Experiment 5: Periodicity In The Activity Of The Elements[1]

In this experiment we will study the stability of *low* oxidation states of the metallic elements - i.e., in the zero oxidation state, the metals themselves. We will examine the relative reactivity (*activity*) of different metals with the hydrogen ion and will 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). But in contrast with the usual general chemistry experiment, we will 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 will 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

$$M(s) + nH_2O(l) \rightarrow M(OH)_n(\text{s or aq}) + \frac{n}{2}H_2(g)$$

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 will 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.

$$M(s) + nH^+(aq) \rightarrow M^{n+}(aq) + \frac{n}{2}H_2(g)$$

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 will use oxidizing metal ions.

$$nM(s) + mN^{n+}(aq) \rightarrow mN(s) + nM^{m+}(aq)$$

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 energy, and its electronegativity.

Dry Lab

1. 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?

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

   $$M(g) + \text{energy} \rightarrow M^+(g) + e^-$$

   How do you think the activity of an element ought to be related to its first ionization energy? Predict a decreasing order of reactivity of the above elements based on their first ionization energies.

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[1] Adapted from *Inorganic Chemistry*, G. Wulfsberg, University Science Books, Sausolito, CA, 2000.

3. 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.

4. The concept of electronegativity is complicated by the fact that there is more than one way of defining and measuring electronegativity. Predict a decreasing order of reactivity of the above elements based on their Allred - Rochow's electronegativities.

Wet Lab

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

2. The following metals are to be tested: Ag, Al, Ca (scrape this as clean as possible), Cu, Hg, Mg, Mn, Na, Ni, Pb, and Zn. *Certain metals require special precautions:*

   • *Sodium* Use only a very tiny cube of metal. Do this reaction in the beaker of water in the hood, behind the glass shield. Cut some fresh sodium and note its color.

   • *Aluminum* is coated with a thin film of tightly adhering oxide that must be cleaned off before its reactions can be observed. To do this, put a tightly crumbled piece of foil 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, 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 the water (leave enough to keep the metal out of contact with the air). Observe whether the metal is reacting with this cold water.

3. Put each of your metals in large test tubes that contain ~ 5 mL of distilled water. Observe whether bubbling occurs, and if so, record which metal gives the most rapid reaction.

4. 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. Observe whether bubbles of H_2 now form. You will also see large static bubbles of hot H_2O forming on the surface of many of the metals.

5. From any unreactive metals (or those that you are not sure about) pour off all but ~ 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.

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

7. Arrange the above eleven metals, insofar as possible, in order of decreasing reactivity (an *activity series*).

8. 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 the following six metals: Cu, Hg, Ag, Mg, Mn, and Zn. Observe whether a reaction occurs (wait 5 minutes 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.

9. As a generalization, how do the activities of metals that react with the Pb^{2+} ion compare with the activity of Pb itself?

10. Devise a series of experiments by which you could 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 the experiments and complete the activity series in part 7. Where would you put Hydrogen in this series?

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.

Additional Questions

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
   g. Pt + $Hg(NO_3)_2$

2. Many of the metals can be conveniently prepared the *thermite* reaction:

$$2\,Al + M_2O_3 \rightarrow 2\,M + Al_2O_3$$

   Which of the following metals could be produced in this way:
   a. Sc
   b. La
   c. U
   d. Cr
   e. Fe
   f. Ca
   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 metals would most likely fail to react with oxygen (under neutral conditions) and hence might be called noble metals?