A miser is ever in want.
--Greek proverb

Redox Reactions

Reactions involving oxidation and reduction processes are very important in our everyday world. They make batteries work and cause metals to corrode (or help to prevent their corrosion). They enable us to obtain heat by burning fuels--in factories and in our bodies.

Many redox reactions are complex. However, *combustion* and *synthesis* (from elements) are two ordinary examples which require very little description. Just a little more involved are the *displacement* reactions, with which this exercise is mainly concerned. Your text book divides these processes into three categories:

- hydrogen displacement
- metal displacement
- halogen displacement

You may remember (?) how to tell if a chemical reaction is occurring by looking at the behavior of a combination of chemicals, but can you *predict* whether or not a reaction like those above will happen?

Displacement reactions involve an element, and a compound containing a "similar" element. "Similar" can mean both metals, or it can simply mean both + or both -. In any case, the general rule that applies is *like displaces like*.

Copper and silver are both metals (both positive in compounds) and are both used for coinage and jewelry. So what will happen if a drop of solution containing silver ions is placed on a piece of copper metal? What will happen if a drop of solution containing copper ions is placed on a piece of silver metal?

Chlorine and bromine are both non-metals (both negative in compounds) and both are used for disinfecting and bleaching. What will happen if chlorine is added to a solution containing bromide ions? What will happen if bromine is added to a solution containing chloride ions?

Permanganate ions (MnO_4^-) react with iron(II) ions (Fe^{2+}) in acid solution. What about the *ratio* in which these ions react? Does the balanced equation correctly predict what happens?

Your task is to answer questions like these about the substances available during this experiment.

Preparing to experiment

You will be provided with the following materials:

1. strips of copper, silver, magnesium and zinc metal
2. synthetic steel wool for cleaning the metal strips
   (DO NOT WET THIS)
3. solutions of $Cu(NO_3)_2$, $AgNO_3$, $Mg(NO_3)_2$, $Zn(NO_3)_2$, HCl
4. solutions containing Cl_2, Br_2 and I_2 (use about 5 drops)
5. solutions of NaCl, KBr, KI (use about 5 drops)
6. hexane (use about 5 drops)
7. small test tubes
8. disposable plastic beral pipets
9. solutions of MnO_4^- and Fe^{2+} ions in equal concentrations
   (i.e., 1 drop of MnO_4^- solution contains the same number of ions as 1 drop of Fe^{2+} solution) [start with at least 50 drops of Fe^{2+}]
10. hand lens

Design an experiment that will enable you to decide which metals will displace each other from solution and which will displace hydrogen from acid solution. (*hint:* the easiest way to do this is to place a drop of each solution on each cleaned metal strip)

Design an experiment that will enable you to decide which halogens will displace each other from solution (see Technique section).

Design an experiment that will enable you to predict the ratio between MnO_4^- and Fe^{2+} in a balanced redox reaction for acidic solution. (hint: MnO_4^- is purple, Fe^{2+} is almost colorless and the products of their reaction are colorless) [*hint:* try a titration!]

Pre-lab take-home quiz

Answer these questions on a separate piece of paper to be turned in the day you do this experiment.

1. What distinguishes a redox reaction from a non-redox reaction? (*hint*: it has to do with electrons—check your reading assignment!!)

2. The evidence that a redox reaction has occurred is similar to the evidence for *any* chemical reaction. There are at least four things to look for when trying to decide if any kind of chemical reaction has happened. What are they?

3. Are all reactions that form compounds from elements redox? Explain.

Techniques

1. Extraction

Sometimes dissolved material is more soluble in one kind of liquid than another. It is also possible that certain properties are more pronounced in a different liquid. Such is the case with the halogens used in this experiment. Each of the halogens has a characteristic color that is best observed in a liquid like hexane rather than one like water. But water and hexane do not mix. However, if the two liquids are shaken with one another, and a halogen is present in the water, it will move into the hexane layer (where it is more soluble) and show its particular color.

In the past such "extractions" have been done by shaking a mixture of the liquids in a stoppered test tube. However, if small amounts (less than 1 mL) of both liquids are used, it is possible to use a plastic pipet or dropper and alternately suction and expel the mixture in rapid sequence, perhaps three times, then let the liquids separate. Hexane is less dense than water and will float to the top where any distinctive color may be noted.

The chemicals

Silver is one of the few metals that can be found native and is also found associated with copper, gold, or lead. It constitutes 1 x 10^{-5} % of the earth's crust. It is more malleable and ductile than any metal except gold and when pure is perhaps the best electrical conductor. It is insoluble in acids except nitric or hot concentrated sulfuric. Most silver salts are light sensitive (they darken on exposure to light) and this property makes them useful in the manufacture of photographic film. Small crystals of silver chloride are used in some photochromic eyeglasses. Absorption of light causes the AgCl to dissociate into Ag and Cl. The finely dispersed silver atoms tint the glass gray. The reverse reaction occurs in subdued light.

Silver has been used in coinage for centuries as well as for jewelry (most often alloyed with gold or copper) and in the manufacture of some laboratory vessels. It is also an ingredient in dental amalgams for filling teeth. Silver has been used to purify drinking water (about 1 part per 20 million), is used in a process for purifying swimming pool water (instead of chlorine) and appears to have no serious toxicity. However, prolonged absorption of silver compounds can lead to grayish-blue discoloration of skin. Many silver salts are irritating to the skin.

Magnesium is one of the most common elements in the crust of the earth, making up about 2.1% of it. In addition to its occurrence in minerals, it is also found in sea water, and in animal and plant organisms.

Magnesium is a silvery-white metal which slowly oxidizes in moist air. It reacts very slowly with water at room temperature, less slowly at 100^{o}C and burns in a current of steam. It reacts readily with dilute acids liberating hydrogen gas. Magnesium also reduces carbon monoxide, carbon dioxide, sulfur dioxide, and nitrogen oxides at red heat. It reacts directly with nitrogen, sulfur, the halogens, and many other elements.

Magnesium is a constituent of light metal alloys, used for manufacturing precision instruments, optical mirrors, in fireworks, flash bulbs and flares.

Copper(II) nitrate (the source of Cu^{2+} in this experiment) is generally sold in hydrated form and is deliquescent (it absorbs water from the environment). It is blue and very soluble in water. It is used in light-sensitive reproductive papers, as a coloring in ceramics, as a mordant in dyeing and printing, and in wood preservatives as a fungicide and herbicide. It is irritating to the skin.

Silver nitrate (the source of Ag^{+} in this experiment) forms colorless, transparent crystals. It is stable and not darkened by light in pure air but darkens in the presence of organic matter and H_2S. It decomposes at low red heat into metallic silver. It is used in photography and the manufacture of mirrors, silver plating, indelible inks, hair dyes, etching ivory and as an important reagent in analytical chemistry.

It has been used as a topical antiseptic in a 0.1 to 10% solution. However, it is caustic and irritating to skin. Silver nitrate stains skin and clothing. These stains will wear off skin in a few days to a week but clothing is generally ruined. Swallowing silver nitrate can cause severe gastroenteritis that may end fatally.

Magnesium nitrate (the source of Mg^{2+} in this experiment) consists of colorless, clear, deliquescent crystals which are readily soluble in water and alcohol. It is used in pyrotechnics.

Zinc nitrate consists of colorless, odorless crystals which are readily soluble in water and very hygroscopic (quickly absorbs water from the air). It is used as a mordant in dyeing. Speaking of a *mordant*, don't you wonder what that is???? Everything seems to be a mordant! Dyes have to be "fixed" in their fabrics or they will wash out. A mordant reacts with the dye to form an insoluble compound, and thus helps prevent it from washing out.

Potassium Bromide (the source of Br^{-} in this experiment) is a white solid which is very soluble in water. It is used in the manufacture of photographic papers and in some engraving processes.

Potassium iodide (the source of I^{-} in this experiment) is a white solid, slightly deliquescent, and prone to oxidation in air. It is used in the manufacture of photographic emulsions, and in table salt and some drinking water to help prevent iodine deficiency disease.

Chlorine is the eleventh most abundant element, making up about 0.19% of the earth's crust. Sea water contains nearly 3% NaCl. It is produced on a large scale by electrolysis of molten chloride or brines. Small amounts for use in the laboratory are often produced by the reaction of MnO_2 and HCl.

Chlorine is a yellowish-green diatomic gas at room temperature. In dilute water and hexane solutions it is essentially colorless. It has a suffocating odor. It forms explosive mixtures with hydrogen and many finely divided metals will burn in chlorine. It combines with all other elements except the noble gases. It is a member of the halogen family.

Chlorine is used for bleaching, purifying water, and making synthetic rubber and plastics. It is a powerful irritant and excessive exposure can cause death.

Bromine is a dark reddish-brown fuming liquid at room temperature, consisting of diatomic molecules. In dilute water and hexane solutions its color varies from golden to dark orange. It is a member of the halogen family and has a chemistry similar to chlorine. It attacks all metals and organic tissues and vaporizes readily at room temperature. Fumes are highly irritating to eyes and lungs.

Bromine is used for bleaching silk, disinfecting spas, and manufacturing anti-knock compounds. Pure liquid bromine on the skin can cause painful, serious burns which heal only slowly. Even aqueous solutions (like in this experiment) should be handled carefully to avoid direct contact.

Iodine [see previous experiment on zinc iodide]

Sodium chloride (the source of Cl^- in this experiment) is, of course, common table salt (the non-iodized version). It occurs in nature as the mineral *halite* and is produced by mining underground deposits as well as from sea water by solar evaporation. It is white in small granular form but large crystals are translucent. The salt sold in the grocery store usually contains some calcium and magnesium chlorides which help absorb water and prevent caking.

Natural salt is the source of essentially all chlorine and sodium as well as of all, or nearly all their compounds (including HCl). It is used for preserving foods (salt curing), in the manufacture of soaps and dyes, in freezing mixtures (for making ice cream!) in dyeing and printing, and in some metallurgy.

Potassium permanganate consists of dark purple or bronze-like crystals and is a strong oxidizing agent. It is used extensively in laboratory work and also in dyeing wood, bleaching, photography, and tanning. Dilute solutions are mildly irritating to the skin and high concentrations are caustic. Potassium permanganate stains skin and clothing like silver nitrate.

Analysis

These questions should be answered in your laboratory notebook following your observations.

1. It is possible to "rank" the metals (and hydrogen) based on their reactions. Look over your observations from the first part of this experiment and list the metals from most reactive to least reactive. Include hydrogen in this list. Compare your list to the activity series on p. 113 in your text and discuss any differences.

2. Write balanced net-ionic equations for the reactions you observed between the metals and their ions (including H^+).

3. It is also possible to "rank" the halogens in a manner similar to the metals, with the most reactive halogen followed by less reactive ones. Use your observations to do this [how can you decide whether the color in the hexane is due to the halogen you added or the product of a possible reaction????]. Fluorine was not used in this experiment. Based on your observations and referring to the periodic table, where do you think fluorine would be placed in your series?

4. Write balanced net-ionic equations for the reactions you observed between the halogens and their ions.

5. Write a balanced redox reaction between MnO_4^- and Fe^{2+} in acidic solution [among the products are Mn^{2+} and Fe^{3+}]. Discuss the ratio between these two ions in the final balanced equation in light of your observations when you mixed the two solutions.