

Experiment 2 (see <http://murov.info/chemexpts.htm> for additional experiments)

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# REDOX REACTIONS

## Learning Objectives

Upon completion of this experiment, students will have experienced:

1. The application of reduction potentials for the prediction of redox reactions.
2. The observation of several commonly encountered oxidation-reduction reactions.

## Text Topics

Balancing of oxidation-reduction reactions, reduction potentials, half reactions.

## Notes to Students and Instructor

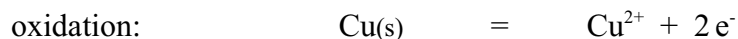
It is important that students prepare for this experiment by determining electrochemical potentials for each reaction that will be tested. For those reactions that are predicted to be spontaneous, predictions of expected observations should be made. The lab manipulations of this experiment should only consume about 1 hour.

## Discussion

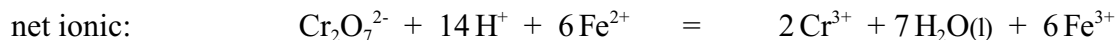
Rusting, bleaching, electroplating, photosynthesizing and burning: what do these chemical changes have in common? They are all examples of processes that involve oxidation-reduction reactions. Electron transfer is the characteristic feature that each of the examples has in common. Identifying oxidation-reduction or redox reactions is a relatively straightforward process. If any of the reactants changes oxidation number during the reaction, the reaction is a redox reaction. As oxidation is a loss of electrons; the element that undergoes an increase in oxidation number (e.g., 2 to 3, 0 to 1, -2 to 0) is oxidized. Reduction is characterized by a decrease in oxidation number (e.g., 2 to 1, 2 to 0, 0 to -1). In some cases, redox is detectable by quick inspection. **If either a reactant or product is in elemental form, the reaction is of necessity a redox reaction.** The only way an element can react or be formed is with a transfer of electrons.

A special class of redox reactions, called single replacement reactions are sometimes used to develop an activity list for metals. The list represents the relative ease of oxidation of a selected group of metals. Today's experiment will utilize a more quantitative method for ranking activity.

Redox reactions can be considered to result from the coupling of an oxidation half reaction with a reduction half reaction. For example, the replacement of silver ion by copper can be broken down into the following oxidation and reduction half reactions:



To arrive at the net ionic equation above, the reduction half reaction was multiplied by 2 to remove electrons from the overall equation when the two half reactions were added together. It would have been fairly simple to write the net ionic equation for this system without using half reactions. However, more complex redox reactions can be very difficult to balance without using the half reaction method. In addition, half reactions are useful in their own right as these are the processes that take place at the electrodes in electrochemical cells and batteries. A second example of the use of half reactions is the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by dichromate ion.



It is possible to determine electrochemical potentials for half reactions. These values are directly related to the driving force for the reaction, and potentials for the two half reactions can be combined algebraically to determine if the overall reaction is spontaneous. The potential  $E^{\circ}$  is related to the standard free energy of a process by  $\Delta G^{\circ} = -nFE^{\circ}$  (where  $F$  is the charge on 1 mol of electrons,  $1 F = 96,485$  coulombs/mol  $\text{e}^{-}$  and  $n$  is the number of electrons transferred in the reaction). A reaction is spontaneous when the free energy change is negative so the potential for a spontaneous reaction must be positive. It should be noted that reversal of the direction of a reaction simply changes the sign of the potential (if it wants to go in one direction, it won't want to go in the reverse direction). As extensive tabulations of half reaction potentials exist, it is possible to calculate potentials and predict spontaneity for a great number of reactions.

To determine if the two examples above would go spontaneously, locate a table of standard reduction potentials. These tables may be found in many chemistry textbooks, online (for example, see section III-B-20 of <http://murov.info/webercises.htm>) or handbooks such as the *CRC Handbook of Chemistry and Physics*.

<u>reaction</u>	<u><math>E^\circ</math></u> <u>(volts)</u>
$\text{Ag}^+ + \text{e}^- = \text{Ag(s)}$	0.80
$\text{Cu}^{2+} + 2 \text{e}^- = \text{Cu(s)}$	0.34
$\text{Cu(s)} + 2 \text{Ag}^+ = \text{Cu}^{2+} + \text{Ag(s)}$	0.46
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$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- = 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O(l)}$	1.33
$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	0.77
$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{Fe}^{2+} = 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O(l)} + 6 \text{Fe}^{3+}$	0.56

The positive potentials for both net ionic equations (0.46 volts and 0.56 volts) indicate both are spontaneous reactions.

## Procedure

In today's experiment, you will use a short table of half reaction potentials to calculate standard potentials for several reactions. For those that have positive potentials, you should also predict possible observations for the reaction when it is tried in the laboratory. For the silver ion - copper system, the potential indicates a spontaneous reaction and we expect to see silver metal plate out on the copper surface while the copper ion entering the solution should turn the solution from colorless to blue.

For each of the reactions listed in the **Results and Discussion** section, write down the net ionic equation and use half reaction potentials to determine the standard potential for the reaction. For those that should be spontaneous, predict the expected observations. Now, using 2 mL of each solution, try all the reactions including those predicted to be non-spontaneous to check for consistency with predictions. Be very careful with the half reactions for hydrogen peroxide as  $\text{H}_2\text{O}_2$  is capable of undergoing either oxidation or reduction (or even both if a catalyst is present). Select the appropriate half reaction for  $\text{H}_2\text{O}_2$  by considering the type of reaction that the other reactant is capable of undergoing. For example, if the reaction calls for the mixing of copper sulfate with hydrogen peroxide, as copper(II) can be reduced but not further oxidized, consider only the oxidation of hydrogen peroxide.

<u>reaction</u>	<u><math>E^\circ</math></u> <u>(volts)</u>
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}(\text{l})$	1.776
$\text{Ce}^{4+} + \text{e}^- = \text{Ce}^{3+}$	1.61
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{2+} + 4\text{H}_2\text{O}(\text{l})$	1.51
$2\text{IO}_3^- + 12\text{H}^+ + 10\text{e}^- = \text{I}_2(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$	1.195
$\text{Br}_2(\text{l}) + 2\text{e}^- = 2\text{Br}^-$	1.066
$\text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- = \text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$	0.94
$\text{ClO}^- + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{Cl}^- + 2\text{OH}^-$	0.89
$\text{Cu}^{2+} + \text{I}^- + \text{e}^- = \text{CuI}(\text{s})$	0.86
$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	0.771
$\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2(\text{aq})$	0.683
$\text{MnO}_4^- + 2\text{H}_2\text{O}(\text{l}) + 3\text{e}^- = \text{MnO}_2(\text{s}) + 4\text{OH}^-$	0.588
$\text{I}_2(\text{aq}) + 2\text{e}^- = 2\text{I}^-$	0.536
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- = [\text{Fe}(\text{CN})_6]^{4-}$	0.36
$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}(\text{s})$	0.337
$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- = \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	0.17
$\text{Cu}^{2+} + \text{e}^- = \text{Cu}^+$	0.153
$\text{Sn}^{4+} + 2\text{e}^- = \text{Sn}^{2+}$	0.15
$\text{S}_4\text{O}_6^{2-} + 2\text{e}^- = 2\text{S}_2\text{O}_3^{2-}$	0.090
$2\text{H}^+ + 2\text{e}^- = \text{H}_2(\text{g})$	0.000
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{H}_2\text{O}_2(\text{aq}) + 2\text{OH}^-$	-0.146
$2\text{CO}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{C}_2\text{O}_4(\text{aq})$	-0.49
$2\text{SO}_3^{2-} + 3\text{H}_2\text{O}(\text{l}) + 4\text{e}^- = \text{S}_2\text{O}_3^{2-} + 6\text{OH}^-$	-0.58
$\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}(\text{s})$	-0.763
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{H}_2(\text{g}) + 2\text{OH}^-$	-0.828
$\text{SO}_4^{2-} + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- = \text{SO}_3^{2-} + 2\text{OH}^-$	-0.92
$\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}(\text{s})$	-2.363
$\text{Na}^+ + \text{e}^- = \text{Na}(\text{s})$	-2.714
$\text{K}^+ + \text{e}^- = \text{K}(\text{s})$	-2.925

Name \_\_\_\_\_ Date \_\_\_\_\_ Lab Section \_\_\_\_\_

**Prelaboratory Problems - *Experiment 2* - Redox Reactions**

1. Write the net ionic equations and determine the standard potentials for the reaction of copper or zinc with tin(IV). Which of the two reactions should be spontaneous?

a. copper + tin(IV)

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

b. zinc + tin(IV)

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

c. spontaneous reaction(s) \_\_\_\_\_

2. Write the net ionic equation and determine the standard potential for the reaction between permanganate and tin(II). From the potential, calculate the free energy of the reaction.

a. permanganate + tin(II)

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

b.  $\Delta G^\circ =$  \_\_\_\_\_

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3. For each of the reactions listed on the following pages (even if it shouldn't go), write down the net ionic equation (NIE), and determine its standard potential. For those with positive potentials, write down your expected observations. Use the following pages for your answers.

Name \_\_\_\_\_ Date \_\_\_\_\_ Lab Section \_\_\_\_\_

## Results and Discussion - *Experiment 2* - Redox Reactions

For each of the reactions listed below (even if it doesn't go), write down the net ionic equation (NIE), and determine its standard potential. For those with positive potentials, write down your expected observations. Attempt to run all the reactions and record your experimental observations.

1. magnesium + 0.1 M zinc sulfate

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

2. copper + 0.1 M zinc sulfate

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

3. zinc + 0.1 M copper(II) sulfate

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

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4. zinc + 3 M hydrochloric acid

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

5. copper + 3 M hydrochloric acid

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

6. 0.1 M potassium iodide + 0.1 M copper(II) sulfate

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_



7.

a. 0.1 M potassium iodide + 0.02 M potassium iodate

[Note: Do not discard after performing 7-a. Proceed to 7-b.]

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

b. Add 1 drop of 6 M hydrochloric acid to the solution from 7-a. Report and explain your observations.

8. 0.1 M potassium iodide + 0.1 M potassium ferricyanide

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

9. 0.1 M iron(III) chloride + 0.1 M potassium iodide

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

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10. 0.1 M iron(III) chloride + 0.1 M potassium bromide

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

11. 3% hydrogen peroxide + 0.1 M cerium(IV) ammonium nitrate (acidic solution)

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

12. aqueous iodine + 1 M sodium thiosulfate (acidic solution)

oxidation half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

reduction half reaction \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

Optional challenge (check with instructor)

13. The following reaction is probably going to be performed under basic conditions. To select appropriate half reactions, you should first run the reaction and devise some tests to identify the product anion that contains sulfur.

3% hydrogen peroxide + 1 M sodium thiosulfate

[Note: Insert a thermometer into the  $\text{H}_2\text{O}_2$  solution and read it before adding the  $\text{Na}_2\text{S}_2\text{O}_3$  solution. After addition, stir with the thermometer and occasionally read the thermometer.]

Describe any qualitative analysis experiments and the results.

List key half reactions (you may have to couple more than 2 half reactions)

NIE \_\_\_\_\_  $E^\circ =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

Temperature reading before addition \_\_\_\_\_

Temperature reading after addition \_\_\_\_\_

Calculate  $\Delta G^\circ$  for this reaction \_\_\_\_\_

Was any temperature change observed for the system consistent with the sign of  $\Delta G^\circ$ ? Explain your answer.

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14. Like the previous reaction, you will need to do some qualitative analysis on the products before trying to figure out the net ionic equation for this reaction. Also consider taking the pH of the solution. This is probably a very complex system and may require that you look up the potentials for half reactions that are not listed in the table.

iron(III) chloride + sodium thiosulfate

Describe any qualitative analysis experiments and the results.

List key half reactions (you may have to couple more than 2 half reactions)

NIE \_\_\_\_\_  $E^{\circ} =$  \_\_\_\_\_

Expected observations \_\_\_\_\_

Experimental observations \_\_\_\_\_

15. Suggest any way you can think of to improve any part(s) of this experiment.
16. Some of the *Learning Objectives* of this experiment are listed on the first page of this experiment. Did you achieve the *Learning Objectives*? Explain your answer.