Electrochemistry and Concentration Effects on Electrode Potentials

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Introduction

You have already studied oxidation-reduction reactions in the previous experiment. You have an understanding of half-reactions and how they contribute to the overall redox reaction. In those experiments, the oxidizing and reducing agents were in the same container. In this experiment, you will see that oxidation-reduction reactions can occur between reactants in separate containers. This happens when electrons are transferred through a wire that connects the two containers. This is the basis of an electrochemical cell.

Before the topic of the electrochemical cell can be explored, you need to understand a few terms. One of the most important is standard reduction potential ($E^{\circ}_{\text{red}}$). Table I located at the end of this experiment has some of the standard reduction potentials needed in this experiment. The standard reduction potential is a quantitative measure of a substance’s tendency to accept electrons under standard conditions (1 atm of gases and 1 M concentration) and is measured in volts. The more positive the reduction potential, the greater the tendency for reduction to occur. For the oxidation half-reaction, the standard oxidation potential ($E^{\circ}_{\text{oxid}}$) for the half-reaction has the same numerical value as the standard reduction potential but the opposite sign. For example, aluminum ion has a standard reduction potential value of –1.65 V (in going to aluminum metal). The standard oxidation potential for aluminum metal is then +1.65 V. The standard cell potential ($E^{\circ}_{\text{cell}}$) is the sum of the standard oxidation and reduction potentials.

To construct a nickel-copper electrochemical cell, for example, you would start by placing a strip of nickel metal into a nickel(II) salt solution. A strip of copper metal is placed into a copper(II) salt solution in a different container. A wire is connected between the nickel strip and the copper strip. Electrons will pass through this wire during the redox reaction. The $E^{\circ}_{\text{red}}$ value for nickel ion is –0.26 V and +0.34 V for copper ion. This means that the Cu$^{2+}$ ion has a greater tendency to accept electrons than the Ni$^{2+}$ ion. Therefore, electrons will pass through the wire from the nickel strip to the copper strip. However, this can only happen if a second connection is provided to complete the electrical circuit. This second connection is called a salt bridge and is placed in both solutions of the two containers. You now have an electrochemical cell. The electrochemical cell is a system that utilizes a spontaneous oxidation-reduction reaction to pump electrons through an electrical circuit. In this example, the nickel half-cell involves nickel metal being oxidized and the copper half-cell involves copper(II) ion being reduced. The metal strips are called electrodes. The oxidation electrode is called the anode and the reduction electrode is the cathode. The cell potential can be measured by connecting a voltmeter between the half-cells. This is what you will do and you can use Figure 1 as a reference to check your set up (as well as asking your instructor).

To predict the observed voltage for this oxidation-reduction reaction, simply add the two half-cell potentials together. Since the copper(II) ion is being reduced in the reaction, its half-reaction
is the reduction, and the nickel half–cell will be an oxidation. The copper electrode voltage will
remain a reduction and the sign of $E^\circ_{\text{red}}$ of Ni$^{2+}$ will be changed to give $E^\circ_{\text{ox}}$

$$
\begin{align*}
\text{Cu}^{2+} + 2e^- & \rightleftharpoons \text{Cu} \quad E^\circ_{\text{red}} = +0.34 \text{ V} \\
\text{Ni} & \rightleftharpoons \text{Ni}^{2+} + 2e^- \quad E^\circ_{\text{ox}} = +0.26 \text{ V}
\end{align*}
$$

**cell reaction**  \(\text{Ni} + \text{Cu}^{2+} \rightleftharpoons \text{Ni}^{2+} + \text{Cu} \quad E^\circ_{\text{cell}} = +0.60 \text{ V}\)

The reading on your voltmeter should be close to +0.60 V. You are not working under standard
conditions, but the ratio of the concentrations is still 1:1. The Nernst equation shows that you
will still measure the standard cell potential. Any differences in the readings would come from
other sources such as resistance in the salt bridge and the concentrations of the two cells not
being exactly the same, for whatever reason.

The second half of this experiment deals with the quantitative effect concentration changes have
on cell voltage as shown by the Nernst equation. In a redox equation

$$
aA(aq) + bB(aq) \rightleftharpoons cC(aq) + dD(aq) \quad (1)
$$

the cell voltage is described by the Nernst equation

$$
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \left( \frac{[C]^c[D]^d}{[A]^a[B]^b} \right) \quad (2)
$$

where $E^\circ_{\text{cell}}$ is the **standard** cell voltage, $E_{\text{cell}}$ is the non-standard voltage and $n$ represents
the total number of electrons transferred in the **balanced** cell reaction. Looking at this equation, you
see that increasing the concentration of the products lowers the voltage of the cell since the log
term will be larger making the value of $E_{\text{cell}}$ smaller.

Equation (2) represents the Nernst equation for the entire cell. It can also be written for a half-
cell. For example, to determine how the concentration of the silver ion affects the total cell
potential, you can first determine how the concentration of the silver ion affects the half-cell
reduction potential. The reaction for the half-cell reduction occurring in today’s experiment is:

$$
\text{Ag}^+ + e^- \rightleftharpoons \text{Ag} \quad (3)
$$

The Nernst equation for reaction (3) is:

$$
E = E^\circ - \frac{0.0591}{1} \log \frac{1}{[\text{Ag}^+]} \quad (4)
$$

The electrochemical cell you are working with will be made up of two half-cells but in this case
one is a saturated calomel electrode while the other is a silver metal electrode. The standard
reduction potential of the calomel electrode is +0.243 V. The cell potential is the sum of the two electrode potentials; one potential contributed by the calomel electrode and one contributed by the silver/silver ion electrode.

You will take three different solutions with a different concentration of silver ion and measure the cell potential by placing both the calomel electrode and the silver electrode into each solution. This will give you three different cell potentials ($E_{cell}$). $E$ will be determined by reference to the calomel standard reduction potential. Knowing the concentration of the silver ion and the value of $n$, you can then find the average standard reduction potential ($E^0$) for the half-reaction by using equation (4).

To find $E$, use the value read off of the potentiometer and the standard reduction potential for the calomel electrode. The easiest way to do this is to think of a number line with both positive and negative numbers. For example, let’s say you read +0.987 V off of the potentiometer when you place the electrodes in the 0.010 M silver ion solution. The value +0.987 V is the distance on the number line (in the positive direction) between the half-cell potential of the calomel electrode and the half-cell potential of the silver electrode. If the difference between the potential values for the calomel electrode and the silver electrode is +0.987 V (the positive sign means to the right of the calomel electrode on the number line), then the reduction potential value for the silver electrode ($E$) is +1.230 V (0.243 + 0.987). Using equation (4), you find your standard reduction potential ($E^0$) for silver to be 1.348 V. If you have a negative cell potential reading, the distance is now to the left of the calomel electrode on the number line. If, for example, the potentiometer reading is –0.439 V, the Ag electrode potential is –0.196 V (–0.439 + 0.243).

The third part of this experiment has you making a saturated AgCl solution in 0.100 M Cl–. You will determine the concentration of the silver ion in this solution using your average $E^0$ value and the measured $E$ (with respect to calomel) with equation (4) and the $K_{sp}$ of AgCl.

Procedure

Part I:

Construct a salt-bridge by completely filling a U-tube with 0.5 M KNO₃ solution and plugging both ends with a cotton ball. Make sure the cotton balls are soaked with the KNO₃ solution.

Place about 25 mL each of 0.10 M zinc(II) sulfate solution, 0.10 M copper(II) sulfate solution, and 0.10 M iron(II) ammonium sulfate solution in 3 separate 50-mL beakers. Label the beakers 'zinc', 'copper', and 'iron'. Clean strips of zinc and copper and an iron nail with steel wool.

**Constructing a Zinc–Copper Electrochemical Cell**

Referring to Figure 1, alligator clip the copper strip to one voltmeter terminal and alligator clip the zinc strip to the other voltmeter terminal. Dip the copper strip in the beaker containing the copper solution and the zinc strip in the beaker containing the zinc solution at the same time. Invert the salt-bridge into both beakers. Note the voltage and remove the salt-bridge immediately. If you have a negative reading on your voltmeter, reverse the connections to the
metal strips and dip salt-bridge again. The metal attached to the black lead is the anode. Record the voltage and identify the anode and cathode of the cell.

Constructing an Iron–Copper Electrochemical Cell

Rinse both ends of the salt-bridge with a little 0.5 M KNO₃ solution. Connect the iron nail to one terminal of the voltmeter as before. Keep the copper strip from Part I attached to the other lead. Dip the metal strips into the proper solution and connect them with the salt-bridge as before. Record a positive reading and identify the anode and cathode.

Constructing an Iron–Zinc Electrochemical Cell

Rinse the ends of the salt-bridge. Keeping the iron nail attached to the voltmeter, replace the copper strip from above with the zinc strip. Dip the metal strips into the corresponding solution and connect them with the salt-bridge as before. Record a positive reading and identify the anode and cathode.

Part II

Be aware that Ag⁺ solutions will stain your skin for several days, so handle the following solutions with care.

1. Place about 25 mL of 0.0010 M Ag⁺ solution in a 50-mL beaker.

2. Attach a calomel electrode to the black lead on the voltmeter and carefully rinse the salt bridge at the tip. Attach a clean (steel wool) strip of silver metal to the red wire of the voltmeter. Dip both electrodes into the Ag⁺ solution, taking care not to have the two electrodes touch. Take the reading 3–5 seconds after placing the electrodes in the solution. The cell potential of the first solution should be between 0.3 and 0.5 V. If it is not see the instructor; you might need to get a new calomel electrode. Rinse the electrodes after reading the cell voltage and repeat this procedure with 0.010 M Ag⁺ and 0.10 M Ag⁺. The reading should increase, but not go above 0.8 V.

Part III

1. Prepare a saturated AgCl solution by adding one drop of 0.10 M Ag⁺ to 25 mL of 0.10 M HCl. Insert the electrodes into this solution and measure the potential as before.

Questions

1. a. Calculate the standard cell potential of a cell constructed from Mg²⁺/Mg and Ni²⁺/Ni (Table I). Which is the anode and which is the cathode?

   b. Using the Nernst Equation, what would be the potential of a cell with \([\text{Ni}^{2+}] = [\text{Mg}^{2+}] = 0.10 \text{ M}\)?

Data Treatment and Discussion
For each electrochemical cell, calculate the standard cell potential in the same manner shown in the introduction section of this laboratory experiment. Include the half-reactions and electrode potential values. Compare the calculated cell potentials to the measured voltages of your electrochemical cells. Describe the possible sources of error.

Using your data from the first three Ag/Ag\(^+\) cell potential readings, determine the average standard reduction potential (E\(^o\)) for silver ion.

Use your average value of E\(^o\) to determine [Ag\(^+\)] in the fourth solution.

Knowing that [Cl\(^-\)] is 0.10 M in the fourth cell, calculate K\(_{sp}\) of AgCl. Compare with a published value of K\(_{sp}\) (give the reference). Describe any source of error.

**Conclusion**

List the cell voltages, average E\(^o\) of Ag/Ag\(^+\), the [Ag\(^+\)] in saturated AgCl, and your K\(_{sp}\) of AgCl.

**Figure 1. Diagram of an Electrochemical Cell**
Table I. Standard Reduction Potentials for Selected Metals

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>$E^\circ_{\text{red}(V)}$</th>
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<tbody>
<tr>
<td>$\text{Mg}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Mg}$</td>
<td>-2.37</td>
</tr>
<tr>
<td>$\text{Al}^{3+} + 3 \text{e}^- \rightleftharpoons \text{Al}$</td>
<td>-1.65</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Zn}$</td>
<td>-0.76</td>
</tr>
<tr>
<td>$\text{Fe}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Fe}$</td>
<td>-0.44</td>
</tr>
<tr>
<td>$\text{Ni}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Ni}$</td>
<td>-0.26</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Cu}$</td>
<td>+0.34</td>
</tr>
<tr>
<td>$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$</td>
<td>+0.80</td>
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