Experiment 21H

ELECTROCHEMISTRY: CORROSION

MATERIALS: 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 and corrosion prevention.

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.   Identify the conditions for "chemical corrosion".
3.   Describe the use of galvanic protection and impressed voltage for corrosion prevention.

PRE-LAB: Complete the Pre-Lab Assignments <u>before</u> coming to lab.

DISCUSSION:

<u>Corrosion</u> can be defined as the deterioration of metals by spontaneous electrochemical reactions between the metal and its environment. Conversion of the metal into its salts can lead to a loss of structural integrity. Our focus will be corrosion of iron, but the problem is not limited to iron-based structures. Aluminum and other important structural metals are also susceptible to corrosion under the proper conditions.

Atmospheric corrosion and chemical corrosion. "<u>Atmospheric corrosion</u>" 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

$$O_2 (g) \ + \ 2 H_2O (\ell) \ + \ 4e^- \ \rightarrow \ 4 OH^- (aq) \tag{1}$$

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

$$Fe (s) \ \rightarrow \ Fe^{2+} (aq) + 2e^- \tag{2}$$
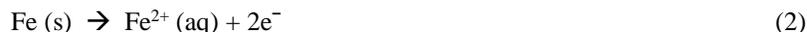
Even if the anode and cathode regions of a cell are made from the same type of metal, atmospheric corrosion will occur if there is a nonuniformity in the dissolved oxygen concentration, such as occurs with the hull of a ship where the dissolved oxygen concentration is greater near the water surface. 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 "<u>chemical corrosion</u>" 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

$$2H^+ (aq) \ + 2e^- \rightarrow \ H_2 (g) \tag{3}$$

An example would be corrosion of iron by battery acid. For more information about naval applications of electrochemistry and corrosion, go to the website https://intranet.usna.edu/ChemDept/_files/documents/navapps/CURRENT/2018%20Documents/sc112-navapp-s18-ch19-corrosion-o2-production-FV.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. The use of a *less* active metal coating such as tin is another barrier method. Among the most important electrical methods for corrosion prevention, widely used in the Navy (and elsewhere), are galvanic protection and impressed voltage. With "<u>galvanic protection</u>" 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 <u>impressed voltage</u>, 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.

Name _____	Section _____
Partner _____	Date _____

PROCEDURE, DATA AND IN-LAB QUESTIONS
Experiment 21H

Part 1: "Atmospheric Corrosion"

In each of these experiments, it's important not to let the electrodes touch each other, in solution. It also helps to hold the electrodes upright so that they don't slide in the beaker.

a) Corrosion cell in pure water

Fill 400 mL beaker ½ full with deionized (DI) water and place it on a white- or light-colored paper. Place Cu & Zn electrodes in beaker (not touching). Attach the voltmeter such that a (+) voltage is obtained and record the voltage and identify which electrode is attached to the red and black wire:

Red wire (cathode) _____

Black wire (anode) _____ Voltage: _____ V

Four possible ½ reactions, and E^o values :

$2H_2O(\ell) + O_2(g) + 4e^- \rightarrow 4OH^-(aq)$ +0.40 V
(atmospheric – uses O_2 from the air)

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ +0.34 V

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ –0.76 V

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ –0.83 V
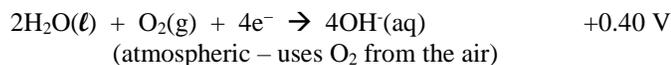
Any reaction that occurs is based on these four possible ½ reactions. Which chemical species are available in significant amounts in the beaker? (circle all that apply)

$H_2O(\ell)$ $O_2(g)$ $OH^-(aq)$ $Cu^{2+}(aq)$ $Cu(s)$ $Zn^{2+}(aq)$ $Zn(s)$ $H_2(g)$

You can only have a chemical reaction when the reactants are available. Recognizing that fact,

Which is the most likely reduction ½ reaction occurring? _____

most likely oxidation ½ reaction? _____

Why did you choose these reactions?

Add a drop of phenolphthalein indicator around each electrode, one at a time:

Color change around Zn? (Y/N) _____ Describe. _____

Color change around Cu? (Y/N) _____ Describe. _____

Switch multimeter to current (mA) setting:

Record observations of color change._____

Record current, with units:_____

b) Corrosion cell in salt water

Dispose of the previous solution in the beaker, clean off the electrodes, then rebuild cell the same as above, but use 0.5 M **NaCl solution** in the beaker instead of water. Attach the voltmeter to obtain a (+) voltage. Record the following:

Voltage: _____

Add phenolphthalein indicator around each electrode, one at a time:

Color change around Zn? (Y/N) _____ Describe._____

Color change around Cu? (Y/N) _____ Describe. _____

Switch multimeter to current (mA) setting:

Record observations of color change._____

Record current, with units:_____

How did the voltage compare to the pure water case?_____

How did the current compare to the pure water case?_____

Why? Explain the observed differences (if any) in voltage and current for cell set up in pure water vs. salt water.

c) Effect of non-uniform O$_2$ concentration

Dispose of solution and clean off the electrodes. Use the small plastic container in the student drawer and fill it **to a depth of ~ ½ inch** with **NaCl solution.** Immerse two Zn strips in the solution on opposite sides of the container. (You can lay them flat on the bottom.) Attach the voltmeter to obtain a (+) voltage. Once you have it all connected, **avoid** <u>agitating the solution.</u>

Voltage: _____

Use a plastic eyedropper or rubber pipet bulb and <u>gently</u> squeeze bubbles of air <u>right next to</u> one of the Zn strips. Try for a long steady stream of bubbles. (Again, agitate the solution as little as possible before/while bubbling.)

What happens to the voltage? _____

Now, slowly squeeze out air bubbles next to the other Zn strip.

What happens to the voltage now? _____

Your actions above created locally higher concentrations of O$_2$(aq) wherever you bubbled the air.   What effect does that have on the cathodic reaction of atmospheric corrosion? (Note that the cathodic (reduction) reaction is the same one you identified on the previous page.)

_____

Which strip of Zn will be the cathode? (Consider the possible half-reactions.) (circle)

    i. Zn where the bubbles were added   ii. Zn strip where bubbles were <u>not</u> added

Which strip of Zn will experience a higher rate of corrosion? (Consider the possible half-reactions.) (circle)

    i. Zn where the bubbles were added   ii. Zn strip where bubbles were <u>not</u> added

Part 2: "Chemical Corrosion" (Effect of HCl acid on Zn metal and Fe metal (nail))

Add 25.0 mL of 3.0 M HCl into a 50 mL beaker. Set up another beaker, full of DI water, right next to the beaker of HCl solution. Take a 4 inch nail and sand the bottom half clean. Also sand the bottom half of a Zn(s) strip. Wipe away all sanding residue, rinse in DI water and <u>completely dry</u> the metals with a paper towel.

Go to one of the **analytical (4 decimal place) balances**. Zero the balance with a 100 mL beaker in place on the balance pan. (Make sure all the doors are closed.) One at a time, place the Zn strip and nail in the beaker and the record the initial mass of each. *In this and all subsequent parts of the lab, make all before and after measurements on the SAME analytical (4 decimal place) balance! Make sure the object is DRY!*

Zn: _____g   Nail:_____g

(In this step DO NOT let electrodes touch!) Simultaneously immerse the two metals (cleaned ends) into the HCl solution, for 3.0 minutes. Observe the sample and agitate periodically. After 3.0 minutes have elapsed, remove both metals from the HCl beaker and swish them around in the beaker of water to remove traces of acid and reaction products.

Observations: _____

Possible ½ reactions:

$$2H_2O(\ell) + O_2(g) + 4e^- \rightarrow 4OH^-(aq) \qquad +0.40 \text{ V}$$
(atmospheric – uses O_2 from the air)

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad 0.00 \text{ V}$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \qquad -0.44 \text{ V}$$

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad -0.76 \text{ V}$$

$$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad -0.83 \text{ V}$$
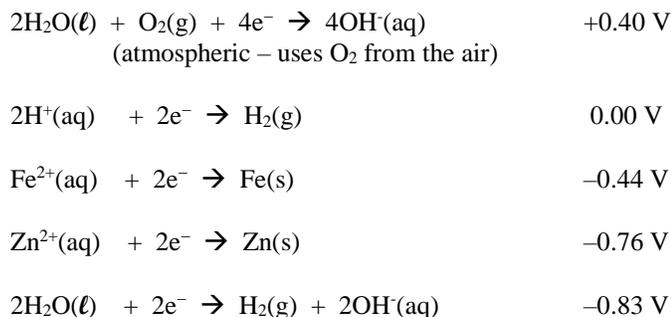
Any reaction that occurs is based on these possible ½ reactions. Which chemical species are available in significant amounts in the beaker? (circle all that apply)

$H_2O(\ell)$ $O_2(g)$ $OH^-(aq)$ $H^+(aq)$ $Fe^{2+}(aq)$ $Fe(s)$ $Zn^{2+}(aq)$ $Zn(s)$ $H_2(g)$

You can only have a chemical reaction when the reactants are available. Recognizing that fact,

Which are the two most likely <u>oxidation</u> ½ reactions occurring? _____

_____

Bubbles at Zn? (Y/N) _____ Identify the gas: _____

Bubbles at Nail? (Y/N) _____ Identify the gas: _____

Which is the most likely <u>reduction</u> ½ reaction occurring? _____

More bubbles at one electrode than the other? (Y/N) _____ Which had more?_____

Think of the spontaneous electrochemical cells based on the oxidation and reduction reactions you just identified. Use them to explain why one electrode bubbled more than the other.

Remove the metals from the water beaker, rinse them with DI water, THOROUGHLY dry them and reweigh on the **same analytical balance** as before. Record final mass of each:

Zn: _____g   Nail:_____g

Part 3: "Galvanic Protection" (Effect of coupling a more active metal to a less active one)

Discard used HCl solution. Obtain a fresh 25.0 mL HCl sample, and a fresh beaker of water.   This time you will see what happens when the metals are connected electrically with a jumper wire.

<u>Re-sand</u> the metal strips; clean, DRY and reweigh them (**analytical balance**), recording initial mass of each:

Zn: _____g   Nail:_____g

Use a jumper wire with alligator clips on each end to connect the **<u>unsanded</u>** parts of the two metals. Simultaneously immerse the two metals (cleaned ends) into the HCl solution, for 3.0 minutes.   Observe the sample and agitate periodically.   After 3.0 minutes have elapsed, remove both metals from the HCl beaker and swish them around the beaker of water to remove traces of acid and reaction products.

Bubbles at zinc? (Y/N) _____ Identify the gas: _____

Bubbles at nail? (Y/N) _____ Identify the gas: _____

More bubbles at one electrode than the other? (Y/N) _____ Which had more?_____

Which electrode is more readily oxidized? (Consider the ½ reactions on the preceding page.) _____

That electrode will be the (circle)   anode   cathode

Remove the metals from the water beaker, rinse them with DI water, THOROUGHLY dry them and reweigh on the same **analytical balance**. Record final mass of each:

Zn: _____g   Nail:_____g

Part 4: "Impressed Voltage" Protection - Effect of applied voltage on same electrodes

Discard the HCl solution in the 50 mL beaker and replace it with 25.0 mL of **0.5 M NaCl** solution. Prepare two 4 inch nails by sanding the lower halves; then clean and dry the nails <u>thoroughly</u>. Mark the head of one nail to identify it as nail #1.   Carefully weigh both nails on the **<u>analytical balance</u>**. Record the initial mass of each:

nail #1 (marked): _____ g   nail #2:_____ g

<u>With no wires attached</u>, turn on the power supply**,** adjust the upper knob to give a 3.0 V setting, and then turn off the power supply. Use jumper wires to attach #1 nail to the (+) terminal and #2 nail to the (-) terminal of the power supply.

Immerse both nails simultaneously into the NaCl solution (do not let them touch). Turn on the power supply. Let it run for 3.0 minutes. (If nothing happens, adjust the lower (current) knob until the red LED turns green.)

(+) Bubbles around nail #1? (Y/N) _____   (-) Bubbles around nail #2? (Y/N) _____

After 3.0 minutes, Turn off the power supply – leave nails undisturbed, answer questions:

Record any color change around nail #1: _____   Note that yellow or yellow-green indicate Fe^{2+}(aq).

Identify the ½ reaction that produced this species: _____

Add a drop of phenolphthalein indicator to the area around #2 nail, and record color change: _____. You have used phenolphthalein before; a pink color is indicative of what ion? _____.

Identify the ½ reaction that produced this species: _____

Now, rinse, thoroughly dry and re-weigh each nail on the **same analytical balance**. Record final masses:

nail #1 (marked): _____ g   nail #2:_____ g

POST-LAB QUESTIONS

(1) Calculate the mass lost by the Zn and Fe metals in the "unconnected" experiment (Part 2). Comment on the differences. Why did one metal corrode (lose mass) more than the other?

(2) Calculate the mass loss for each metal (Zn and Fe) in the "connected" experiment (Part 3). How do the mass differences demonstrate the concept of sacrificial anode or galvanic protection?

(3) In Part 4 you connected each nail to the + or – terminals of the power supply. Calculate the mass loss for each nail.

Mass loss #1 (marked) : _____ (+ terminal)   Mass loss #2: _____ (– terminal)

Does this make sense? <u>Explain</u> the observed changes in terms of oxidation and reduction processes.

Describe the "impressed voltage" cell of Part 4. Fill in ½ reactions, add heads to upper arrows to show direction of electron flow, label electrodes as #1 or #2. (NOTE- pay attention to polarity at the power supply!)

nail (electrode) #_____   nail (electrode) #_____

half-reaction: half-reaction:

_____   _____

Name _____   Section _____
                                                                            Date _____

Pre-Lab Exercises
Experiment 21H

1   a. The type of corrosion which results when battery acid is spilled on a wrench is:

i. atmospheric corrosion   ii. chemical corrosion   iii. pitting corrosion   iv. stress corrosion

     b. The type of corrosion which results when a wrench is left in damp grass is:

i. atmospheric corrosion   ii. chemical corrosion   iii. pitting corrosion   iv. stress corrosion

2. Common methods to limit or prevent corrosion include (1) use of corrosion-resistant materials; (2) applying impervious coatings; (3) galvanic protection; and (4) impressed voltage. Which method best describes the following circumstances?

     a. Gold (Au) is used for electrical contacts.

i. corrosion-resistant material   ii. impervious coating   iii. galvanic protection   iv. impressed voltage

     b. The hull is kept attached to a power supply when in port.

i. corrosion-resistant material   ii. impervious coating   iii. galvanic protection   iv. impressed voltage

     c. The bulkhead is painted gray.

i. corrosion-resistant material   ii. impervious coating   iii. galvanic protection   iv. impressed voltage

     d. A metal can is plated with tin (Sn).

i. corrosion-resistant material   ii. impervious coating   iii. galvanic protection   iv. impressed voltage

3. In the corrosion of iron, the iron would act as the _____ and have a _____ electrode sign (polarity).

i. anode___positive   ii. anode___negative   iii. cathode___positive   iv. cathode___negative

4. In the corrosion of iron, the rust that forms will often appear _____. (Check the Naval Applications module https://intranet.usna.edu/ChemDept/_files/documents/navapps/ADDITIONAL-INFO/Corrosion%20Chapter.pdf if you are not sure.)

i. at the site of the anode   ii. at the site of the cathode   iii. somewhere between anodic and cathodic regions

iv. only when water is excluded.

USE OF THE DIGITAL MULTIMETER

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 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 <u>no</u> current flow in the meter, and the electrochemical process under investigation 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 <u>red wire</u> is attached to the <u>cathode</u> when the voltmeter displays a <u>positive</u> value. Make your connections to get positive voltages; knowing which electrode is the cathode will help you analyze the chemical behavior of the system.
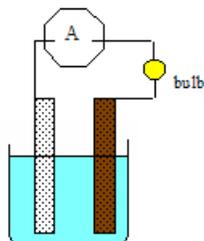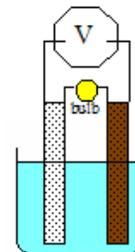
Making Current Readings When a multimeter is set to one of the current (amps) scales, the electrochemical process is not stopped by any opposing forces, as in the case when electrical potential is being measured. Instead, the current produced by the process is passed through the meter where it measured. 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 <u>within</u> 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.

Read in volts (V)

Read in microamps (μA)

DC voltage settings

DC current settings

Read in millivolts (mV)

Read in mA

RED WIRE

BLACK WIRE

DC current readings, instrument will adjust the scale automatically

DC voltage readings, instrument will adjust the scale automatically

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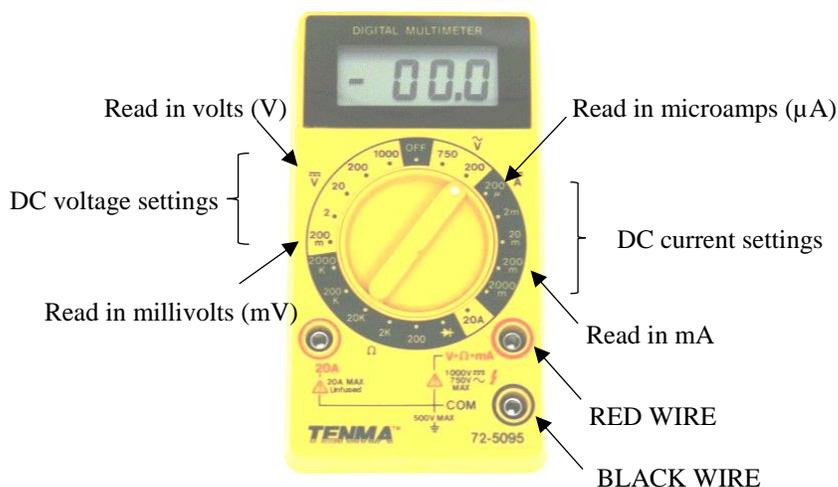
Here are some general rules for reading the meters. Follow these to get consistent results.

1. Always write down the UNITS with your values.

2. For the **TENMA** multimeter, 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!). If the meter simply shows a constant number "1" on the left side of the display, you are off-scale. Go to the next <u>higher</u> scale.

3. For the **EXTECH** multimeter, when reading voltage, use the V_{DC} setting. The instrument will adjust the scale automatically. When reading current, start with the μA setting, if needed you can go to the next higher scale (mA). If "OL" appears in the display during a measurement, you are off-scale. Go to the next <u>higher</u> scale.