APPENDICES

TOPIC 6: Electrochemistry

Appendix 1 - An Introduction to Oxidation-Reduction (BLM)

In Part I of this experiment you will observe some possible oxidation-reduction reactions involving several metals and metallic ions. The results can be used to estimate the ease of reduction of the metallic ions relative to each other.

In Part II you will make a similar comparison of the relative ease of reduction of the three halogen elements Cl_2, Br_2, and I_2. Specifically, you will determine which of these halogens is capable of removing electrons from which of the halide ions, $C1^-_{(aq)}$, $Br^-_{(aq)}$, or $I^-_{(aq)}$. From this information you will be able to arrange the halogen element-halide ion half- reactions in order of decreasing ease of reduction.

PROCEDURE

PART I

a. Obtain small, clean strips of the metals zinc, copper, and lead. Also have available the following 0.l mol/L solutions: $Zn(N0_3)_2$, $Cu(N0_3)_2$, and $Pb(N0_3)_2$.

b. Record your observations of the reactions of each metal in each solution. For each combination, use 3 ml of solution in a 13 x 100 mm test tube and a small freshly cleaned strip of metal.

PART II

PRELIMINARY OBSERVATIONS

a. In separate test tubes, obtain about 3 ml of the three halogens in solution: in the first, chlorine in water, $Cl_{2(aq)}$; in the second, bromine in water, $Br_{2(aq)}$; and in the third, iodine in water containing ethanol (I_2 is only very slightly soluble in water).

b. Add 15 drops of hexane to each. Fit with a stopper, then shake each test tube vigorously for a few seconds. Note the color of the hexane phase which contains the dissolved halogen. (Make sure you know which is the hexane layer.)

c. Put about 3 ml of 0.1 mol/L NaCl in a clean test tube, about 3 ml of 0.1 mol/L KBr in a second. and 3 ml of 0.1 mol/l KI in a third test tube. Add 15 drops of hexane to each test tube. Fit with a stopper, then shake each test tube for a few seconds. Note the color of the hexane layer.

PART II

TEST FOR SPONTANEOUS OXIDATION-REDUCTION REACTIONS

d. Put about 3 ml of 0.1 Mol/L KBr in one test tube and about 3 ml of 0.1 mol/L KI in another. To each test tube add 15 drops of hexane. Add 1 ml of a fresh solution of chlorine in water to each. Stopper and shake both test tubes for a few seconds. Note the color of the hexane phase and compare with the preliminary tests in Part II, steps a and b.

e. Repeat the test outlined in step d, except use 0.1 mol/L NaCl and 0.1 mol/L KI. Use 5 drops of bromine water in place of the chlorine water. After adding the bromine water, stopper the tubes and shake as directed above. Record your results.

f. Repeat the test outlined in step d, except use 0.1 mol/L NaCl and 0.1 mol/L KBr, and use 5 drops of iodine water in place of the chlorine water. Add iodine water, stopper the tubes and shake as directed above. Record your results.

Some Follow-up Questions

1. Which of the metallic ions tested was reduced by two metals? Which was reduced by only one of the metals? Which was reduced by none of the metals?

2. Arrange the metallic ion-metal half reactions, $M^{2+}_{(aq)} + 2e^- \rightarrow M_{(s)}$, in a column in order of decreasing ease of reduction.

3. Write balanced, total reactions for the cases in which oxidation-reduction reactions between metals and metallic ions were observed.

4. Which of the halogens tested was reduced by two of the halide ions? Which halogen was reduced by only one halide ion? Which halogen was not reduced by any of the halide ions used?

5. Arrange the halogen element-halide ion half-reactions in a column in order of decreasing ease of reduction.

6. Write balanced, total reactions for the cases in which oxidation-reduction reactions occurred between halide ions and halogens.

7. Use the additional information given below to construct a series of all seven half- reactions discussed in this experiment. Add the half-reaction $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$ to your list in the appropriate place.

   Put the list in order of decreasing ease of reduction.

a. $Ag^{+}_{(aq)}$ is less easily reduced than $Br_{2(aq)}$ and more easily reduced than
$I_{2(aq)}$.

b. $I_{2(aq)}$ is less easily reduced than $Ag_{(aq)}$ and more easily reduced than $Cu_{2(aq)}$.

8. Use the list constructed in question 7 to answer the following:

   a. Would it be feasible to store a solution of copper sulfate in a container made of metallic zinc? Explain.
   b. Would it be feasible to store a solution of copper sulfate in a container made of metallic silver? Explain.
   c. Would you expect jewelry made from an alloy of silver and copper to tarnish (oxidize) in a laboratory where fumes of bromine are present? Explain your reasoning.

Appendix 2: An Introduction to Oxidation-Reduction – Teacher Background

PURPOSE
To establish experimentally the relative electron-gaining tendency of three metals and three halogen elements.

NECESSARY MATERIALS (per student or pair)

1213 X 100mm test tubes
2 solid rubber stoppers, size #00 (or cork size #3)
6 metal strips: 2 of copper, 2 of lead, 2 of zinc

Solutions and reagents:
9 ml 0.1 *M* $Cu(NO_3)_2$ [24.2 g $Cu(NO_3)_2 \cdot 3H_2O$/liter]
9 ml 0.1 *M* $Pb(NO_3)_2$ [33.1 g $Pb(NO_3)_2$/liter]
9 ml 0.1 *M* $Zn(NO_3)_2$ [29.8 g $Zn(NO_3)_2 \cdot 6H_2O$/liter]
6 ml 0.1 *M* NaBr (10.3 g NaBr/liter)
6 ml 0.1 *M* NaI (15 g NaI/liter)
6 ml 0.1 *M* NaC1 (5.8 g NaCl/liter)
5 ml chlorine water (saturated; see lab hint 2)
4 ml bromine water (1 ml Br_2/200 ml H_2O; see lab hint 3)
4 ml iodine in water-ethanol solution (see lab hint 4)
9 ml hexane (C_6H_{14}) (see lab hint 5)

LABORATORY HINTS

The preparation for each solution MUST be done in a correctly functioning fume hood.

1. Two strips of each metal are sufficient if the student does not test the metal with the nitrate of the same metal. Three pieces of each metal are needed if this is done.

2. To make saturated chlorine water, slowly pass chlorine gas from a lecture bottle of compressed gas into the needed amount of water, or set up a chlorine gas generator as follows. Use a long-stem funnel and delivery tube in a 2-hole stopper inserted in a 250-ml flask. Add about 40 ml of concentrated HCl to about 10 g of MnO_2 in the flask, and warm gently. Use a fume hood. This procedure generates enough chlorine gas to prepare 1 liter of chlorine water.

3. Prepare bromine water by dissolving about 1 ml of bromine in 200 ml of water. Bromine can be prepared by heating 10 g of KBr with 2 g of MnO_2 and 15 ml of 9 *M* H_2SO_4 in a glass retort and allowing the bromine to flow into a tube of water. The solution for this experiment need be only lightly colored to be concentrated enough. i.e a very small amount of bromine produced. The retort is used to avoid

rubber or cork stoppers as bromine will react with organic materials.

CAUTION: Avoid getting liquid bromine on your skin. It produces very painful, slowly healing burns.

4. Dissolve about 0.25 g of $I_{2(s)}$ in 50 ml of ethanol, and add 350 ml of water.

PRELAB DISCUSSION

Little is needed if the student has read the experiment carefully. Instruct students to set up solutions as directed in Part I and then check them every 5 or 10 minutes while continuing with Part II.

SAMPLE WRITEUP

PART I

	$Cu(NO_3)_2$ solution	**$Pb(NO_3)_2$ solution**	**$Zn(NO_3)_2$ solution**
Copper	N.R.	N.R.	N.R.
Lead	Dark coating forms	N.R.	N.R.
Zinc	Dark coating forms	Crystals form on zinc stip	N.R.

PART II

Preliminary Observations with hexane

$Cl_{2(aq)}$ + C_6H_{14} → no color
$Br_{2(aq)}$ **+** C_6H_{14} → brownish-red color in C_6H_{14} layer
$I_{2(aq)}$ + C_6H_{14} → pink color in C_6H_{14} layer
0.1 *M* NaCl + C_6H_{14} → no color
0.1 *M* KBr + C_6H_{14} → no color
0.1 *M* KI + C_6H_{14} → no color

PART II (continued)

Test for Spontaneous Oxidation-Reduction Reactions

0.1 *M* KBr + $Cl_{2(aq)}$ + C_6H_{14} → orange-brown color in C_6H_{14} layer
0.1 *M* KI + $C1_{2(aq)}$ + C_6H_{14} → purple-pink color in C_6H_{14} layer
0.1 *M* NaC1 + $Br_{2(aq)}$ + C_6H_{14} → orange-brown color in C_6H_{14} layer
0.1 *M* KI + $Br_{2(aq)}$ + C_6H_{14} → purplish color in C_6H_{14} layer
0.1 *M* NaCl + $I_{2(aq)}$ + C_6H_{14}→ pink color in C_6H_{14}layer
0.1 *M* KBr + $I_{2(aq)}$ + C_6H_{14} → pink color in C_6H_{14} layer

Follow-up Questions for Discussion:

1. Which of the metallic ions tested was reduced by two metals? Which was reduced by only one of the metals? Which was reduced by none of the metals?
   $Cu^{2+}_{(aq)}$ was reduced by both lead and zinc.
   $Pb^{2+}_{(aq)}$ was reduced by zinc only.
   $Zn^{2+}_{(aq)}$ was not reduced by either copper or lead.

2. Arrange the metallic ion-metal half reactions, $M^{2+}_{(aq)} + 2e^- \rightarrow M_{(s)}$, in a column in order of decreasing ease of reduction. Add the half-reaction $Ag_{(aq)} + e^- \rightarrow Ag_{(s)}$ to your list in the appropriate place.
   $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$
   $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$
   $Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$
   $Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

3. Write balanced, total reactions for the cases in which oxidation-reduction reactions between metals and metallic ions were observed.

$$Pb_{(s)} \rightleftarrows Pb^{2+}_{(aq)} + 2e^-$$
(oxidation half-reaction)

$$2e^- + Cu^{+2}_{(aq)} \rightleftarrows Cu_{(s)}$$
(reduction half-reaction)

$$Pb_{(s)} + Cu^{2+}_{(aq)} \rightleftarrows Pb^{2+}_{(aq)} + Cu_{(s)}$$
(total reaction)

$$Zn_{(s)} \rightleftarrows Zn^{2+}_{(aq)} + 2e^-$$
(oxidation half-reaction)

$$2e^- + Cu^{+2}_{(aq)} \rightleftarrows Cu_{(s)}$$
(reduction half-reaction)

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftarrows Zn^{2+}_{(aq)} + Cu_{(s)}$$
(total reaction)

$$Zn_{(s)} \rightleftarrows Zn^{2+}_{(aq)} + 2e^-$$
(oxidation half-reaction)

$$2e^- + Pb^{+2}_{(aq)} \rightleftarrows Pb_{(s)}$$
(reduction half-reaction)

$$Zn_{(s)} + Pb^{2+}_{(aq)} \rightleftarrows Zn^{2+}_{(aq)} + Pb_{(s)}$$

(total reaction)

4. Which of the halogens tested was reduced by two of the halide ions? Which halogen was reduced by only one halide ion? Which halogen was not reduced by any of the halide ions used?

   Chlorine was reduced by both $Br^-_{(aq)}$ and $I^-_{(aq)}$.
   Bromine was reduced by $I^-_{(aq)}$ only.
   Iodine was not reduced by either $Br^-_{(aq)}$ or $Cl^-_{(aq)}$.

5. Arrange the halogen element-halide ion half-reactions in a column in order of decreasing ease of reduction.
   $Cl_{2(aq)} + 2e^- \rightarrow 2Cl^-_{(aq)}$
   $Br_{2(aq)} + 2e^- \rightarrow 2Br^-_{(aq)}$
   $I_{2(aq)} + 2e^- \rightarrow 2I^-_{(aq)}$

6. Write balanced, total reactions for the cases in which oxidation-reduction reactions occurred between halide ions and halogens.

$2e^- + Cl_{2(aq)} \rightleftarrows 2Cl^-_{(aq)}$ *(reduction half-reaction)*

$2Br^-_{(aq)} \rightleftarrows Br_{2(aq)} + 2e^-$ *(oxidation half-reaction)*

$Cl_{2(aq)} + 2Br^-_{(aq)} \rightleftarrows 2Cl^-_{(aq)} + Br_{2(aq)}$ *(total reaction)*

$2e^- + Cl_{2(aq)} \rightleftarrows 2Cl^-_{(aq)}$ *(reduction half-reaction)*

$2I^-_{(aq)} \rightleftarrows I_{2(aq)} + 2e^-$ *(oxidation half-reaction)*

$Cl_{2(aq)} + 2I^-_{(aq)} \rightleftarrows 2Cl^-_{(aq)} + I_{2(aq)}$ *(total reaction)*

$2e^- + Br_{2(aq)} \rightleftarrows 2Br^-_{(aq)}$ *(reduction half-reaction)*

$2I^-_{(aq)} \rightleftarrows I_{2(aq)} + 2e^-$ *(oxidation half-reaction)*

$Br_{2(aq)} + 2I^-_{(aq)} \rightleftarrows 2Br^-_{(aq)} + I_{2(aq)}$ *(total reaction)*

7. Use the additional information given below to construct a series of all seven half- reactions discussed in this experiment. Add the half-reaction $Ag^+_{(aq)} \rightarrow Ag_{(s)}$ to your list in the appropriate place.
   Put the list in order of decreasing ease of reduction.
   a. $Ag^+_{(aq)}$ is less easily reduced than $Br_{2(aq)}$ and more easily reduced than
      $I_{2(aq)}$.
   b. $I_{2(aq)}$ is less easily reduced than $Ag_{(aq)}$ and more easily reduced than $Cu_{2(aq)}$.
   $Cl_{2(aq)} + 2e^- \rightleftarrows 2Cl^-_{(aq)}$

$Br_{2(aq)} + 2e^- \rightleftarrows 2Br^-_{(aq)}$
$Ag^+_{(aq)} + e^- \rightleftarrows Ag(s)$
$I_{2(aq)} + 2e^- \rightleftarrows 2I^-_{(aq)}$
$Cu^{2+}_{(aq)} + 2e^- \rightleftarrows Cu_{(s)}$
$Pb^{2+}_{(aq)} + 2e^- \rightleftarrows Pb_{(s)}$
$Zn^{2+}_{(aq)} + 2e^- \rightleftarrows Zn_{(s)}$

8. Use the list constructed in question 7 to answer the following:
   a. Would it be feasible to store a solution of copper sulfate in a container made of metallic zinc? Explain.
   b. Would it be feasible to store a solution of copper sulfate in a container made of metallic silver? Explain.
   c. Would you expect jewelry made from an alloy of silver and copper to tarnish (oxidize) in a laboratory where fumes of bromine are present? Explain your reasoning.

(a) A solution of copper sulfate would contain $Cu^{2+}_{(aq)}$ and would react with a container made of $Zn_{(s)}$ since $Cu^{2+}_{(aq)}$ is reduced by zinc as shown in the list in question 7.
(b) The $CuSO_4$ solution would not react with a container made of $Ag_{(s)}$ because it is $Ag^+_{(aq)}$ which is reduced by $Cu_{(s)}$. $Ag_{(s)}$ is not a strong enough reducing agent to reduce $Cu^{2+}_{(aq)}$.
(c) One should expect such jewelry to tarnish, since both $Ag_{(s)}$ and $Cu_{(s)}$ reduce $Br_{2(aq)}$. It is expected that $Br_{2(g)}$ would have the same effect. Of course, a laboratory with any appreciable concentration of bromine fumes would be uninhabitable.

POSTLAB DISCUSSION

Some interpretation of the results for Part II will probably be necessary. The following may be helpful.

Chlorine does not color C_6H_{14}. Iodine in C_6H_{14} is a deep purple if very concentrated, although an attempt has been made to keep the solution dilute enough that a pink-lavender shade should result. Bromine in C_6H_{14} is red when concentrated, and straw-colored when diluted. Unless these differences in color receive comment, students may fail to identify the bromine in C_6H_{14} in different concentrations.

Since Cl_2 will be reduced by both I^- and Br^-, the color of the C_6H_{14} layer will show I_2 and Br_2 for Part II(d). When Br_2 water is added, no reaction takes place with Cl^-, although the student may not be able to determine this, since a Br_2 color in C_6H_{14} would mask any Cl_2 even if it were produced. With the recommended concentrations, all the Br_2 should be used in replacing I^-, and the resulting color in C_6H_{14} should be due only to I_2.

With iodine solution, no reactions occur, and only the color of I_2 in C_6H_{14} will be observed. A comparison of the color resulting with 5 drops of the iodine solution added to 5 ml of NaI and 1 ml C_6H_{14} will convince the student that none of the I_2 has reacted with the Cl^- or Br^-.

TABLE of Standard Reduction Potentials

Greatest Affinity for Electrons

Most Easily Reduced

Strongest Oxidizing Agent

Weakest Oxidizing Agent

Least Easily Oxidized

Half reaction	E (volts)
$F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}$	+2.87
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)}$	+1.77
$MnO_{4(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.52
$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$	+1.50
$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$	+1.36
$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33
$MnO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.28
$1/2O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_{(l)}$	+1.23
$Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$	+1.06
$AuCl^-_{4(aq)} + 3e^- \rightarrow Au_{(s)} + 4Cl^-_{(aq)}$	+1.00
$NO^-_{3(aq)} + 4H^+_{(aq)} + 3e^- \rightarrow NO_{(g)} + 2H_2O_{(l)}$	+0.96
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	+0.80
$1/2Hg^{2+}_{2(aq)} + e^- \rightarrow Hg_{(l)}$	+0.79
$Hg^{2+}_{(aq)} + 2e^- \rightarrow Hg_{(l)}$	+0.78
$NO^-_{3(aq)} + 2H^+_{(aq)} + e^- \rightarrow NO_{2(g)} + H_2O_{(l)}$	+0.78
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$	+0.77
$O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_{2(aq)}$	+0.68
$I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$	+0.53
$Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$	+0.52
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	+0.34
$SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow SO_{2(g)} + 2H_2O_{(l)}$	+0.17
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+_{(aq)}$	+0.15
$Sn^{4+}_{(aq)} + 2e^- \rightarrow Sn^{2+}_{(aq)}$	+0.15
$S_{(s)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2S_{(g)}$	+0.14
$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$	0.00
$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$	-0.13
$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$	-0.14
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$	-0.25
$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$	-0.28
$Se_{(s)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2Se_{(g)}$	-0.40
$Cr^{3+}_{(aq)} + e^- \rightarrow Cr^{2+}_{(aq)}$	-0.41
$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$	-0.44
$Ag_2S_{(s)} + 2e^- \rightarrow 2Ag_{(s)} + S^{2-}_{(aq)}$	-0.69
$Te_{(s)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2Te_{(g)}$	-0.72
$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$	-0.74
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	-0.76
$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)}$	-0.83
$Mn^{2+}_{(aq)} + 2e^- \rightarrow Mn_{(s)}$	-1.18
$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$	-1.66
$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$	-2.37
$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$	-2.71
$Ca^{2+}_{(aq)} + 2e^- \rightarrow Ca_{(s)}$	-2.87
$Sr^{2+}_{(aq)} + 2e^- \rightarrow Sr_{(s)}$	-2.89
$Ba^{2+}_{(aq)} + 2e^- \rightarrow Ba_{(s)}$	-2.90
$Cs^+_{(aq)} + e^- \rightarrow Cs_{(s)}$	-2.92
$K^+_{(aq)} + e^- \rightarrow K_{(s)}$	-2.92
$Rb^+_{(aq)} + e^- \rightarrow Rb_{(s)}$	-2.92
$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$	-3.00

Least Affinity for Electrons

Least Easily Reduced

Weakest Oxidizing Agent

Most Easily Oxidized

Strongest Reducing Agent