Experiment 21H

FV 2/8/11

ELECTROCHEMISTRY: CORROSION

MATERIALS: Ag, Cu, Zn strips; sandpaper; 20d bright common nails; 3 M HCl; 0.5 M NaCl; DC power supply; various electrical leads; plastic pipets; digital multimeter; phenolphthalein in dropper bottles; 50 mL (2), 400 mL beakers; 25 mL graduated cylinder

PURPOSE: The purpose of this experiment is to illustrate the principles and practical aspects of corrosion.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Explain how atmospheric corrosion occurs, and how it results in the eating away of metal.
2. Describe the use of galvanic protection and impressed voltage for corrosion prevention.

PRE-LAB: Complete the Pre-Lab Assignment before coming to lab.

DISCUSSION:

Atmospheric corrosion and chemical corrosion. Atmospheric corrosion occurs when dissolved oxygen is reduced at the cathode of an electrochemical cell. In the absence of other reducible chemical species, dissolved oxygen is a viable candidate for reduction, via the half-reaction

$$O_2\,(aq) + 2\,H_2O + 4e^- \rightarrow 4\,OH^- \qquad (1)$$

If a metal sufficiently high on the activity series, such as iron, is electrically coupled to a region in contact with dissolved oxygen, the metal will undergo oxidation (i.e., it will corrode). For the case of iron, the oxidation reaction is

$$Fe\,(s) \rightarrow Fe^{2+}\,(aq) + 2e^- \qquad (2)$$

Even if the anode and cathode regions of a cell are made from the same type of metal, atmospheric corrosion will occur if there is a nonuniformity in the dissolved oxygen concentration, such as occurs with the hull of a ship where the dissolved oxygen concentration is greater near the water surface. These concentration differences are enough to cause the different regions of the same piece of metal to act anodically or cathodically. Although atmospheric corrosion is certainly caused by chemical action, the term chemical corrosion is usually used to describe a different process, one that results in the liberation of hydrogen and the uniform destruction of the metal. The oxidation reaction is the same as equation (2), but the reduction reaction is

$$2H^+\,(aq) + 2e^- \rightarrow H_2\,(g) \qquad (3)$$

An example would be corrosion of iron by battery acid. For more information about naval applications of electrochemistry and corrosion, go to the website http://www.chemistry.usna.edu/navapps/PDF/Corrosion.pdf .

Corrosion Prevention. There are a number of methods used to stop or slow down the spontaneous corrosion of iron. Barrier methods, such as coating the metal with paint or grease, are the simplest means to protect the iron. These work by preventing the three necessary reactants of atmospheric corrosion, iron, water and oxygen, from coming together. Among the most important electrical methods, widely used in the Navy (and elsewhere), are galvanic protection and impressed voltage. With galvanic protection, the Fe is electrically coupled to a more active element, typically Zn. The Zn corrodes sacrificially, protecting the Fe. Zinc plates are attached to the hulls of ships, both large and small, to perform this function. With impressed voltage, an electrical power supply is connected to the iron, and continually feeds electrons to it. This maintains the iron in a reduced state. This method of protection is typically used when ships are tied up in port.

PROCEDURE:

Atmospheric Corrosion

1. In a single, 400 mL beaker about ½ full of distilled water, place Cu and Zn strips, making sure that they are not in contact with each other. Place the beaker on a sheet of white paper (not the hood sill!) and attach the leads to the digital multimeter. Measure the positive voltage, if any, noting which lead is attached to which metal.

✍ **Answer in-lab question #1 on page 4.**

2. Add a few drops of phenolphthalein indicator to the liquid in the beaker and wait for about a minute. Do not agitate the solution. Is there any evidence to confirm that the half-reaction you have proposed does, in fact, occur? Now switch the multimeter to the appropriate current (amps) setting, and wait for about a minute (again, don't agitate). Record the measured amperage, and any observations that provide evidence to confirm that the half-reaction you have proposed does occur. Shake both of the metal strips to disperse any buildup of chemical products, and switch the multimeter back to the voltage setting to see if the reaction continues.

✍ **Answer in-lab question #2 on page 4.**

3. Repeat steps 1 and 2, but this time immerse the Cu and Zn metal strips in a solution of 0.50 M NaCl, instead of distilled water. Again, use white paper, don't agitate the liquid, and look carefully. How do your observations differ from those previously made? Save your 0.50 M NaCl solution for the next part.

4. Study the effect of non-uniform dissolved oxygen concentration as follows. In the small plastic container found in the student drawer under the hood, add 0.50 M NaCl solution until the depth is about ½". Immerse two strips of Zn metal in this solution, on opposite sides of the plastic container. (Either fully immersed or standing up along the long edge is OK.) Attach the leads from the digital multimeter so that the voltage is positive. Once connected, avoid agitating the liquid. Measure and record the voltage. Now, with a plastic pipet or pipet bulb, slowly squeeze bubbles of air in the liquid right next to one of the zinc strips. Record any effect this has on the voltage. Confirm this effect by slowly squeezing out air bubbles next to the other zinc strip.

✍ **Answer in-lab question #3 on page 4.**

5. Add a few drops of phenolphthalein indicator to the solution. Switch the multimeter to the appropriate current (amps) setting, allowing the cell to actively discharge. Continue bubbling air near one of the zinc strips.

✍ **Answer in-lab question #4 on page 4.**

Chemical Corrosion and Galvanic Protection

6. Place 25.0 mL of 3 M HCl in a 50 mL beaker. Use distilled water to completely fill another 50 mL beaker and place it adjacent to the first. Take a 4" iron nail and lightly sand the bottom 1.5" to clean the surface. Use a <u>dry</u> paper towel to wipe off any sanding residue and weigh the nail on the analytical balance. Do not touch the prepared surface after cleaning. Take a Zn strip and clean, weigh and handle the Zn in the same manner.

Initial weight of nail_____ Initial weight of Zn strip_____

In kinetics, timing matters! Read the next step in its entirety before doing anything.

7. You are going to measure the rate of corrosion of the two metals when they are subject to chemical attack for a 2 minute period, so have a clock ready to time the experiment. Simultaneously immerse the cleaned ends of the two metal strips into the beaker containing the HCl solution. Keep them in the solution for exactly 2 minutes, agitating them both periodically. MAKE SURE THAT THE METALS DO NOT TOUCH EACH OTHER. Observe and record the behavior at each metal. After the 2 minute period has elapsed, remove both metals from the HCl solution and immediately place them in the distilled water bath prepared earlier. Swish them around to remove any traces of the HCl. Remember not to handle the reacted surfaces.

8. Use a paper towel to THOROUGHLY dry the metals, and weigh them again on the analytical balance.

Final weight of nail_____ Final weight of Zn strip_____

9. Take the Fe nail and Zn strip just reacted and clean the same area of each as done before. (Lightly sand, wipe with a dry paper towel, and do not handle the cleaned ends.) Weigh them again on the analytical balance. Use a wire with alligator clips on both ends to connect the head of the nail to the uncleaned top of the Zn strip.

Initial weight of nail_____ Initial weight of Zn strip_____

In kinetics, timing matters! Read the next step in its entirety before doing anything.

10. You are going to repeat the measurement of the rate of corrosion, but now with the metals electrically connected. Simultaneously immerse the cleaned ends of the two metal strips into the beaker containing the HCl solution. Keep them in the solution for exactly 2 minutes, agitating them both periodically. Observe and record the behavior at each metal. After the 2 minute period has elapsed, remove both metals from the HCl solution and immediately place them in the distilled water bath prepared earlier. Swish them around to remove any traces of the HCl. Remember not to handle the reacted surfaces.

11. Use a paper towel to THOROUGHLY dry the metals, and weigh them again on the analytical balance. Discard the HCl solution down the drain, flushing with water.

Final weight of nail_____ Final weight of Zn strip_____

✍ **Answer in-lab questions #5 and #6 on page 5.**

Impressed Voltage for Corrosion Protection

12. Place 25.0 mL of 0.5 M NaCl in a 50 mL beaker. Use distilled water to completely fill another 50 mL beaker and place it adjacent to the first. Use a marker to mark the heads of two 4" Fe nails, to help distinguish them. Lightly sand the bottom 1.5" of each nail to clean the surfaces. Use a <u>dry</u> paper towel to wipe off any sanding residue and weigh the nails (separately) on the analytical balance. Do not touch the prepared surfaces after cleaning.

Initial weight of nail A_____ Initial weight of nail B_____

13. Switch the small power supply to the 3V setting. Locate two leads which have alligator clips at both ends. Use one to connect the red (+) post of the power supply to the head of nail #1; similarly connect the black (-) post to the head of nail #2.

In kinetics, timing matters! Read the next step in its entirety before doing anything.

14. You are going to measure the rate of corrosion of the two nails when subject to chemical attack for a 2 minute period, but now connected to an external (impressed) voltage. Simultaneously immerse the cleaned ends of the two nails into the beaker containing the NaCl solution, and turn on the power supply. Keep them in the solution for exactly 2 minutes, agitating them both periodically. MAKE SURE THAT THE NAILS DO NOT TOUCH EACH OTHER. Observe and record the behavior at each metal, and any changes to the solution After the 2 minute period has elapsed, turn off the power supply, remove both nails from the NaCl solution and immediately place them in the distilled water bath prepared earlier. Swish them around to remove any traces of the electrolyte or residues. Remember not to handle the reacted surfaces.

15. Use a paper towel to THOROUGHLY dry the nails, and weigh them again on the analytical balance. Discard the NaCl solution down the drain, and clean the residue out of the beaker.

Final weight of nail A_____ Final weight of nail B_____

✍ **Answer in-lab questions #7 and #8 on page 5.**

✍ **Answer in-lab summary questions #9 and #10 on page 5.**

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✍ IN-LAB QUESTIONS ✍
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1. Based on the multimeter connections and voltage reading, which metal strip is acting as the anode and which is acting as the cathode? Write out the anode half-reaction.

anode _____ anode reaction:

cathode _____

Since there are no metal ions available, the water (or something dissolved in it) must be involved in the cathode reaction. Use a table of standard reduction potentials (like Table 19.1 of your text) and list some possible reduction reactions. Based on the E^o values, which is the most likely? Verify your conclusions with your instructor.

2. What evidence did you observe to suggest that the proposed reduction reaction was occurring? Why was this observed only when the multimeter was in the current-measuring mode, and not the voltage-measuring mode? (If you are unsure about this, check the paragraphs on "*How multimeters work*" in the Discussion section.)

3. What was the effect of bubbling air near one of the Zn strips? Explain how this observation is consistent with the explanation of atmospheric corrosion of a ship's hull, sitting in water, referred to in the Discussion section. What are the two half-reactions? Which zinc strip will gradually be eaten away?

4. How does the phenolphthalein help confirm the reactions postulated above? Verify with your instructor that your analysis of these observations is correct.

5. Calculate the mass lost by each metal in procedure step 7 (unconnected) and in procedure step 10 (connected). The mass loss is proportional to the rate of corrosion in each case. How do the mass changes demonstrate the concepts of "galvanic protection" and "sacrificial anode"?

6. You probably noticed that the nail bubbled MORE when connected to the Zn than it did when unconnected. Explain this observation. Have your instructor check your answers on the last two questions.

7. Calculate the mass lost by each nail in procedure step 14. One nail should show almost no mass loss. To which pole (+ or -) of the power supply was this one connected? Explain WHY the corrosion rate of this metal was so low.

8. Use a chemical reaction and explain what was happening at the other electrode, which suffered a significant mass loss. Write out the reaction that resulted in bubble formation at this electrode. Can these two reactions explain the precipitate you observed? Have your instructor check your answers on the last two questions.

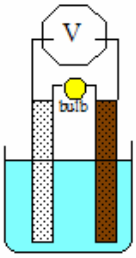
9. Explain why the atmospheric corrosion was so much more effective in the 0.5 M NaCl compared to when it was carried out in distilled water.

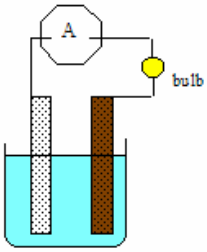
10. Explain why attaching a piece of Zn metal to the hull of a ship helps protect the hull from unwanted corrosion (assume the hull is iron-based). Why would this protection not be effective if the zinc were attached to a painted section of the hull?

USE OF THE TENMA DIGITAL MULTIMETER

As described in the discussion, a multimeter can measure several important electrical properties, namely voltage, current and resistance. We will only be interested in the first two for this experiment. Because the instrument functions differently for these different measurements, it is important that it be set up properly to make them. Because it has multiple scales in each case, it is also important that you read it properly to get meaningful data. This sheet provides a brief description of proper use of the device.

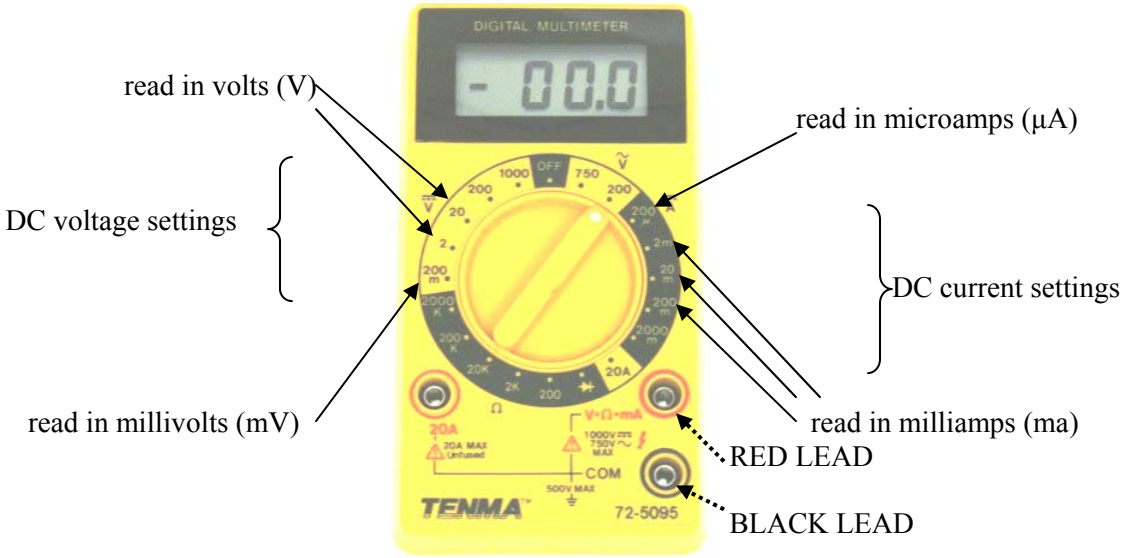
Making Voltage Readings As discussed earlier, when the multimeter is set to one of the voltage scales, it acts as a potentiometer. This measures the voltage difference between two points of a circuit by creating an equal (but opposite) electromotive force and applying it to the circuit until the current going through the meter is reduced to zero. Thus, when a multimeter is set to one of the voltage scales, there is no current flow in the meter, and the electrochemical process being investigated is actually stopped. What you read is based on the voltage that was applied to stop current flow. For this to work properly, the two leads of the meter must be placed ACROSS the circuit, touching the two points of interest (usually the electrodes). See the drawing at right. Also, note that the red wire is attached to the cathode when the voltmeter displays a positive value. Make your connections to get positive voltages; knowing which electrode is the cathode will help you analyze the chemical behavior of the system.





Making Current Readings When a multimeter is set to one of the current (amps) scales, the electrochemical process is not stopped by any opposing forces, as in the case when electrical potential is being measured. Instead, the current produced by the process is passed through the meter where it measured. Thus for current readings, the meter must be IN the circuit. See the drawing at left.

Reading Values of Voltage or Current Because there are different scales on the meter, and even different units within the voltage scales or current scales, it is essential that you note what position you set the dial to, and to always include the units with your readings. Shown below is an image of the meter face. The label at each setting (e.g. 200m) indicates the maximum reading on that scale.



Here are some general rules for reading the meters. Follow these to get consistent results.

1. Always write down the UNITS with your values.
2. **Always use the LOWEST setting that gives a meaningful reading,** because it will provide the greatest precision and accuracy. When reading voltage, start with the 200m scale, and then go up. (You will never need the 200V or 1000V settings!) When reading current, start with the 200µ scale, and then go up. (You will never need the 2000m scale!) NOTE: If the voltage or current were completely unknown, you would probably start with a high scale, and go down to the lowest with a good reading, in order to protect the meter. That will not be a problem here.
3. If the meter simply shows a constant number "1" on the left side of the display, you are off-scale. Go to the next higher scale.

Name _____ Section _____
Date _____

Pre-Lab Exercises
Experiment 21H

1. a. Use the table of standard reduction potentials in your text to calculate E^o_{cell} for the reaction:

Cu^{2+} (aq) + Zn (s) → Cu (s) + Zn^{2+} (aq)

b. Which species is being reduced in the reaction as written?

i. Cu^{2+}(aq) ii. H_2O(l) iii. Zn(s) iv. Zn^{2+}(aq)

c. If a Galvanic cell were made from this reaction, which electrode would be the anode?

i. Cu(s) ii. Zn(s) iii. Pt(s)

d. How could E_{cell} be increased above the E^o_{cell} value?

i. add more Zn(s) ii. add more Cu(s) iii. increase [Cu^{2+}(aq)] iv. increase [Zn^{2+}(aq)]

2. Zinc plates attached to iron hulls act as "sacrificial anodes" to prevent corrosion. This is an example of:

i. impressed voltage ii. electrolysis iii. passivation iv. galvanic protection