EXPERIMENT 7

Periodicity in the Activity (Electromotive) Series of Metals

This experiment is assigned on page 318 of the text.

FOR THE INSTRUCTOR

This experiment can be performed in three ways:

1. The instructor shows the video titled "Periodicity in the Activity (Electromotive) Series of the Elements," found at uscibooks.aip.org/videos/, and has the students, in groups, fill out the worksheets (attached at the end of the experiment). (The instructor should either provide graph paper or a spreadsheet program that will produce a graph of results, and provide a method for the students to report their results and conclusions.)
2. The instructor demonstrates selected reactions and the students, in groups, record and discuss the results, and answer the questions. This experiment is too involved to do in whole as a demonstration, so I select four metals from the list of varying activity but which have no complications (i.e. not Al). Before class I heat a beaker of hot water. The reactions of active metals with the ions of less-active metals take 15 minutes or so, so I do these in large test tubes ahead of time, and show the test tubes after asking the class to devise the procedure.
3. The students perform the experiment in the laboratory (perhaps in pairs), then record their results, discuss the results, and answer the questions.

SOLIDS OR SOLUTIONS REQUIRED: The metals should, in general, be in the form of granules or powders rather than as massive chunks: Ag, Al, Ca, Cu, Hg, Mg, Mn, Na (under toluene), Ni, Pb, Zn. The five solutions needed are:

6 M HCl

1 M $AgNO_3$ (8.5 g/50 mL)

0.5 M $CuSO_4$ (12.5 g 5-hydrate/100 mL)

0.5 M $Hg(NO_3)_2$ (17.1 g 1-hydrate/100 mL, and add enough conc. HNO_3 to dissolve the precipitate that forms).

0.5 M $Pb(C_2H_3O_2)_2$ (16.3 g 3-hydrate, with a few mL conc. acetic acid/100 mL).

FOR THE STUDENTS

PURPOSE. In this experiment, we study the stability of low oxidation states of the metallic elements (i.e., in the zero oxidation state, the metals themselves). We examine the relative reactivity (activity) of different metals with the hydrogen ion and list the different elements in order of decreasing reactivity with the hydrogen ion (such a list is called an activity or electromotive series of elements). In contrast with the usual general chemistry experiment, we also attempt to discover the periodicity in such an activity series so that we can also predict the activities of other metals not yet tested and also gain some insight into the bonding that occurs in metals.

The reaction of some metals with standard 1 M hydrogen ion is dangerously exothermic, so we begin our tests by studying the reactivity of metals with pure cold water, in which the concentration of the hydrogen ion is only 10^{-7} M. In terms of predominant species such a reaction can usually be summarized as

$$M(s) + n\,H_2O \rightarrow M(OH)_n + n/2\,H_2(g) \qquad (A.1)$$

Only very reactive metals undergo this reaction with cold water; their relative activity will be judged by the relative rate of evolution of H_2. If this reaction is not perceptible, we try to speed the rate of the reaction by using hot water.

Metals that show no activity to hot water will then be reacted with cold (roughly 1 M) hydrochloric acid:

$$M(s) + n\,H^+(aq) \rightarrow M^{n+}(aq) + n/2\,H_2(g) \qquad (A.2)$$

If cold hydrochloric acid produces no reaction, then hot hydrochloric acid will be tested.

A certain number of metals fail to react with the hydrogen ion at all; these are said to be less active than hydrogen and are listed below it in an activity series. To rate their relative activity, stronger oxidizing agents than H^+ must be used; we use oxidizing metal ions.

$$n\,M(s) + m\,N^{n+}(aq) \rightarrow m\,N(s) + n\,M^{m+}(aq) \qquad (A.3)$$

Part I. Forming Hypotheses

There are more than 80 metals in the periodic table; testing all these would be very time consuming and very expensive too. If we can find some form of periodicity in the tendency of metals to react with oxidizing agents, we will not need to test all 80 metals or memorize the results. Let us first form hypotheses as to how a metal's activity might relate to each of these fundamental properties of a metal: its position in the periodic table, its ionization potential, and its electronegativity.

A. Recalling general chemistry, describe how metallic properties of an element (such as their activities) relate to their position in the periodic table. Can you use this principle to predict the order of decreasing activity of the elements Ag, Al, Ca, Cu, Hg, Mg, Mn, Na, Ni, Pb, and Zn? Why or why not?

B. The first ionization energy (or first ionization potential) is the energy required to remove one electron from a gaseous atom of an element to produce a +1 ion:

$$M(g) + \text{energy} \rightarrow M^+(g) + e^- \qquad (A.4)$$

How do you think the activity of an element ought to be related to its first ionization potential? Table 6.5 on page 363 of the text presents the first ionization energies of the elements. Predict a decreasing order of reactivity of the above elements based on their first ionization energies.

C. How do you think the Pauling electronegativity of an element and its activity might be related? Predict a decreasing order of reactivity of the above elements based on their Pauling electronegativities. [Lead goes to Pb^{2+} in this experiment, so the Pauling electronegativity for Pb(II) should be used to predict the activity of lead.]

D. The concept of electronegativity is complicated by the fact that there is more than one way of defining and measuring electronegativity. Allred and Rochow's scale of electronegativity is presented later in Table 9.9 on page 559 of the text. Predict a decreasing order of reactivity of the above elements based on their Allred-Rochow electronegativities.

Part Ii. Testing Your Hypothesis

A. Heat a 400-mL beaker of water on a ringstand to near boiling. This will be used from time to time throughout the experiment.

B. The following metals are to be tested: Ag, Al, Ca, Cu, Hg, Mg, Mn, Na, Ni, Pb, and Zn. *Certain metals require special precautions*:

Sodium—Use only a very tiny cube of metal. Do not point the test tube of water at anyone; do this reaction in the hood behind the glass shield.

Aluminum is coated with thin films of tightly adhering oxide that must be cleaned off before its reactions can be observed. To do this, put a few granules of the metal in a large test tube with 2 mL H_2O and 2 mL 6 M HCl. Heat in the hot water bath until vigorous reaction just begins (a few minutes are required), then quickly remove the test tube, dilute the acid with cold distilled water, pour off the diluted acid, half-fill the test tube with distilled water, pour this off, and again half-fill the test tube and pour off nearly all of the water (leave enough to keep the metal out of contact with the air). Observe whether the metal is reacting with this cold water—if not, go immediately to Step **D**.

C. Put a few granules of each of your metals in large test tubes that contain about 5 mL of distilled water. Observe whether bubbling occurs, and if so, which metal gives the most rapid reaction.

D. If you observe no reaction with cold water (or if you observe only a very faint reaction), put the test tube in your hot water bath (which should be very hot but not boiling). Observe whether bubbles of H_2 now form.

E. From any unreactive metals pour off all but about 2 mL of the water, then add 2 mL of 6 M HCl. Observe over a period of a few minutes; note the relative bubbling rates.

F. For any metals that are still unreactive, put the test tube in the beaker of almost-boiling water and heat for a few minutes. Note relative bubbling rates.

G. Arrange the above 11 metals, insofar as possible, in order of decreasing reactivity (an activity series).

H. In each of six test tubes, place 2 mL of 0.5 M $Pb(C_2H_3O_2)_2$ solution. To each test tube, add a few granules (or one drop) of the following six metals: Cu, Hg, Ag, Mg, Mn, and Zn. Observe whether reaction occurs (wait 10 mins before deciding "no reaction"). The Pb^{2+} ion [in $Pb(C_2H_3O_2)_2$] is capable of oxidizing which of these metals? What is the observed product? Write balanced equations for the reactions that occur.

I. As a generalization, how does the activity of metals which react with the Pb^{2+} ion compare with the activity of Pb itself?

J. Devise a series of experiments by which you can determine the relative positions of the metals Ag, Cu, and Hg in the activity series, using any of the following reactants: Ag(s), Cu(s), Hg(l), 1 M $AgNO_3$, 0.5 M $Hg(NO_3)_2$, 0.5 M $CuSO_4$. Carry out and describe the experiments and your results, and complete the activity series in Step G.

Part III. Conclusions

Decide which periodic property of a metallic element (periodic table position, ionization potential, Pauling electronegativity, Allred–Rochow electronegativity) correlates most strongly with the activity of metals. Justify your choice.

Part E Questions that are included in Exercise 6.32, page 375

1. Based on your conclusions, predict the products of the following reactions (if they go), and describe the vigor of the expected reaction: (a) Cu + AuCl; (b) La + H_2O; (c) Au + HBr; (d) Ti + HCl; (e) Be + H_2O; (f) U + HCl; and (g) Pt + $Hg(NO_3)_2$.
2. Many of the metals can be conveniently prepared by the thermite reaction:

$$2\,Al + (e.g.)\ M_2\,O_3 \rightarrow 2\,M + Al_2\,O_3 \qquad (A.5)$$

   Which of the following metals could be produced in this way: (a) Sc; (b) La; (c) U; (d) Cr; (e) Fe; (f) Ca; and (g) Bi.
3. Many of the least-active metals have been prized by humans for ages for their durability (and scarcity); these are sometimes referred to as the noble metals. Which of the metals would most likely fail to react with oxygen (under neutral conditions) and hence might be called noble metals?

Alternate Version of the Experiment

This version is for students who carried out an activity series experiment in general chemistry. Go through this experiment omitting Part II, the experimental part; substitute your data sheet (or a textbook activity series) for this experiment. Draw up your hypothesis in Part III for the elements you tested or for the elements in your textbook activity series.

PERIODICITY IN THE ACTIVITY (ELECTROMOTIVE) SERIES OF METALS WORKSHEET

Name of team __________________________

Members of team __________________________

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Your goals:

- To examine relative reactivity (activity) of the different metals with the hydrogen ion.
- To list the different elements in order of decreasing reactivity with the hydrogen ion. Such a list is called an activity or electromotive series of elements.
- To discover the periodicity in such an activity series.

PERIODICITY IN THE ACTIVITY (ELECTROMOTIVE) SERIES OF METALS WORKSHEET

Name of team ______________________

Part I

Formulating a hypothesis on how a metal's activity might relate to its atomic properties

Choose one of the following atomic properties which you hypothesize might most affect its activity.

- The size of the metal ion formed.
- The charge of the metal ion.
- The Pauling electronegativity of the metal.
- The Allred-Rochow electronegativity of the metal.
- The ionization energy of the metal atom.

Write your observations in the table.

Fill in the blanks in the following statements.

We hypothesize that the activity (reactivity) of a metal will **increase** when its

(choose one of the above atomic properties) ____

(choose "increases" or "decreases") ____

The reason that this might be so is ____

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You have 5 minutes to decide!

PERIODICITY IN THE ACTIVITY (ELECTROMOTIVE) SERIES OF METALS WORKSHEET

Name of team ________________________

Part I

Predicting an activity series of selected metals based on your hypothesis

(Example: $Ag < Al \leq Au \ll Ac$)

The metals you have to test and the ions that they form upon reacting are the following:

Metal and ion	Radius of ion	Charge of ion	Pauling Electronegativity	Allred–Rochow Electronegativity	Ionization energy*
$Ag \rightarrow Ag^{+}$	129		1.93	1.42	731
$Al \rightarrow A1^{3+}$	67		1.61	1.47	578
$Ca \rightarrow Ca^{2+}$	114		1.00	1.04	590
$Cu \rightarrow Cu^{2+}$	87		1.90	1.75	746
$Hg \rightarrow Hg^{2+}$	116		2.00	1.44	1007
$Mg \rightarrow Mg^{2+}$	86		1.31	1.23	738
$Mn \rightarrow Mn^{2+}$	97		1.55	1.60	717
$Na \rightarrow Na^{+}$	116		0.93	1.01	496
$Ni \rightarrow Ni^{2+}$	83		1.91	1.75	737
$Pb \rightarrow Pb^{2+}$	133		1.87	1.55	716
$Zn \rightarrow Zn^{2+}$	88		1.65	1.66	906

*Units are kJ/mol.

Your predicted activity series (order of increasing reactivity):

____

PERIODICITY IN THE ACTIVITY (ELECTROMOTIVE) SERIES OF METALS WORKSHEET

Name of team ________________________

Part II
Testing your hypothesis

- Write your observations in the table.
- Make notes about the relative rates of reactivity of the metals.

Metal	Reaction with *cold* water	Reaction with *hot* water	Reaction with *cold* HCl	Reaction with *hot* HCl	Reaction with Ag^+	$\mathcal{E}^o$	Observations
Ag							
Al							
Ca							
Cu							
Hg							
Mg							
Mn							
Na							
Ni							
Pb							
Zn							

Your observed activity series (order of increasing reactivity):

____

PERIODICITY IN THE ACTIVITY (ELECTROMOTIVE) SERIES OF METALS WORKSHEET

Name of team ________________________

Part III
Graphing your data

- On the graph, plot the $\mathcal{E}^o$ values for the metals you tested versus their values of the atomic property you selected.
- Decide from the appearance of this plot whether the data support or refute your hypothesis.

If you believe your hypothesis:

- State your conclusion at the bottom of the graph, in the form:

  "We confirm that the activity of a metal tends to increase when its ________________________ (choose an atomic property) ________________________ (increases *or* decreases)."
- You are done. Turn in your plot and conclusion to the instructor.

If you decide that your graph refutes your original hypothesis, you still have a chance to win:

- Select an alternate atomic property to which activity could be related.
- On the graph, plot the $\mathcal{E}^o$ values for the metals you tested versus their values of the alternate atomic property you selected. Be sure to label the axes of your plot.
- Decide from the appearance of this plot whether the data support or refute your hypothesis.
- State your conclusion at the bottom of the graph, in the form:

  "We find that the activity of a metal tends to increase when its ________________________ (choose an atomic property) ________________________ (increases *or* decreases)."
- Turn in your new plot and conclusion to the instructor.

After all graphs have been turned in, the winning hypothesis will be revealed!