Two Activity Series: Metals and Halogens

- Learn to identify Active metals.
- Learn about the Halogens.
- Learn about Oxidation-Reduction reactions.
- Learn about Single Replacement reactions.

In this laboratory exercise we will determine the relative Activity of various metallic elements and the relative Activity of the Halogens. Our first task will be to define what is meant by the “Activity” and then to develop a scheme which will allow us to measure the Activity. There is a distinct commonality between how the Activity of the Metals and the Activity the Halogens are defined. This commonality has its origins in the Oxidation-Reduction nature of the Activity definitions.

Activity of the Metals

The elemental metals under consideration in this experiment are:

Calcium (Ca)
Copper (Cu)
Iron (Fe)
Lead (Pb)
Lithium (Li)
Magnesium (Mg)
Potassium (K)
Silver (Ag)
Sodium (Na)
Tin (Sn)
Zinc (Zn)

Metals are substances which have three characteristic properties:

1) Metals are shiny or lustrous.
2) Metals are malleable and ductile.
3) Metals are good conductors of electricity and heat.

As a general rule, the Elements toward the bottom-left corner of the Periodic Table are metals, and those toward the upper-right corner are non-metals; transitioning from one region of the Table to the other through the metalloids. This transition is not abrupt, however. As a result, the change from metallic to non-metallic character is gradual as we move across a Period or up a Group. Elements become less metallic as we go across a Period from left to right. And, as we proceed down a Group the Elements become more metallic; cf. the Group 4A elements:
<table>
<thead>
<tr>
<th>Element</th>
<th>Metallic Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>non-metal</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>metalloid</td>
</tr>
<tr>
<td>Germanium (Ge)</td>
<td>metalloid</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>metal</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>metal</td>
</tr>
</tbody>
</table>

The primary difference between the elemental metals is the ease with which they undergo chemical reactions. The elements toward the bottom-left corner of the Period Table, which have the most metallic character, are chemically very reactive, and, hence, are the most Active metals. These metals very readily shed their electrons to form cations.

The Activity of the metals can be evaluated by means of their ability to undergo a chemical reaction in a Single Replacement reaction. In single replacement reactions, one metal displaces another metal, or hydrogen, from a compound or aqueous solution. In general, this can be represented as:

$$M' + M''Z \rightarrow M'Z + M''$$  \hspace{1cm} (Eq. 1)

where $M'$ is the metal which will displace $M''$. The metal $M'$ that displaces $M''$ does so because it has a greater tendency to undergo a reaction. The metal $M'$ is said to be more "Active" than $M'$. Thus, the Activity of a metal is a measure of its ability to compete in a single replacement reaction. An Activity Series is a sequence of metals arranged according to their Activity.

Very Active metals (Class I: Active Metals) will react directly with water at Room Temperature, displacing hydrogen and producing the hydroxide. Rubidium, an Alkali Metal, is an example of a very Active metal:

$$2 \text{ Rb(s)} + 2 \text{H}_2\text{O} \rightarrow 2 \text{RbOH(aq)} + \text{H}_2(\text{g})$$  \hspace{1cm} (Eq. 2)

The bubbling off of the hydrogen gas is indicative of this reaction. The Single Replacement nature of this reaction can be seen if we re-write the chemical formula for water as H-OH.

$$2 \text{ Rb} + 2 \overset{\text{H}}{\text{HOH}} \rightarrow 2 \text{RbOH} + \text{H}_2$$  

Here, the Rb is more Active than Hydrogen, hence the reaction occurs. If we make an assignment of Oxidation Numbers, we can see this reaction is also an example of an Oxidation-Reduction reaction. The rubidium is oxidized from a 0 oxidation state to a +1 oxidation state.
Because of their extremely high Activity, the Alkali Metals are frequently stored under an inert liquid, such as Mineral Oil, to prevent them from reacting with the oxygen of the atmosphere.

Less Active metals (Class II: Less Active Metals) will not be able to displace hydrogen from water, but can displace hydrogen from an aqueous acid. As example, consider manganese, which only slowly reacts with water at Room Temperature, but reacts vigorously with the strong acid HCl:

\[
2 \text{Mn}(s) + 6 \text{HCl}(aq) \rightarrow 2 \text{MnCl}_3(aq) + 3 \text{H}_2(g) \quad \text{(Eq. 3)}
\]

The manganese has displaced the hydrogen to produce the chloride salt, which is soluble in the aqueous environment in which the reaction takes place. (In a classic example of circular reasoning, one property of an Acid is that they will dissolve Active Metals.) This too is an Oxidation-Reduction reaction.

It is important to protect these metals from exposure to acids. For example, Aluminum, a member of this class of metals, is used in beverage cans that are lined with a plastic coating to prevent contact with the acidic soft drinks they contain.

Finally, metals of low Activity (Classes III and IV: Structural and Coinage Metals) have to be compared one against another. Suppose we wish to compare the Activity of copper and cobalt. We can look at the following reactions:

\[
2 \text{Co}(s) + 3 \text{CuCl}_2(aq) \rightarrow 2 \text{CoCl}_3(s) + 3 \text{Cu}(s) \quad \text{(Eq. 4)}
\]

\[
\text{Cu}(s) + \text{Co(NO}_3)_3(aq) \rightarrow \text{No Reaction} \quad \text{(Eq. 5)}
\]

Since cobalt displaces copper, but copper does not displace cobalt, we can see cobalt is more Active than copper. Hence, cobalt appears before copper in the Activity Series. And, again, the displacement of copper by cobalt is an Oxidation-Reduction reaction.
A technical point; we can actually perform this experiment by placing a drop of CuCl\(_2\) solution on a clean strip of cobalt metal. A darkening spot on the cobalt is indicative of a reaction. Likewise, the second reaction can be tested by placing a drop of Co(NO\(_3\))\(_3\) solution on a clean strip of copper metal and observing that no change takes place.

Because metals in the *Coinage Metal* class are so inert, they are ideal for making jewelry and coins. We will not sub-divide the *Structural* and *Coinage Metals*.

Thus, we will arrange the above mentioned metals into an Activity Series based on their ability to undergo oxidation in Single Replacement reactions. We will do this by first examining which metals react, and how vigorously they react, with Room Temperature water; *Class I: Active Metals*. Those which do not react appreciably with water, will be tested against aqueous HCl; *Class II: Less Active Metals*. Finally, comparative tests will be performed on those metals which show no reactivity with water or aqueous acid. These are *Class III and IV: Structural and Coinage Metals*.

It must be borne in mind that we are not controlling for a number of factors, surface area, completeness of oxide removal, etc., so there may be occasional ambiguities in placing pairs of metals within the Series. However, on the whole, our scheme will provide us with results that are consistent with others. Later in the course we will discuss how to quantify our Activity measure using electrochemical potential measurements.

*Activity of the Halogens*

The Halogens (*Latin* for salt-former), Group 7A of the Periodic Table of the Elements, react with most of the other elements in the Periodic Table to form a wide range of Ionic and Covalent compounds.
The exceptional reactivity of these elements is tied to their common valence shell electron configuration; each being one electron shy of a Noble Gas octet. In most of their reactions, the Halogens act as Oxidizing Agents and display a wide range of Oxidation States.

<table>
<thead>
<tr>
<th>Halogen</th>
<th>Common Oxidation States</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>F⁻¹</td>
</tr>
<tr>
<td>Cl</td>
<td>Cl⁻¹, Cl⁺¹, Cl⁺³, Cl⁺⁵, Cl⁺⁷</td>
</tr>
<tr>
<td>Br</td>
<td>Br⁻¹, Br⁺¹, Br⁺³, Br⁺⁵, Br⁺⁷</td>
</tr>
<tr>
<td>I</td>
<td>I⁻¹, I⁺¹, I⁺³, I⁺⁵, I⁺⁷</td>
</tr>
<tr>
<td>At</td>
<td>At⁻¹</td>
</tr>
</tbody>
</table>

You should note the Oxidation States for these elements tend to vary in units of two. This is true in general and is because the electrons about an atom tend to form pairs; bonding pairs or lone pairs. During chemical reactions the electrons will tend to re-shuffle, with some chemical bonds breaking and some forming, as pairs. This range of Oxidation States is evident in the Oxyanions formed by Chlorine:

<table>
<thead>
<tr>
<th>Anion</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>Chloride Ion</td>
</tr>
<tr>
<td>ClO⁻</td>
<td>Hypochlorite Ion</td>
</tr>
<tr>
<td>ClO₂⁻</td>
<td>Chlorite Ion</td>
</tr>
<tr>
<td>ClO₃⁻</td>
<td>Chlorate Ion</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>Perchlorate Ion</td>
</tr>
</tbody>
</table>

In their elemental state the Halogens form diatomic molecules; F₂, Cl₂, Br₂, and I₂. Additionally, these elements display a strong regularity in their physical properties:

<table>
<thead>
<tr>
<th>Halogen</th>
<th>Appearance</th>
<th>mp (°C)</th>
<th>bp (°C)</th>
<th>Atomic Radium (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flourine</td>
<td>Brownish Gas</td>
<td>-219</td>
<td>-188</td>
<td>72</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Yellow-Green Gas</td>
<td>-101</td>
<td>-34.0</td>
<td>100</td>
</tr>
<tr>
<td>Bromine</td>
<td>Reddish Liquid</td>
<td>-7.2</td>
<td>59.5</td>
<td>114</td>
</tr>
<tr>
<td>Iodine</td>
<td>Purple Solid</td>
<td>114</td>
<td>185</td>
<td>133</td>
</tr>
</tbody>
</table>

As you study chemical bonding and intermolecular forces, you will learn the reason for this regularity.

This regularity extends to the chemistry of the Halogens as well. Therefore, we expect the Activity of these elements to display a distinct trend within the Group. In this context, we will define the Activity of these elements as the ability to participate in a Replacement Reaction:

\[ X_2(aq) + 2 Y^-(aq) \rightarrow 2 X^-(aq) + Y_2(aq) \]  \hspace{1cm} (Eq. 6)

If \( X_2 \) reacts with \( Y^- \) and \( Y_2 \) does not react with \( X^- \), then we say \( X_2 \) is more Active than \( Y_2 \). (Note the definition is the reverse of that used for the metals. Here Activity is associated with the ability to gain electrons, whereas in metals it is associated with the ability to lose electrons.)
In each case, we will generate the desired Halogen in an aqueous environment and then add a solution of the Salt of the reacting Halide. A small amount of the non-polar solvent Cyclohexane will then be added. Because Halogen molecules are also non-polar, they will tend to migrate into the Cyclohexane and will produce a distinctive color:

<table>
<thead>
<tr>
<th>Halogen</th>
<th>Color in Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>Yellow-Green</td>
</tr>
<tr>
<td>Bromine</td>
<td>Orange-Brown</td>
</tr>
<tr>
<td>Iodine</td>
<td>Pink-Purple</td>
</tr>
</tbody>
</table>

Thus, we will generate each Halogen and then add the appropriate Halide. Cyclohexane will then be added to extract any Halogens present from the Water. The color of the Cyclohexane solution will then be an indication of which Halogen is present. From this information we will be able to ascertain whether or not a chemical reaction has taken place between the Halogen and the Halide. And, based on this reactivity information, a ranking of Halogen Activity can be constructed.
Pre-Lab Safety Questions

1. Consult an SDS for Chlorine, Bromine and Iodine. What First Aid measures should be taken if any of these substances get on your skin?

2. Do a short internet search for an NFPA 704 Fire Diamond for Hydrogen. What is the Degree of Hazard for Hydrogen's flammability?

3. What is the Lower Explosive Limit and the Upper Explosive Limit for a gas? Additionally, what is the Autoignition Temperature of a substance? What are these values for Hydrogen gas? How many liters of Hydrogen gas will be released if 1.0g of Zinc metal reacts completely with sufficient Hydrochloric Acid? [At Room Temperature and 1 atm pressure, 1 mol of gas will occupy 24.4 L. Think in terms of Avogadro's Hypothesis!]
Procedure

Activity of the Metals

Test for Class I: Active Metals

Put about 2.5 cm of water in each of 8 appropriately labeled test tubes. To each test tube, add a small piece of each metal (Cu, Fe, Pb, Mg, Sn, Zn). Note which react with water, and which do not. Also note the vigorousness of the reactions.

- The surface of some of the metals may have to be cleaned with a piece of Steel Wool to remove any oxide coating. This is especially true for Al and Mg which form particularly tough oxide coats. (You may want to wear a pair of gloves while doing this.)

For the remaining metals (Ca, Li, K, Na), put about 20mL of water into a 100mL beaker. Place your wire screen over the beaker. In the Fume Hood, add a small piece of the metal; this can be obtained from your laboratory instructor. Repeat this for each metal. Note which react with water, and which do not. Also note the vigorousness of the reactions.

- We will take as a given that Silver does not react with Water, so no observations regarding this metal is required here.

Test for Class II: Less Active Metals

For those metals which did not react with water, or those which reacted very slowly, decant the water from the test tube. Into each of these test tubes, add about 5 mL of 6M HCl. Note the vigorousness of any reactions.

- We will again take it as a given that Silver does not react with Acid.

For any metal which does not react with the acid:

- Decant off the aqueous acid solution.
- Rinse off the metal pieces with water. Dry them.
- Return the metal pieces to the appropriately marked container.

At this point, we will also confirm the gas being bubbled off has properties consistent with that of Hydrogen gas. Hydrogen gas reacts explosively with Oxygen gas, provided the two are well mixed together:

\[ 2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(l) \]
So, any of our samples that generate copious amounts of hydrogen gas can be tested for combustion of the gas. Zinc will make for a good choice here.

**In the fume hood, and away from other sources of hydrogen:**

1) Add 5 -10mL of 6M HCl(aq) to a large test tube. Prop this up in a large beaker.
2) Drop 2-3 pieces of Zinc into the solution. Allow the reaction to proceed for a minute or two.
3) When the vapors spill out of the test tube, test them with a flaming splint. Repeat the test several times to determine the time interval required to get a vigorous reaction.

**Test for Class III and IV: Structural and Coinage Metals**

Finally, for each of those metals which do not react with acid, obtain a strip of the metal containing small wells. Clean the surface of each well with a piece of Steel Wool. Small glass dowels are available for this purpose. (You may want to wear a pair of gloves for this.) The surface needs to be extremely clean and shiny. Place a few drops of each of the solutions of the other metal salts. Note which exhibit signs of reaction.

**Activity of the Halogens**

All of the Halogen Reactions should be performed in the Fume Hood.

**Chlorine Production and Testing**

1. Into 2 small test tubes, add 10 drops of 5% NaClO and 5 drops of cyclohexane. Now add 5 drops of 6M HCl to each test tube. Check the Cyclohexane layer for a color change.

\[
\text{ClO}^\text{-}(aq) + \text{Cl}^- (aq) + 2 \text{H}^+(aq) \rightarrow \text{Cl}_2(aq) + \text{H}_2\text{O}
\]

2. To one test tube, add 4 drops of 0.5M Br\(^-\). Agitate and check the Cyclohexane layer for a color change.

3. To the other test tube, add 6-8 drops of 0.5M I\(^-\). Agitate and check the Cyclohexane layer for a color change.

**Bromine Production and Testing**

1. Add a pinch (~0.1g) of KBr and a pinch of MnO\(_2\) to a test tube and mix. Add 2 drops of Water and 3 drops of conc. H\(_2\)SO\(_4\). Mix. Add 10 drops of Water and 5 drops of Cyclohexane. Mix well. Check the color of the Cyclohexane layer.

\[
4 \text{Br}^- (aq) + \text{MnO}_2(s) + 4 \text{H}^+(aq) \rightarrow \text{MnBr}_2(aq) + \text{Br}_2(aq) + 2 \text{H}_2\text{O}
\]
Discard into a Waste Container.

2. Add 5 drops of Water, 5 drops of Bromine Water and 5 drops of Cyclohexane to each of two test tubes. Mix and note the color of the Cyclohexane layer.

3. To one test tube, add 2 drops of 0.5M Cl\(^-\). Agitate and check the Cyclohexane layer for a color change.

4. To the other test tube, add 2 drops of 0.5M I\(^-\). Agitate and check the Cyclohexane layer for a color change.

**Iodine Production and Testing**

1. Add a pinch (~0.1g) of KI and a pinch of MnO\(_2\) to a test tube and mix. Add 2 drops of Water and 3 drops of conc. H\(_2\)SO\(_4\). Mix. Add 10 drops of Water and 5 drops of Cyclohexane. Mix well. Check the color of the Cyclohexane layer.

   \[
   4 \text{I}^{(aq)} + \text{MnO}_2(s) + 4 \text{H}^+(aq) \rightarrow \text{MnI}_2(aq) + \text{I}_2(aq) + 2 \text{H}_2\text{O}
   \]

   Discard into a Waste Container.

2. Add 8 drops of Water, 2 drops I\(_3^-\) solution and 5 drops of Cyclohexane to each of two test tubes. Mix and note the color of the Cyclohexane layer.

3. To one test tube, add 2 drops of 0.5M Cl\(^-\). Agitate and check the Cyclohexane layer for a color change.

4. To the other test tube, add 2 drops of 0.5M Br\(^-\). Agitate and check the Cyclohexane layer for a color change.
Data Analysis

Activity of the Metals

Class I: Active Metals

For each metal that reacts directly with water, write a balanced chemical equation representing the reaction.

For Class II: Less Active Metals

For each metal that reacts directly with acid, write a balanced chemical equation representing the reaction.

Hints: The presence of Fe$^{3+}$ in aqueous solutions is indicated by a yellow/orange color. Cu$^{2+}$ is indicated by a slight blue color. Pb$^{2+}$ is the common form of lead in an aqueous environment. Likewise, tin normally exists as Sn$^{2+}$ when dissolved in Water.

For Class III and IV: Structural and Coinage Metals

For each observed reaction, write a balanced chemical equation representing the reaction.

Activity Series

Based on these observations, arrange the metals into an Activity Series, with the most Active listed first and the least Active listed last.

Compare this Series with that listed in the Course Textbook.

Activity of the Halogens

For each Halogen-Halide reaction observed to take place, write a balance Chemical Equation.

Activity Series

Based on these observations, arrange the halogens into an Activity Series. Based on the observed trend, you should be able to include Fluorine and Astatine in your ranking.
Post Lab Questions

1. In each of the following, identify the Oxidation State of the metallic element:
   - NaOH \( x_{\text{Na}} = \) ____
   - MnO_4^- \( x_{\text{Mn}} = \) ____
   - Ni \( x_{\text{Ni}} = \) ____
   - Sn(NO_3)_2 \( x_{\text{Sn}} = \) ____
   - FeO \( x_{\text{Fe}} = \) ____
   - Fe_2O_3 \( x_{\text{Fe}} = \) ____

2. In our procedure we have been careful to use a non-oxidizing Acid; HCl. An oxidizing Acid, such as Nitric Acid (HNO_3), contains an anion that is responsible for the oxidation of the metal. For instance, Nitric Acid will oxidize Copper according to:
   \[
   \text{Cu(s)} + 4 \text{HNO}_3(\text{aq}) \rightarrow \text{Cu(NO}_3)_2(\text{aq}) + 2 \text{NO}_2(\text{g}) + 2 \text{H}_2\text{O}
   \]
   Show the Nitric Acid is acting as an Oxidizing Agent by explicitly assigning Oxidation States to the Nitrogen in each species participating in the reaction. Unlike Copper, Gold will not dissolve in Nitric Acid. *Aqua Regia* is instead required. What is *Aqua Regia* and how does it act on Gold?

3. In each of the following interhalogen compounds, identify the Oxidation State of the Iodine
   - IF \( x_1 = \) ____
   - IF_3 \( x_1 = \) ____
   - IF_5 \( x_1 = \) ____
   - IF_7 \( x_1 = \) ____

What do you notice about the highest Oxidation State achieved by Iodine? Could it go higher?