2+}$ - Cr$_2$O$_7^{2-}$ Titration

Section F. Lead-Acid Automobile Battery

Requires one three-hour class period to complete
The overall goal in this series of experiments in electrochemistry is to be able to identify, write, balance, and apply common reduction-oxidation (electron transfer) reactions. You should also be able to construct a variety of electrochemical cells, both voltaic and electrolytic, and be able to use standard electrochemical instrumentation and conventions to measure and calculate standard reduction potentials. Finally, you should be able to apply the Nernst law to potentiometric titrations with microelectrode sensing of redox reaction potentials.

**CAUTION:** Solutions of many transition metal ions, e.g., Pb$^{2+}$, Cu$^{2+}$, and Sn$^{2+}$, are toxic. Even though you will be using only very small amounts of these solutions, it is important to exercise caution when using these chemicals. It is also important to observe the hazardous waste regulations in this experiment. All transition metal ion solutions and waste will be collected and disposed of by the instructors and technical staff. Acids and bases, e.g., H$_2$SO$_4$ and NH$_3$, are also corrosive and toxic. Please use these solutions with caution. If you get any of these chemicals on your hands, wash well with cold water and report to your instructor.

### Section A. Redox Reaction Investigations

**Goals:**

1. To study a redox reaction involving copper and zinc species.
2. To describe and characterize some of the electrochemical properties of the reaction.

**Experimental Steps:**

1. Clean your plastic reaction surface.
2. Obtain 4 pieces each of copper metal (Cu$(_6)$) and zinc metal (Zn$(_6)$) from Reagent Central. Use tweezers to transfer the metal pieces to the surface.
3. Drop 2 drops of 1 M CuSO$_4$ solution onto the top of a piece of Zn$(_6)$.
4. Drop 2 drops of 1 M ZnSO$_4$ solution onto the top of a piece of Cu$(_6)$.
5. Study each of the solution-metal interfaces with your hand lens.
   - Describe and record what you see.

**NOTE:** The discoloration of the Zn$(_6)$ is due to the formation of finely divided Cu$(_6)$ at the zinc metal surface. The chemical reaction is a spontaneous reaction in which an electron transfer is taking place, and it is called a reduction-oxidation, or redox, reaction:

\[
\text{Cu}^{2+} + \text{Zn}(_6) \rightarrow \text{Cu}(_6) + \text{Zn}^{2+}
\]

- What half-reactions (one a reduction, the other an oxidation) can be written for this redox reaction?
• How many electrons are being transferred from Zn\(_{\text{(s)}}\) to Cu\(^{2+}\)?
• Which is the reducing agent and which is the oxidizing agent in this titration?
• Is this redox reaction a homogeneous or a heterogeneous reaction?
• Why does the Cu\(_{\text{(s)}}\) produced in the redox reaction look very different from the copper metal piece?
• Do you think that the redox reaction has a large or small equilibrium constant?

6. Design a simple experiment to prove that Cu\(^{2+}\) disappears in the reaction and is replaced by Zn\(^{2+}\) ions in solution.

7. Look at the piece of copper metal with ZnSO\(_4\) on it.

• Describe the surface of the metal.

   NOTE: A good way to do this is to remove the ZnSO\(_4\) drops with a cotton swab and compare the copper surface with another copper piece.

The nonspontaneous reaction, i.e., the redox reaction that did not occur, is

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

• Does this reaction have a small or a large equilibrium constant?

8. Look at the spontaneous reaction again.
• What are the oxidation numbers for Cu\(_{\text{(s)}}\), Zn\(_{\text{(s)}}\), Cu\(^{2+}\), and Zn\(^{2+}\) and for sulfur and oxygen in SO\(_4^{2-}\)?

9. Leave the metal pieces on the plastic surface because you will be using them in the next section.

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**Section B. A Small-Scale Electrochemical Cell**

**Goals:**

(1) To construct a small-scale electrochemical cell using the redox system investigated in Section A. (2) To learn how to use a multimeter to measure electrochemical cell potentials and be able to use the appropriate sign conventions to calculate standard reduction potentials from cell potentials.

**Experimental Steps:**

1. Obtain a multimeter from your instructor. Set up the meter to measure DC voltage. Use the two needle probes (red and black).

   NOTE: If you don’t know how to do this, check with your instructor.

2. Place a small rectangular piece of filter paper (already cut for you) onto the plastic surface.

3. Place a piece of Cu\(_{\text{(s)}}\) and a piece of Zn\(_{\text{(s)}}\) onto the paper about 3 cm apart.

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The diagram below illustrates the locations of the solutions delivered in Steps 4–6.

4. Deliver 2 drops of 1 M CuSO₄ to the paper just at the edge of the copper metal so that the solution soaks under the metal piece.

5. Deliver 2 drops of 1 M ZnSO₄ to the paper so that it soaks under the zinc metal piece.

6. Deliver 2 drops 1 M KNO₃ to the dry paper in between the wet circles.

   NOTE: The KNO₃ solution will spread out and run into the part of the paper wet with CuSO₄ and ZnSO₄.

7. Switch the multimeter on and touch the red probe to the piece of copper metal and the black probe to the piece of zinc metal.
   - Read and record the voltage. Don't forget the sign!

8. Reverse the probes.
   - Record what happens to the sign and switch the meter off.

The voltage (potential) that you have just recorded is the electrochemical cell voltage of a cell, which is made up of two half-cells joined electrically by wires (the probes) and the salt bridge solution (KNO₃). The sign conventions in these types of cell voltage measurements are sometimes confusing and are not easy to understand. The multimeter has two probes: red and black. The red is the positive terminal; the black is the negative terminal. The probes are touched to the electrodes in the cell, and the measured voltage will have a positive sign if the black probe is on the anode and the red probe is on the cathode. If the sign of the measured voltage is negative, then the reverse of the above is true: The black probe is on the cathode, and the red probe is on the anode.

REMEMBER: The anode is the electrode at which oxidation occurs. The cathode is the electrode at which reduction occurs.

The voltage read in Step 7 should be positive. Since the black probe is on Zn(s), this must be the anode.
   - Write the half-reaction occurring at Zn(s).
   - Write the half-reaction occurring at the cathode (Cu(s)).

The standard reduction potential E° for
\[ \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}_{(s)} \]
is 0.34 V (measured against a standard hydrogen electrode). This value can now be used to calculate the standard reduction potential for \[ \text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}_{(s)} \]

At the anode the half-reaction is \[ \text{Zn}_{(s)} \rightleftharpoons \text{Zn}^{2+} + 2e^-, \quad E^o_{\text{ox}} \]
and at the cathode the half-reaction is \[ \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}_{(s)}, \quad E^o_{\text{red}} = 0.34 \text{ V} \]
The sum of these two half-reactions is the cell reaction \[ \text{Cu}^{2+} + \text{Zn}_{(s)} \rightleftharpoons \text{Cu}_{(s)} + \text{Zn}^{2+}, \quad E^o_{\text{cell}} = E^o_{\text{ox}} + E^o_{\text{red}} \]

- Calculate \( E^o_{\text{ox}} \), the standard oxidation potential for \[ \text{Zn}_{(s)} \rightleftharpoons \text{Zn}^{2+} + 2e^- \]
and then reverse the sign to obtain the standard reduction potential for \[ \text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}_{(s)} \]

- You might want to practice your skills by writing the half-reactions for the case of the measured voltage from Step 8.
- Calculate the equilibrium constant for the spontaneous redox reaction \[ \text{Cu}^{2+} + \text{Zn}_{(s)} \rightleftharpoons \text{Cu}_{(s)} + \text{Zn}^{2+} \]
by using the relationship

\[ \log_{10} K = \frac{nE^o_{\text{cell}}}{0.0592} \quad \text{at } 25^\circ\text{C} \]

where \( K \) is the equilibrium constant, \( n \) is the number of electrons transferred in the redox reaction, and \( E^o_{\text{cell}} \) is the standard cell potential.
NOTE: Equilibrium constants for redox reactions cannot be found in the usual reference literature (as can equilibrium constant for acid-base reactions, etc.). Redox reaction equilibrium constants are generally calculated from standard reduction potential data.

Section C. An Electrochemical Series from Cell Data

Goals: (1) To construct a series of electrochemical cells. (2) To obtain cell potentials for the calculation of standard reduction potentials.

Discussion: The standard potential data obtained in this section may then be used to interpret corrosion phenomena, design voltaic and electrolytic cells, and arrange reduction reactions into an electrochemical series.

Experimental Steps: 1. Obtain a 9 cm filter paper and make a cell template similar to the template shown in the diagram below.

2. Write on each sector the atomic symbols of the metals, as shown.
3. Place the cutout paper into the lid of a clean, dry plastic petri dish.
4. Use your tweezers to transfer the appropriate metal pieces (e.g., Ag(s) wire, Cu(s) squares, etc.) to each sector. 
   NOTE: Make sure they are arranged in the order shown.
5. Drop 2 drops of the appropriate metal ion solutions onto the paper at the edge of each metal piece so that each metal is contacting the solution (as in Section B).
6. Drop 1 M KNO₃ salt bridge solution into the middle so that it soaks outwards and contacts all the other wet areas. Try not to use too much!
7. Switch the multimeter to measure DC voltage and start making measurements with the red probe on Ag(s) and the black on Cu(s). Don't forget the sign!
8. Now keep the red probe on Ag(s) and make measurements by moving the black probe around the circle in a clockwise manner.
   - Record voltages and signs.

9. Move the red probe to Cu(s) and continue around with the black probe. When you have finished, switch the meter off.
   NOTE: The measurements made on Mg(s) and Al(s) will be very unstable. Just try to obtain an approximate voltage.
   - Make a table of the cells and their cell voltages in your notebook.
   - Use the principles that you learned in Section B to calculate the standard reduction potentials for each half-cell, given that the $E^\circ$ for
     \[
     \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu(s)}
     \]
     is 0.34 V.
     Note that $E^\circ$ for a half-reaction is not dependent on the coefficients, provided, of course, that the reaction is balanced, i.e., $E^\circ$ for
     \[
     \text{Ag}^{+} + e^- \rightleftharpoons \text{Ag(s)}
     \]
     is the same as $E^\circ$ for
     \[
     2\text{Ag}^{+} + 2e^- \rightleftharpoons 2\text{Ag(s)}
     \]

10. Arrange the standard reduction potentials and corresponding half-reactions in order, starting with the most negative at the top of the table and ending with the most positive at the bottom.
   - Which is the strongest oxidizing agent in the table?
   - Which is the strongest reducing agent in the table?
   The literature value of $E^\circ$ for the half-reaction,
     \[
     \text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe(s)}
     \]
   is −0.44 V.
   - Compare your value for steel.
   - Why are they so different?
   - If you wanted to design a battery from relatively common materials that produced a voltage of about 1 V, which cell reaction would you choose?
   - Why were the measurements on Mg(s) and Al(s) so difficult?

11. Clean up by placing the filter paper and metal pieces in the appropriate waste containers.
Section D. Electrographic Analysis of Metals

Goal: To carry out a chemical analysis of an unknown metal sample by making the sample the anode of an electrolytic cell.

Experimental Steps:
1. Obtain from Reagent Central the following items: a petri dish, a piece of aluminum foil and a piece of filter paper (both already cut for you), a 9 V battery, and leads with clips.
2. Place the foil into the petri dish.
3. Place the filter paper onto the foil and add 2 or 3 drops of 1 M KNO₃ to the paper.
4. Place a clean nickel (the coin!) onto the paper.
5. Clip an electrical lead to the foil and clip the other end of it to the negative terminal of the battery.
6. Clip the other lead to the positive terminal of the battery and then touch the other end to the coin for no longer than 3 seconds.
7. Remove the coin, lift up the paper, and place it on a small piece of microtowel. Drop 1 or 2 drops of dimethylglyoxime reagent onto the paper.
   • Observe the result with your hand lens.

NOTE: You may carry out similar experiments with other kinds of scrap metals. You must be able to carry out a qualitative test for the metal ion produced in the electrolytic cell. A good test for iron is to add 2 drops of H₂O₂ followed by 1 drop of NH₄CN. A red-brown coloration indicates Fe³⁺.
   • Which metal is the cathode and which is the anode in this experiment?
   • What half-reaction is occurring at the coin?
   • Do you think that the electrolysis could be carried out with a standard 1.5 V battery?
   • Whose picture is on a nickel?

Section E. Nernst's Law and Potentiometric Redox Titrations

Goals: (1) To be able to use potentiometric techniques to analyze the progress of redox titrations. (2) To graphically interpret the titration data using Nernst's Law.

Section E. Part 1. The Ce⁴⁺ – Fe²⁺ Titration

Experimental Steps:
1. Clean a 1 x 12 well strip. Shake to remove any water.
2. Using a clean 24-well tray, obtain a small volume of 0.06 M Fe²⁺ solution in one well and, in another well, a small volume of 0.01 M Ce⁴⁺ solution.
3. Use good wash, rinse, fill, and transfer technique to fill large-drop microburets with Fe²⁺ and Ce⁴⁺ solutions.

4. Deliver 1 drop of Fe²⁺ to each well of the 1 x 12 strip.

5. Carry out a serial titration of the Fe²⁺ by adding 1 drop of Ce⁴⁺ to the first well, 2 drops Ce⁴⁺ to the second well, and so on. Stir.

6. Clip a piece of pencil lead into the red spring-clip probe of the multimeter and a piece of copper wire into the black spring-clip probe. Switch the multimeter to read DC voltage.

   NOTE: The spring clips slip onto the needle probes. The pencil lead is the sensing microelectrode, and the copper wire is the reference microelectrode.

7. Hold a spring clip with electrode in each hand and dip the electrodes into the solution in the first well. Record the voltage. Do not touch the electrodes together.

8. Dip the electrodes in each of the wells for the titration.
   • Record the voltages.

9. Switch the meter off.

10. Now add 1 drop of ferroin indicator to each of the wells and stir.
     • Record the number of drops of Ce⁴⁺ required to produce an end point color change.
     • Plot a graph of solution voltage (vertical axis) versus number of drops of Ce⁴⁺. Draw the best smooth line through the points. (The graph is called a potentiometric titration curve.)

   NOTE: The redox reaction occurring during the titration is

   \[ \text{Fe}^2+ + \text{Ce}^4+ \rightleftharpoons \text{Fe}^3+ + \text{Ce}^{3+} \]

   The Ce⁴⁺ (cerium(IV) ion) is the oxidizing agent that oxidizes Fe²⁺ to Fe³⁺. The equilibrium constant for the redox reaction may be calculated from the standard reduction potentials:

   \[ \text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} \quad E^o = 0.77 \text{ V} \]

   \[ \text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+} \quad E^o = 1.44 \text{ V} \]

   At each point in the titration, equilibrium is achieved because the redox reaction is fast — this titration is analogous to the acid-base titrations you studied earlier. The concentrations of the various species are changing during the titration. At the beginning the [Fe²⁺] is 0.06 M, and at the equivalence point, it is very small because it has all reacted with the added Ce⁴⁺. The nonstandard concentrations (they are not 1 M!)
require that the Nernst law be used to see how the voltage of the titration solution changes. The Nernst law is

\[ E = E^\circ - \frac{0.0592}{n} \log_{10} Q \]

where \( E \) is the potential (voltage) at some concentration other than standard, \( E^\circ \) is the standard potential, 0.0592 is a constant (it equals 2.303 RT/F when \( T = 298 \, K \)), \( n \) is the number of electrons transferred, and \( Q \) is the reaction quotient. \( Q \) is simply the concentration of each product to the power of the coefficient of each reactant multiplied together.

For the redox titration reaction in this experiment,

\[ \text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+} \]

The Nernst law is

\[ E = E^\circ - \frac{0.0592}{n} \log_{10} Q \left( \frac{[\text{Fe}^{3+}][\text{Ce}^{3+}]}{[\text{Fe}^{2+}][\text{Ce}^{4+}]} \right) \]

and \( E^\circ = 1.44 \, V \) = 0.77 V for the reaction. As the titration proceeds and the concentrations of \( \text{Fe}^{2+}, \text{Ce}^{4+}, \text{Fe}^{3+}, \) and \( \text{Ce}^{4+} \) change, the \( E \) for the solution is measured (sensed) by the pencil lead (graphite) electrode in reference to the copper wire electrode. The reference electrode potential stays constant during the titration.

### Section E. Part 2. The Fe\(^{2+} - \text{Cr}_2\text{O}_7^{2-}\) Titration

**Experimental Steps:**

A potentiometric redox titration of \( \text{Fe}^{2+} \) with \( \text{Cr}_2\text{O}_7^{2-} \) (dichromate ion) may be carried out in a manner exactly analogous to the \( \text{Ce}^{4+} - \text{Fe}^{2+} \) titration described in Part 1.

1. Serially titrate 1 drop of 0.06 M \( \text{Fe}^{2+} \) with 0.002 M \( \text{K}_2\text{Cr}_2\text{O}_7 \) solution. A suitable indicator is diphenylamine sulfonate. The redox reaction is

\[ \text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightleftharpoons 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O} \]

The \( \text{H}^+ \) is already in the titration solutions, which are made to be 1 M in \( \text{H}_2\text{SO}_4 \).

3. Plot the potentiometric titration curve. Write the Nernst law for this titration.

\[ \text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+} \quad E^\circ = 0.77 \, \text{volt} \]

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E^\circ = 1.33 \, \text{volt} \]
Section F. The Lead-Acid Automobile Battery

**Goals:**
(1) To build a single-cell, lead-acid battery. (2) To charge it to produce the electrode surface conditions necessary for the system to act as a battery.

**Experimental Steps:**
1. Half-fill a well of a 24-well tray with 1 M H₂SO₄ solution.
2. Place 2 small strips of lead metal (Pbₙₜ) into the solution in the well so that they do not touch.
3. Clip electrical leads to the 9 V battery and clip an electrical lead to each strip of lead metal.

   **NOTE:** There will be an immediate vigorous reaction as the H₂SO₄ is electrolyzed. *Do not allow the lead strips to touch!*

   • What will happen if they do touch?
4. Unclip the battery and examine the strips of lead.

   **NOTE:** One of the strips is a clean Pbₙₜ surface; however, the other has a brownish-colored layer of PbO₂ₙₜ on the surface. The initial charging reaction involves the electrolysis of dilute sulfuric acid,

   \[ 2\text{H}_2\text{O}(l) \rightleftharpoons 2\text{H}_2\text{O}(g) + \text{O}_2(g) \]

   and the dioxygen oxidizes the Pbₙₜ surface to PbO₂ₙₜ. Once the electrode surfaces are established, then the overall discharge-charge reaction is

   \[ \text{Pb}_n\text{t} + \text{PbO}_2\text{n}(s) + 2\text{H}_2\text{SO}_4(aq) \xrightarrow{\text{discharge}} \xleftarrow{\text{charge}} 2\text{PbSO}_4\text{n}(s) + 2\text{H}_2\text{O}(l) \]