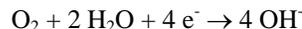


The truth that many people never understand, until it is too late, is that the more you try to avoid suffering the more you suffer because smaller things begin to torture you in proportion to your fear of suffering. --Thomas Merton

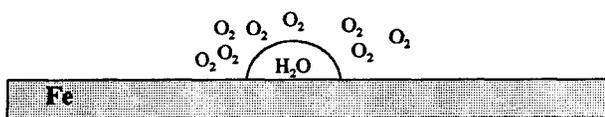
Corrosion of Iron

So far we have looked at electrochemical processes which are useful in some way. Spontaneous reactions occurring in galvanic cells generate electric potential. Non-spontaneous reactions which we can force to occur in plating or other electrolytic cells also have their utility. But by far the most significant and undesirable spontaneous electrochemical process is *corrosion*. The most common example is the rusting of iron metal or iron alloys such as ordinary carbon steel. Corrosion costs this country billions of dollars each year in replacement and maintenance costs. From a purely economic point of view, then, it would be helpful to understand corrosion processes.

Most metals react with oxygen, as a glance at the Standard Reduction Potential table will show. The reduction half-reaction of oxygen in moist air has a potential of +0.40 V:



With the notable exceptions of gold and silver, most common metals will form spontaneous redox couples with this half-reaction. In dry air corrosion is very slow or nonexistent (why?). One way to visualize what is happening in the corrosion of a metal like iron is to focus on what happens in and around a drop of water on the metal surface:

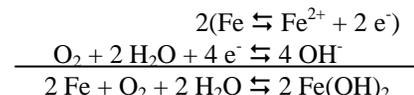


The oxygen in the air around the water slowly diffuses into the drop. It is the liquid water that brings the dissolved gas into contact with the metal. At the surface of the iron beneath the water drop the following half-reaction may occur:

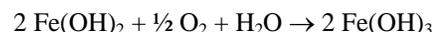


The potential for this half-reaction is +0.44 v. Taken together the two processes constitute only the first step in the creation of what we commonly refer to as "rust".

The net reaction for this first simple step is therefore:



Iron(II) hydroxide is insoluble but its green color is almost never observed because it is ordinarily further oxidized by the oxygen:



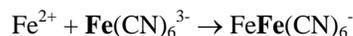
The final product (when dry) has the reddish-brown flaky character we associate with rust. Although the reaction that produces Fe(OH)₂ is technically an equilibrium process (all electrochemical processes are) the value of K_c is very large (>10⁹⁹ at 298 K) and left unchecked it will go to completion. But the rate is relatively slow under normal atmospheric conditions and so it is still possible to manipulate the equilibrium somewhat by changing appropriate factors.

The *rates* of corrosion reactions--and presumably their mechanisms--vary widely. Factors which influence the progress of the net reaction in the first step of the oxidation of iron may have an effect on the overall rate. The nature of the oxide product is also very important in affecting the extent of the corrosion. For example, aluminum is a very active metal, but its oxide, Al₂O₃, is very dense and forms a thin protective layer on the metal which discourages further corrosion. In contrast, iron rust (hydrated forms of Fe₂O₃ such as reddish-brown Fe(OH)₃) is typically flaky and easily crumbles off to continually expose fresh metal for reaction.

Although the mechanism for corrosion is not always well understood, it is clear how to prevent it. The surface of the metal must be protected from contact with oxygen. Paints, oils and other coatings are often used for this purpose. But it is also possible to take advantage of the electrochemical nature of the process by providing competition for the unwanted reaction in the form of an oxidation that requires less energy than the corrosion of the metal. For example, buried steel pipes can be protected from corrosion by attaching a piece of a more active metal to them. As the more active metal is oxidized, it continually supplies electrons to the steel pipe, thus preventing (or at least slowing) its oxidation [recall, oxidation is the *loss* of electrons].

What conditions favor corrosion? What kinds of metal combinations work best for corrosion protection? These are some of the questions you will investigate in this experiment.

You can follow the progress (or lack of progress) of the reaction by using an interesting indicator called "ferroxyl". The solution contains phenolphthalein and potassium hexacyanoferrate(III)--K₃[Fe(CN)₆]. The hexacyanoferrate(III) ion reacts with Fe²⁺ ions to form an intense blue complex ion called *prussian blue* which has been used for years in carbon papers, blue-printing inks, typewriter ribbons, and artists pigments:



The indicator is very sensitive and will detect extremely small quantities of Fe²⁺. The additional presence of phenolphthalein may help you to further follow the progress of the corrosion process.

Preparing to experiment

You will be provided with the following materials:

1. 0.10 M HCl solution*
2. the following solutions or liquids containing "ferroxyl":
distilled water
tap water
0.10 M NaCl
0.10 M NaOH
3. "ferroxyl" indicator
4. strips of iron metal
5. thin strips of the following metals: Cu, Zn, Mg, Sn
6. four small alligator clips
7. steel wool
8. hand lens

*see **Technique** section

Design a series of experiments to investigate the following:

- the relative rate of corrosion with the available liquids or solutions
- the ability of various metals to "protect" iron from corrosion (see **Technique** section) (*hint*: pick the solution from above that has the *second* fastest rate of reaction)

Technique

1. Preparation of the iron strips

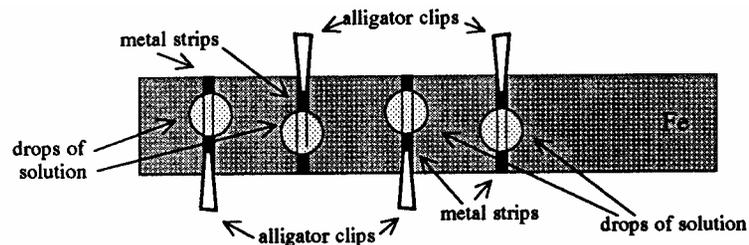
It is very important to clean the iron strips thoroughly before beginning any part of the experiment. Use steel wool to clean the entire surface and be especially vigilant about any signs of rust. Wipe off the strip with a dry paper towel before experimenting to avoid interference by pieces of steel wool. It is equally important to rinse and dry the strips completely when you are finished with the experiment.

2. Using HCl with "ferroxyl" indicator

The HCl solution does not have the indicator pre-mixed because of the remote possibility that small amounts of toxic HCN gas might be generated on long standing in the bottle. You should place a drop of HCl on the strip where you want it and then add a small drop of indicator to it.

3. Testing for corrosion protection by other metals

In order to obtain meaningful results you must have good electrical contact between the thin metal strips and the iron strip. Cleaning the metals with steel wool is a very good idea. Then use the small alligator clips to attach the strips to the iron. Be sure the clips actually "bite" into the metal (especially with the Sn which is quite thin) and hold the thin strips against the iron. You can test all of the metals on one strip using an arrangement such as shown below:



Notice that the drops of whatever solution you choose should extend far enough to contact both the thin metal strip and the iron. The alligator clips have been placed on alternate sides to help keep the Fe strip level so that the drops will not run off. You will find that the thin metal strips are longer than the width of the Fe strip. You should fold the extra length over the edge to help hold the thin strip against the iron.

4. Clean up

Once again, it is VERY important that the strip be rinsed thoroughly at the end of the experiment and dried completely. Iron will rust rapidly in the lab because of the chemical fumes present in small concentrations. If the thin metal strips have survived they can also be cleaned and dried for re-use. You should also rinse the dry the alligator clips if they get solution on them.

The Chemicals

Potassium hexacyanoferrate(III) is a solid consisting of ruby-red crystals. Aqueous solutions slowly decompose on standing and are somewhat light sensitive. It is used chiefly for blueprints, in photography, calico printing, in electroplating and for the tempering of iron and steel.

Analysis

1. Which solution showed the slowest rate of corrosion? The fastest? How do the solutions in between rank? Explain why you think the results turned out the way they did. Your explanation should take into account the electrochemical nature of corrosion and the net reaction for the first step of iron corrosion. Be sure to mention the sodium hydroxide solution in particular.

2. The blue color of the "ferroxyl" indicator tells you that Fe^{2+} has been produced. The pink color of phenolphthalein indicates that the solution is becoming basic. Explain the appearance of the drops in which corrosion occurred. Specifically, why are the colors segregated the way they were?

3. Why is the sodium hydroxide solution pink?

4. Sodium chloride and calcium chloride are commonly used to de-ice roads in the eastern part of the country (by lowering the freezing point of the slush). When this salty slush is splashed up onto automobiles it has an undesirable effect on them. Based on your observations, why is this so?

5. Explain your observations for the "protected" metal combinations in light of the activity series.

6. Magnesium is a very active metal which, like aluminum, rapidly develops an oxide coating that prevents further corrosion AND masks the reaction of the metal with water (remember the **Periodic Properties** experiment?). When employed as a sacrificial metal, however, the preferential oxidation of magnesium provides a constant clean surface. What evidence did you see for the reaction of magnesium with water when used to protect the iron?

7. Go to the Standard Reduction Potential table in your text and find the water half-reaction that will combine with the oxidation half-reaction of magnesium and account for all of the observations you made (including any color changes). Write the net reaction that occurs between magnesium and water.

[This protective aspect of magnesium versus iron actually has a relatively recent practical application that is not connected with corrosion. The U.S. Army developed (along with Zesto Therm company) a heat pack for warming the infamous MREs or "meal, ready-to-eat". The heater consists of magnesium metal, sodium chloride and powdered iron all mixed into a porous pad enclosed in cardboard. When water is poured onto this package and it is placed underneath an MRE it quickly heats up as the reaction you have observed takes place. $\Delta H = -355 \text{ kJ/mol Mg.}$]