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Electrochemical Cells
AP Chemistry Laboratory #21

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Introduction

Oxidation–reduction reactions form a major class of chemical reactions. From the reactions of oxygen with sugars, fats, and proteins that provide energy for life to the corrosion of metals, many important reactions involve the processes of oxidation and reduction. In this three-part lab, these reactions are studied by constructing various electrochemical cells and measuring the voltage generated. From these measurements, a reduction series is generated, the concentration of copper ions in solution determined, and the K_{sp} of silver chloride calculated.

Concepts

- Half-cell reaction
- Nernst equation
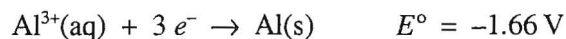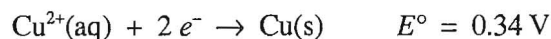- Standard reduction potential
- Spontaneous reaction

Background

An electrochemical cell results when an oxidation reaction and a reduction reaction occur, and their resulting electron transfer between the two processes occurs through an external wire. The oxidation and reduction reactions are physically separated from each other and are called _half-cell reactions_. A half-cell can be prepared from almost any metal in contact with a solution of its ions. Since each element has its own electron configuration, each element develops a different electrical potential, and different combinations of oxidation and reduction half-cells result in different voltages for the completed electrochemical cell.

The _standard reduction potential_ is the voltage that a half-cell, under standard conditions (1 M, 1 atm, 25 °C), develops when it is combined with the standard hydrogen electrode, that is arbitrarily assigned a potential of zero volts. A chart of reduction half-cell reactions, arranged in order of decreasing standard reduction potential, shows the relative ease of reduction of each substance listed. The more positive the reduction potential, the easier the reduction. A spontaneous cell (a battery) can be constructed if two half-cells are connected internally using a salt bridge, and externally using a metallic connector. In an electrochemical cell, the reaction listed in the standard reduction potential chart with the more positive voltage occurs as a reduction, and the reaction listed with the less positive voltage reverses and occurs as an oxidation reaction. The cell voltage

can be found by adding the voltages listed in the table, with the value of the voltage for the oxidation reaction becoming the negative of its reduction reaction voltage.

As an example, consider a cell made up of copper and aluminum half-cells.

$$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s) \qquad E^° = 0.34\,V$$

$$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s) \qquad E^° = -1.66\,V$$

The copper reaction has the more positive potential and remains a reduction reaction. The aluminum reaction with the less positive (more negative) potential is reversed and becomes an oxidation reaction. Its potential is now an oxidation potential:

$$Al(s) \rightarrow Al^{3+}(aq) + 3\,e^- \qquad E^° = +1.66\,V$$
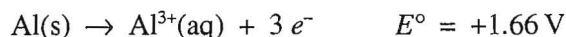
The reduction potential and the oxidation potential are added to find the cell voltage:

$$3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq)$$
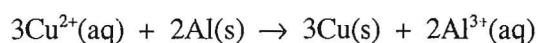
$$E^°_{cell} = E^°_{reduction} + E^°_{oxidation}$$

$$E^°_{cell} = 0.34\,V + 1.66\,V = 2.00\,V$$

A positive value for $E^°_{cell}$ indicates the oxidation–reduction reaction, as written, is *spontaneous*.

A cell representation such as the following: $Zn(s)\,|\,Zn^{2+}(1.0\,M)\,||\,Cu^{2+}(0.0010\,M)\,|\,Cu(s)$ means that a cell is constructed of zinc metal dipping into a 1.0 M solution of Zn^{2+}. The symbol "|" refers to a phase boundary. The symbol "||" indicates a salt bridge between the zinc ion solution and the copper ion solution. The second half-cell is copper metal dipping into a 0.0010 M solution of copper ions. The anode is on the left (where oxidation occurs) and the cathode is on the right (where reduction occurs).

In this laboratory a "standard" table of electrode potentials is constructed. A value of 0.00 volts is assigned to the electrode made from zinc metal in a 1.0 M solution of zinc ions. The voltage values should correlate with those found in published tables, differing only by the value of $E^°$ for the standard zinc electrode. Published standard values are measured in solutions that have very small electrical resistance. The resistance of the experimental cell will probably cause a lowering of measured values from the ideal values.

The table of standard potentials assumes that all ion concentrations are 1.0 M, gas pressures are 1 atm, and temperature is 25 °C. Calculations of potentials under nonstandard conditions can be made using the *Nernst equation:*

$$E = E^° - \frac{RT}{nF}\,\ln Q$$

where E = the measured cell potential, $E^°$ = the standard cell potential, R is the gas constant (8.314 J/mol·K), T is the temperature (K), n = the number of moles of electrons transferred as shown by the oxidation–reduction equation, and F is the Faraday constant (9.65×10^4 C/mol). Q is the reaction quotient: the actual concentrations of products and reactants substituted into the equilibrium constant expression.

Using base 10 or common logarithms the expression can be written:

$$E = E° - \frac{2.303\,R\,T}{n\,F}\,\log Q$$

Substituting for the constants 2.303, R, and F, and using a temperature of 25 °C (298K) the expression can be simplified to:

$$E = E° - \frac{0.0592V}{n}\,\log Q$$

A measurement of the cell potential, E, under nonstandard conditions, can be used to calculate the value of Q, which can then be used to determine unknown concentrations of ions actually present in a solution.

Experiment Overview

The purpose of Part 1 of this laboratory is to construct a table listing the reduction potentials of a series of metal ions, in order of ease of reduction. The series of microscale half-cells is constructed by placing a piece of metal into a 1.0 M solution of its ions for each metal in the series. The metals chosen are copper, iron, lead, magnesium, silver, and zinc. The half-cells are connected by a salt bridge constructed of a strip of filter paper soaked in a solution of potassium nitrate. The zinc half-cell is chosen as the reference standard, and all potentials are measured with respect to the zinc electrode.

In Part 2, the Nernst equation is applied to the voltage measurement of a cell with nonstandard copper ion concentration. A solution of 0.0010 M Cu^{2+} is prepared, and the voltage of the cell: $Zn(s)\,|\,Zn^{2+}(1.0\ M)\,\|\,Cu^{2+}(0.0010\ M)\,|\,Cu(s)$ is measured. The measured voltage is compared to that calculated from the Nernst equation. In the final section, the solubility product constant of silver chloride, AgCl, is determined from the Nernst equation and the voltage of a cell in which the zinc half-cell is connected to a solution containing a trace of Ag^+ ions in a 1.0 M solution of sodium chloride, NaCl.

Pre-Lab Questions
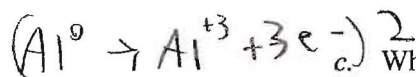
The following data were measured using a nickel electrode as the reference standard:

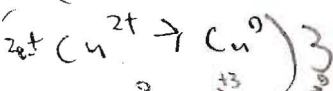|	**Potential, volts**
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$	+0.62
$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s)$	+0.00
$Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$	−0.15
$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	−1.38

1. Which ion is most easily reduced?
   Copper is most easily reduced

2. Which metal is most easily oxidized?
   Aluminum is most easily oxidized

3. The copper and aluminum electrodes are connected to form a battery.

   a. Which is the anode? Aluminum

   b. Which is oxidized? Copper

$((Al^0 \rightarrow Al^{+3} + 3e^-) \, 2$

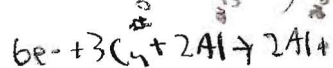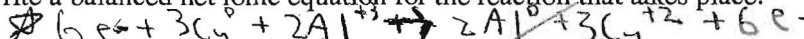$2^+ (Cu^{2+} \rightarrow Cu^0) \, 3$

$6e^- + 3Cu + 2Al \rightarrow 2Al + 3Cu$

c. What will be the battery voltage? $-1.38 + .62 = -0.76v$

d. Write a balanced net ionic equation for the reaction that takes place.

$6e^- + 3Cu^0 + 2Al^{+3} \rightarrow 2Al^0 + 3Cu^{+2} + 6e^-$

4. A solution is prepared in which a trace or small amount of Fe^{2+} is added to a much larger amount of solution in which the $[OH^-]$ is 1.0×10^{-2} M. Some $Fe(OH)_2$ precipitates. The value of K_{sp} for $Fe(OH)_2 = 8.0 \times 10^{-10}$.

a. Assuming that the hydroxide ion concentration is 1.0×10^{-2} M, calculate the concentration of Fe^{2+} ions in the solution.

b. A battery is prepared using the above solution with an iron wire dipping into it as one half-cell. The other half-cell is the standard nickel electrode. Write the balanced net ionic equation for the cell reaction.

c. Use the Nernst equation to calculate the potential of the above cell.

Materials

Chemicals

Cupric nitrate solution [Copper(II) nitrate], $Cu(NO_3)_2$, 1.0 M, 3 mL   Copper foil, Cu

Ferric nitrate solution [Iron(III) nitrate], $Fe(NO_3)_3$, 1.0 M, 2 mL   Iron nail, Fe

Lead nitrate solution [Lead(II) nitrate], $Pb(NO_3)_2$, 1.0 M, 2 mL   Lead foil, Pb

Magnesium nitrate solution, $Mg(NO_3)_2$, 1.0 M, 2 mL   Magnesium ribbon, Mg

Silver nitrate solution, $AgNO_3$, 1.0 M, 2 mL   Silver foil, Ag

Zinc nitrate solution, $Zn(NO_3)_2$, 1.0 M, 2 mL   Zinc strip, Zn

Sodium chloride solution, NaCl, 1.0 M, 10 mL   Potassium nitrate solution, KNO_3, 1.0 M, 10 mL

Equipment

Reaction plate, 24-well   Beral-type pipets, graduated, 10

Graduated cylinder, 10-mL   Filter paper

Wires and alligator clips   Voltmeter

Test tubes, 13 × 150 mm, 3   Beaker, 50-mL

Steel wool or sandpaper

Safety Precautions

Silver nitrate solution is toxic by ingestion and irritating to body tissue. It also stains skin and clothing. Lead nitrate solution is toxic by ingestion and inhalation; irritating to eyes, skin, and mucous membranes. Zinc nitrate solution is slightly toxic by ingestion; it is corrosive to body tissue. Cupric nitrate solution is slightly toxic by ingestion and irritating to skin, eyes, and mucous membranes. Ferric nitrate solution is corrosive to body tissue. Magnesium nitrate solution is a body tissue irritant. Wear chemical splash goggles and chemical-resistant gloves and apron. Wash hands thoroughly with soap and water before leaving the laboratory.

Procedure

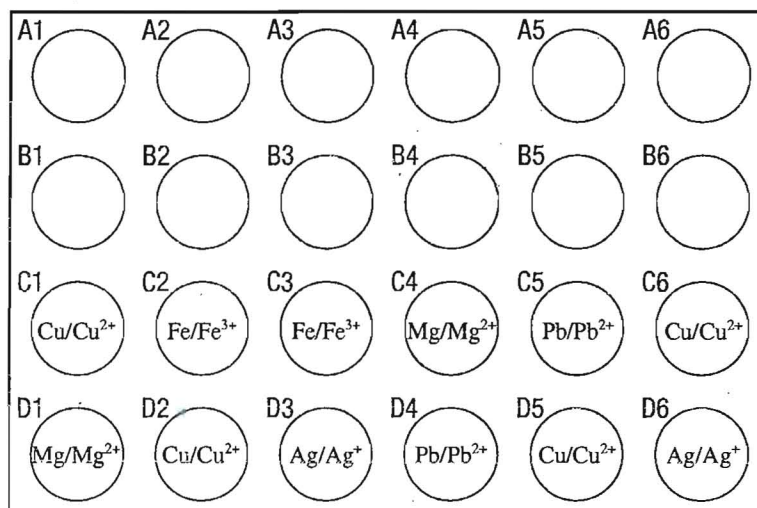### *Part 1. Determine Reduction Potentials*

1. Prepare a test cell to measure the voltage of the copper and zinc half-cells. Using a graduated Beral-type pipet, put approximately 2 mL of 1.0 M $Zn(NO_3)_2$ solution in one of the center wells of a 24-well plate. With a new pipet, put approximately 2 mL of 1.0 M $Cu(NO_3)_2$ in an adjacent well.

2. Polish small strips of zinc and copper metal with sandpaper or steel wool, and place each metal in the appropriate well containing the solution of its ions.

3. Take a small strip of filter paper that has been soaked in KNO_3 solution, and drape it across the wells so that one end dips in the solution in each well. This acts as the salt bridge. Use a fresh strip of paper for each measurement in the procedure.

4. Use a voltmeter to measure the potential difference between the two half-cells. Connect the negative terminal of the voltmeter to the zinc electrode. Use the most sensitive scale that is practical. Make note as to which electrode is the anode and which is the cathode. When the voltmeter reads a positive voltage, the electrode connected to the positive terminal is the cathode and is undergoing reduction, while oxidation is occurring at the electrode connected to the negative (or common) terminal, the anode.

5. Prepare half-cells in other wells of the 24-well plates. Make a diagram of the order of the solutions in the wells. The other four solutions are 1.0 M $Fe(NO_3)_3$, 1.0 M $Pb(NO_3)_2$, 1.0 M $Mg(NO_3)_2$, and 1.0 M $AgNO_3$. An example is shown below.
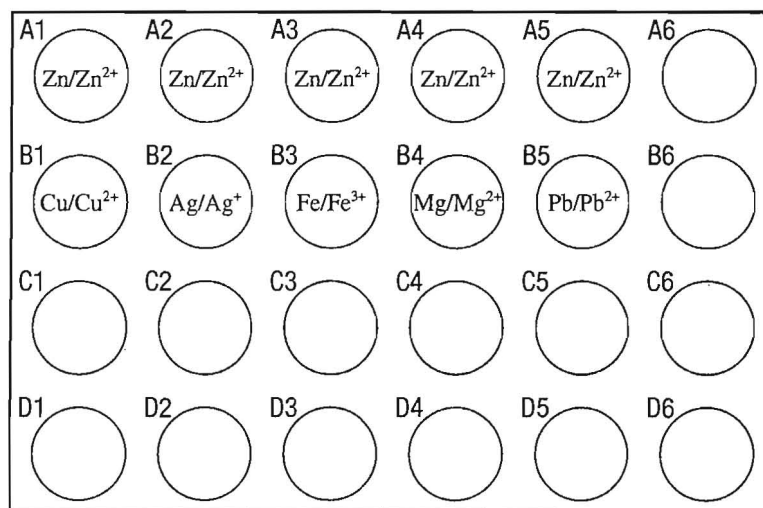
6. Use a new pipet to put approximately 2 mL of each 1.0 M solution into their designated wells.

7. Polish the metals with sandpaper or steel wool so that they are shiny, and insert them into the well that contains the ion of the same metal.

8. Use fresh strips of filter paper soaked in 1.0 M potassium nitrate as salt bridges. The electrodes to be tested are:

$$Ag\,|\,Ag^+ \qquad Mg\,|\,Mg^{2+}$$
$$Cu\,|\,Cu^{2+} \qquad Pb\,|\,Pb^{2+}$$
$$Fe\,|\,Fe^{3+} \qquad Zn\,|\,Zn^{2+}$$
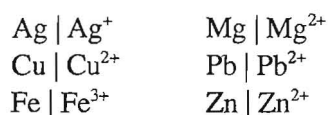
9. Designate the zinc electrode as the standard electrode. Measure the potential difference between the zinc electrode and each of the other electrodes. Note which terminal is the anode and which is the cathode in each case. Record the data in the Part 1 Data Table.

10. Measure the potential difference between at least six combinations of the various electrodes. Record your data, including the equation for each cell reaction, in the second Part 1 Data Table. An example of six combinations set up in the 24-well plate is shown below.

A1	A2	A3	A4	A5	A6
B1	B2	B3	B4	B5	B6
C1 Cu/Cu^{2+}	C2 Fe/Fe^{3+}	C3 Fe/Fe^{3+}	C4 Mg/Mg^{2+}	C5 Pb/Pb^{2+}	C6 Cu/Cu^{2+}
D1 Mg/Mg^{2+}	D2 Cu/Cu^{2+}	D3 Ag/Ag^+	D4 Pb/Pb^{2+}	D5 Cu/Cu^{2+}	D6 Ag/Ag^+

Part 2. Change Ion Concentration

Prepare a 0.0010 M $Cu(NO_3)_2$ solution as follows (steps 1–3).

1. Dilute the 1.0 M $Cu(NO_3)_2$ to 0.0010 M. Begin by counting 18 drops of distilled water into a small test tube, and add 2 drops of the 1.0 M $Cu(NO_3)_2$ solution.

2. Mix well by pouring back and forth from one test tube to another. This solution is now 0.10 M.

3. Repeat this dilution process two more times to give a final concentration of 0.0010 M.

4. Pour some of this 0.0010 M $Cu(NO_3)_2$ solution into one of the wells in the well plate. Add a piece of polished copper foil and measure the voltage against the standard zinc electrode.

A representation of the cell is:

$$Zn(s) \mid Zn^{2+}(1.0\ M) \parallel Cu^{2+}(0.0010\ M) \mid Cu(s)$$

Record the data in the Part 2 Data Table.

Part 3. Solubility Product of AgCl

1. Pour 10 mL of 1.0 M NaCl solution into a 50-mL beaker.

2. Add one drop of 1.0 M $AgNO_3$ to the NaCl solution and stir well. Almost all of the silver ions will combine with chloride ions to precipitate AgCl. Since there is such a large excess of Cl^- ions, it can be assumed that the concentration of Cl^- is still 1.0 M. The concentration of Ag^+, which is limited by the K_{sp} of AgCl, will be very small.

3. Pour some of the solution into one of the wells in the well plate and add a silver metal electrode. Measure the potential difference between this half-cell and the zinc half-cell.

A representation of the cell is:

$$Zn(s) \mid Zn^{2+}(1.0\ M) \parallel Ag^+(unknown\ M) \mid Ag(s)$$

4. Record the voltage in the Part 3 Data Table.

Part 1. Data Tables

(Ch.2) B Battery notes
Podcasts

Voltage of each half-cell versus the zinc electrode

	Voltage	Anode	Cathode
Zn versus Ag	1.15 V	Zinc	Ag
Zn versus Cu	.54		Cu
Zn versus Fe	.93		Fe
Zn versus Mg	.23 V		Mg
Zn versus Pb	.08		Pb

Predicted and Measured Cell Potentials

Anode	Cathode	Equation for the Cell Reaction	Predicted Potential from Experimental Data	Measured Potential
Fe^0	Cu^{+2}	$6e^- + 3Cu + 2Fe \rightarrow 3Cu + 2Fe + 6e^-$	.20 V	.09
Cu^0	Ag^+	$2e^- + Cu^0 + 2Ag \rightarrow Cu^{+2} + 2Ag + 2e^-$	.40 V	.34 V
Pb^0	Ag^+	$2e^- + Pb + 2Ag \rightarrow Pb^{+2} + 2Ag + 2e$	.75 V	.83 V
Fe^0	Pb^{+2}	$6e + 3Pb + 2Fe^{+3} \rightarrow 3Pb^{+2} + 2Fe + 6e$	.70	.76
Pb^0	Cu^{+2}	$2e + Cu^0 + Pb^{+2} \rightarrow Cu^{+2} + Pb^0 + 2e$	.40 V	.43 V
Fe^0	Ag^+	$3e + 3Ag^0 + Fe^{+3} \rightarrow 3Ag^0 + Fe^0 + 3e$	.40 V	.41 V

Part 2. Data Table

	Voltage	Anode	Cathode
$Zn(s) | Zn^{2+}(1.0 M) || Cu^{2+}(0.0010 M) | Cu(s)$		Zn^{+2}	Cu^{+2}

Equation for Cell Reaction	Predicted Potential	Measured Potential
$Zn + Cu + Zn^{2+} \rightarrow Cu^{+2} + Zn^0 + 2e|$		

Part 3. Data Table

	Voltage	Anode	Cathode
$Zn(s) | Zn^{2+}(1.0 M) || Ag^+(unknown M) | Ag(s)$			

Equation for Cell Reaction	Calculated [Ag⁺]	Calculated K_{sp} AgCl	Reported K_{sp} AgCl

Calculations *(Show all work on a separate sheet of paper.)*

Part 1

1. Write reduction equations for each metal ion, arranging the equations in decreasing order of measured potential in the table below. Include zinc in the table, using 0.00 volts as the potential of the $Zn | Zn^{2+}$ half-cell. Record the accepted standard potentials using the hydrogen electrode as standard, and calculate the difference between the two standard values.

Reduction Equations for Each Ion Arranged in Decreasing Order of Potential:

①   ②

Reduction Equation	Electrode Potential using Zinc as the Standard, $E°_{Zn}$	Accepted Electrode Potential using Hydrogen as Standard, $E°$	① - ② $E°_{Zn} - E°$
$Ag^0 \rightarrow Ag^{+1} + 1e-$	$1.15 V$	$10.8 + 0.76 = 1.56$	$-0.41 V$
$Fe^{+2} \rightarrow Fe^{+3} + 1e-$	$0.93 V$	$-0.44 + 0.76 = 0.32$	$0.61 V$
$Cu^0 \rightarrow Cu^{+2} + 2e-$	$0.53 V$	$0.34 + 0.76 = 1.1$	$-0.57 V$
$Mg^0 \rightarrow Mg^{+2} + 2e-$	$0.23 V$	$-2.37 + 0.76 = -1.61$	$-1.38 V$
$Pb^0 \rightarrow Pb^{+2} + 2e-$	$0.08 V$	$-0.13 + 0.76 = 0.63$	$-0.55 V$

2. Use the electrode potentials from the above table to predict the voltages of the six half-cell combinations selected in Part 1, step 10. Record this value and which metal is the cathode and which is the anode in the second Part 1 Data Table for each combination. Compare the predicted and measured potentials.

Part 2

Write a balanced net ionic equation for the reaction occurring in the cell in Part 2. Record this equation in the Part 2 Data Table. Use the Nernst equation to calculate what the expected voltage should be. Record this value in the Part 2 Data Table. Compare this value to the measured voltage.

Part 3

1. Write a balanced net ionic equation for the reaction occurring in the cell. Use the Nernst equation to calculate the concentration of the Ag^+ ion. Record this value in the Part 3 Data Table.

2. Calculate the value of the solubility product of AgCl. Compare the calculated value to a reported value. Record this value in the Part 3 Data Table.

Post-Lab Questions

1. What is an electrode potential?
   The voltage a battery can create

2. Did the ranking of reduction equations agree with that in a published chart of $E°$ values?
   No

3. How should the values found using the zinc electrode as a standard compare with those in the $E°$ table that are based on the standard hydrogen electrode? Did they?
   They didn't because Hydrogen has a different voltage than Zinc.

4. What factors can cause a difference between experimental and reported values?
   (Voltage set to wrong setting) Machine errors, human errors (can't keep salt bridges from touching the leads

5. What does a negative value for a standard potential indicate?
   It is taking energy in.

6. How did the change in concentration of the copper ions in Part 2 affect the cell potential? Is this change in agreement (qualitatively) with that which would be predicted by LeChâtelier's Principle? Did the calculated and measured values agree? They didn't agree, this is most likely because the salt bridges kept touching the leads which caused us to get the wrong data.

7. Explain how the AgCl solubility product was determined.