

Electrolysis and Electroplating

Lab #4, Chem 36

Spring 2009

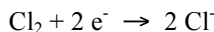
Introduction

Reactions that involve a change in the number of electrons at a particular location require a reduction or oxidation process to take place. This lab is designed to provide an example of the reduction/oxidation (redox) processes. In general, all redox reactions can be written as a sum of half reactions, where a half reaction is defined as a specific type of reaction where electrons appear explicitly as reactants or products. Consider for example the reasonably typical redox reaction of Na metal and Cl₂ gas to form NaCl.

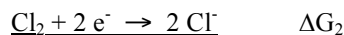
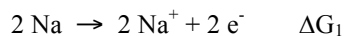
In the first half reaction, Na metal forms Na⁺. Since the oxidation state of Na increases, Na is oxidized during the course of the reaction.



In the second half reaction Cl forms Cl⁻. Since the oxidation state of Cl decreases, Cl is reduced during the course of the reaction.



Adding the reactions together requires a consideration of the overall *electron* stoichiometry. In this way the total number of electrons consumed or produced can be balanced and therefore can be canceled out of the “whole” reaction. As a direct result of balancing the number of electrons the total sum of the oxidation states of the reactants must be equal to the total sum of oxidation states of the products, i.e. total oxidation state is conserved in redox reactions.



Redox reactions, just like any other reaction, correspond to a change in the overall free energy of the system. But unlike other reactions, the total amount of driving force in redox reactions is usually expressed in terms of the reaction potential, E. E is

an experimental quantity that is easily measured by using an electrode to act as an electron source (oxidation) or sink (reduction), and measuring the voltage at which the half reaction occurs.

Reaction potential, E, and free energy, G, are directly proportional and under standard conditions this expression takes a very simple form first discovered by Michael Faraday.

$$\Delta G = -nFE$$

Here ΔG is the standard free energy, n is the number of electrons involved in the half reaction, E is the reaction potential, and F is the Faraday constant. F basically corresponds to the number of coulombs in a mole of electrons. A coulomb (C) corresponds to a fundamental quantity of charge, which for our purposes can be thought of as defining the more familiar unit of current the ampere (A). One ampere corresponds to the motion of one coulomb of charge per second. So current is a measure of the charge flowing through a wire per unit time.

$$\text{Amperes} = \text{Coulombs}/(\text{time in seconds}) = C/s$$

The value of the Faraday constant in terms of coulombs per mole of electrons is F = 96,485 C/mol.

When considering the addition of half reactions in terms of reaction potentials, E, the rule is that free energies are additive. In this way, the number of electrons is dealt with properly. For instance, from the example given above:

$$\Delta G_{\text{tot}} = \Delta G_1 + \Delta G_2$$

$$-n_{\text{tot}}FE_{\text{tot}} = -n_1FE_1 + (-n_2FE_2)$$

For the experiments done in this lab a variety of half and whole reactions will be examined. The currents and mass changes involved during these reactions will be measured quantitatively. The experimental data acquired will be used to estimate Faraday's constant and/or Avogadro's number.

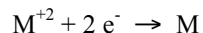
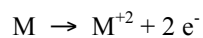
The reactions are all of the electroplating type, so a

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short discussion of the chemistry of Cu, Zn, and Mg is in order. Cu, Zn, Mg all have relatively stable +2 oxidation states and unstable +1 oxidation states. So the general form of the half reactions taking place in the following reactions will either be oxidation of the metal to the +2 oxidation state or reduction of the divalent cation.



It is important to remember the two electron nature of the individual reactions in order to relate the total number of electrons to the amount of deposited metal formed during the electroplating reaction(s).

Experimental

1. Obtain two Cu electrodes, one Zn electrode and a 30 mL beaker from the stockroom.
2. Polish the bottom 2/3 of the electrodes with Emory paper and bend each electrode so that it hangs over the edge of the 30 mL beaker. This is the electrolytic cell for the experiment.
3. Rinse the electrodes with distilled water and then with acetone. Allow them to dry and then mark all of the electrodes so that they can be distinguished unambiguously from each other.
4. Weigh each of the dried electrodes on the analytical balance and record the weights.

Part 1

1. Obtain 25 mL of 1 M CuSO₄ from the reagent bottle. If the solution is cloudy, gravity filter it into the 30 mL beaker. Take the two Cu electrodes and place the electrodes on opposite sides of the beaker.
2. Use one of the alligator clips coming from the multimeter to attach to one of the Cu electrodes and the other alligator clip to attach to the negative terminal of the battery. Set the multimeter to measure current with a sensitivity of 200 mA. DO NOT attach the other electrode until the TA has inspected your experimental setup including the electrodes and the overall

circuit.

3. As soon as the connection is made between the electrode and the resistor, start timing and measuring the current in mA every 30 seconds. Stop timing and measuring the current when the circuit is broken (at around the 8 min mark). This is a key measurement for the experiment as the mass of metal being electroplated or electrodissolved depends on both the exact current and the amount of time the cell is in operation. Note carefully if the appearance of the electrodes changes during the course of the experiment.
4. After carefully disconnecting the circuit, gently dip the electrodes into a beaker of distilled water and then rinse very gently with a little acetone in the fume hood. This washes off any residual electrolysis solution. Be careful not to shake, touch or wipe the active electrode surface as this may dislodge some of the material that has been deposited on the electrode. The entire point of the experiment is to relate how much material has been deposited or lost in relation to how much current (in amperes) passed through the circuit over a set time (i.e. charge in coulombs).
5. Once the electrodes have dried, weigh them on the analytical balance.

Part 2

1. Pour about half of the used CuSO₄ electrolysis solution into a test tube.
2. With tweezers drop a small piece of Mg into the solution and leave it there for several minutes.
3. Remove the "Mg" and examine it carefully. From the observations explain what happened to the Mg and draw a balanced equation.

Part 3

1. Pour the other half of the used CuSO₄ electrolysis solution into a test tube.
2. With tweezers drop a small piece of Zn into the solution and leave it there for several minutes.
3. Remove the Zn and examine it carefully. From the observations explain what happened to the Zn and draw a balanced equation.

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Part 4

1. Obtain 25 mL of 1 M ZnSO_4 solution from the reagent bottle. If the solution is cloudy, gravity filter it into the 30 mL beaker. Place one Cu electrode and one Zn electrode on opposite sides of the beaker.
2. Use one of the alligator clips coming from the multimeter to attach to the Cu electrode and the other alligator clip to attach to the negative terminal of the battery. Set the multimeter to measure current with a sensitivity of 200 mA. DO NOT attach the other electrode until the TA has inspected your experimental set up including the electrodes and the overall circuit.
3. As soon as the connection is made between the electrode and the resistor start timing and measuring the current in mA every 30 seconds. Stop timing and measuring the current when the circuit is broken at around the 8 min mark. This is a key measurement for the experiment as the mass of metal being electroplated or electrodissolved depends on both the current and the amount of time the cell is in operation. Note carefully if the appearance of the electrodes changes the course of the experiment.
4. After carefully disconnecting the circuit, dip the electrodes gently into a beaker of distilled water and then rinse very gently with a little acetone in the fume hood. This washes off any residual electrolysis solution. Be careful not to shake, touch or wipe the active electrode surfaces as this may dislodge some of the material that has been deposited on the electrode. The entire point of the experiment is to relate how much material has been deposited or lost in relation to how much current (in amperes) passed through the circuit over a set time (i.e. charge in coulombs).
5. Once the electrodes have dried, weigh them on the analytical balance.

Waste

Pour the left over solution into the appropriately labeled bottle in the hood.

Calculations

Parts 1 & 4

1. Write a balanced reaction for the reaction occurring at the cathode.
2. Determine the mass change that occurred at the cathode.
3. Multiply the average current (in amperes) by the elapsed time (in seconds) to calculate the total charge (in coulombs) passed during the course of the experiment.

$$\text{Coulombs (C)} = \text{Average Amperes} \times \text{Time (sec)}$$

4. Using Faraday's constant, $F = 96,485 \text{ C/mol}$ electrons, calculate the total mole of electrons passed and the mass of the metal that theoretically could have been deposited at the cathode.
5. Determine % metal recovered.
6. Assuming that the yield of deposition was in fact 100%, determine the moles of metal deposited. From the number of coulombs passed during the experiment and the two electron stoichiometry, estimate the value of Faraday's constant.
7. Knowing that the charge on an electron is $1.602 \times 10^{-19} \text{ C}$, estimate Avogadro's number.

Parts 2 & 3

Figure out/propose what individual half reactions are occurring. Add the two half reactions together to derive a balanced overall equation that describes what is happening at the surface of the Mg or Zn.