

Experiment 42B

FV 9Sep17

THERMODYNAMICS OF AN ELECTROCHEMICAL CELL

MATERIALS: 12x75 test tubes (3); 10 mL graduated cylinder (2); 150 mL beaker; 4" Ag and Zn wire electrodes; 2.5" x 0.5" x 0.25" sponge salt bridges; hot plate; fine steel wool; digital multimeter with alligator clip leads; small rubber bands; glass marker; thermometer with rubber stopper for test tube; test tube rack; 0.50 M AgNO₃; 0.25 M Zn(NO₃)₂; 1.5 M NaNO₃; 3 M HCl.

PURPOSE: The purpose of this experiment is to explore the thermodynamics of an electrochemical cell, and the relationships of energy, work and power associated with this spontaneous electron-transfer (oxidation-reduction) redox reaction.

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

1. Understand the relation between work and free energy in an electrochemical cell.
2. Use experimental data to derive thermodynamic quantities for an electrochemical reaction.
3. Understand the correspondence between theoretical expressions and graphical methods of data analysis.
4. Distinguish energy, work and power in an electrochemical system.

DISCUSSION:

Thermodynamics is not simply an academic exercise focused on arcane pursuits like determining equilibrium quantities or predicting the direction of some reaction. The development of thermodynamics was associated with very important practical engineering issues, such as the efficiency of engines and power requirements of processes. To a large extent these both relate to the use of energy - how energy is transformed from one form into another, such as the chemical energy available in a tank of gasoline being converted into the motion of an automobile. Clearly there are multiple steps involved in that case, e.g. chemical energy to heat as the fuel burns; heat to pressure in engine cylinders, pressure to mechanical motion of the pistons as the gaseous products expand, etc. A battery is an example of a modern energy conversion device. In a battery, the electrons transferred between reactants in an oxidation-reduction reaction can be used to do work - heating a toaster, powering a light bulb, or running a computer. The work that is done in the environment (the *surroundings*) comes from the change in energy of the chemicals in the battery (the *system*) as the reaction proceeds. The free energy change for a reaction ($\Delta_r G$) represents the maximum work available from a reaction, if spontaneous, or the minimum energy required to drive the process, if non-spontaneous. A battery, of course, encapsulates a spontaneous reaction, so it provides energy for work. Recharging that same battery would be an example of a non-spontaneous reaction; the surroundings must do work on the system in order to restore the chemical reactants to their original higher energy condition. These maximum and minimum values of work corresponding to $\Delta_r G$ are only encountered in the specialized (and impossible) circumstances of thermodynamic reversibility, but are useful outer limits for engineering evaluations. And, electrochemical cells probably come closest to thermodynamic reversibility of any energy conversion device.

To relate the Gibbs free energy to electrical work, first consider the more familiar mechanical work. Work can be defined as the energy transfer that occurs as a mass is moved through a distance against an opposing force. Lifting a barbell from the floor to a position above your head is a simple example. You, as the weightlifter, supply the force to overcome gravity and move the weight. You exchange energy with the barbell - some of your chemical potential energy stores are depleted as you do the work, and the barbell gains additional gravitational potential energy as the work is done on it.

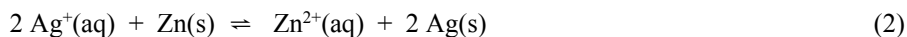
Mass is the property of matter influenced by the gravitational force F_g , as described in Newton's law of gravitation ($F_g = Gm_1m_2/r^2$, where m_1 and m_2 are the masses of two particles separated by a distance r and G is the gravitational constant). Charge is the property of matter influenced by the electrostatic force F_e , as described in Coulomb's law ($F_e = kq_1q_2/r^2$, where q_1 and q_2 are two charges separated by a distance r and k is a constant). So, the corresponding description of electrical work, w_{elec} , can be the energy transfer that occurs as a charge is moved through an electrical potential energy difference. This can be expressed as

$$w_{elec} = q \cdot E \quad \text{or} \quad w_{elec} = n \cdot F \cdot E \quad (1)$$

where q is the charge (in coulombs, C) and E is the electrical potential difference (in volts, V). One joule of work is associated with moving a coulomb of charge across a potential energy difference of one volt, so $1 \text{ V} = 1 \text{ J/C}$. That will relate voltage and energy units. In the wires of an electrical circuit, the charge is carried by moving electrons, but each

electron carries only a very small charge, 1.602×10^{-19} C. So, the charge is typically described in terms of the number (n) of moles of electrons exchanged in a reaction, where each mole contains Avogadro's number of electron charges. The latter quantity (symbolized F) is called the Faraday constant, and has the value of 96485 coulombs/mole e^- .

A battery (or cell) provides the electrical potential energy difference (voltage) to drive the electrons through the circuit. The cell does work on a charge to move it from the low energy terminal to the high energy terminal. The energy of the cell that is transferred in the form of work comes from the chemical potential energy change that occurs as the chemical reaction of the battery proceeds. The reaction for the cell you will use is:



To be useful as a portable energy source, the reaction must be spontaneous, so $\Delta_r G < 0$. Since $\Delta_r G$ represents the maximum non-PV work that can be obtained from the cell (and we will assume that all of it is electrical), we can relate $\Delta_r G$ to the voltage obtained from the cell.

$$\Delta_r G = -n \cdot F \cdot E \quad (3)$$

The negative sign appears because of the convention that E is positive for spontaneous cells.

The definition of $\Delta_r G$ is

$$\Delta_r G = \Delta_r H - T \Delta_r S \quad (4)$$

where $\Delta_r H$ and $\Delta_r S$ are the enthalpy change and entropy change for a reaction, respectively. We know that $\Delta_r G$ is strongly dependent on temperature, while $\Delta_r H$ and $\Delta_r S$ are constant over a small temperature range. In this experiment we will examine the change in voltage of a cell, $\Delta E/\Delta T$, over a small temperature range. Combining equations (3) and (4), and treating derivatives as finite differences, provides the following from the experimental measurements.

$$-\frac{\Delta(\Delta G)}{\Delta T} = n F \left(\frac{\Delta E}{\Delta T} \right) = \Delta S \quad (5)$$

Substituting for ΔG and ΔS in the definition of Gibbs Free Energy (equation (4)) gives

$$-\frac{\Delta H}{nF} = E - T \left(\frac{\Delta E}{\Delta T} \right) \quad \text{or} \quad E = \frac{\Delta E}{\Delta T} T - \frac{\Delta H}{nF} \quad (6)$$

The last expression has the form of a straight line for a plot of cell voltage E vs absolute temperature T . The slope of the line ($\Delta E/\Delta T$) is related to the entropy change of the reaction $\Delta_r S$ through equation (5) and the intercept is related to the enthalpy change of the reaction $\Delta_r H$ through equation (6).

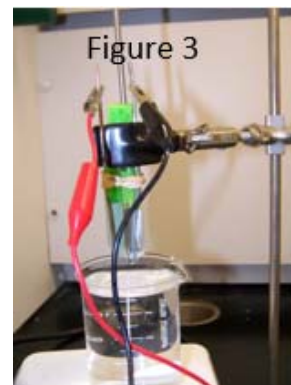
Finally, a note about "power". This term is used in everyday language as the equivalent of energy, but they are not synonymous. Power is the *rate* of delivering energy (or the *rate* of work done), and not the energy or work itself. One joule of energy delivered over one second corresponds to one watt of power; $1 \text{ W} = 1 \text{ J/s}$. So a fairly dim 60 W light bulb uses 60 J of energy per second. If that same 60 J of energy is delivered in one millisecond, as might happen in a strobe light, the power would be $60 \text{ J} / 1 \times 10^{-3} \text{ s} = 60 \text{ kilowatts (kW)}$. The strobe appears much brighter, but it is the same energy change, merely a different rate. You have probably seen or heard of the kilowatt-hour (kWh) unit used by electric utility companies. As the product of the rate of energy delivery multiplied by the time period, the kilowatt-hour is properly a unit of energy.

References

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PROCEDURE

1. Use the rubber band to hold the three small test tubes tightly together, with all openings on the same end of the assembly, and the rubber band about midway along the length. Label one test tube A (for Ag) and another Z (for Zn). Set up a ring stand with a standard pinch clamp at about a 10" height. Adjust the pinch clamp to a size that will grip and firmly hold the assembly of the three test tubes.
2. Obtain ~ 7 mL of 0.50 M AgNO_3 solution in one of the graduated cylinders, and ~ 7 mL of 0.25 M $\text{Zn}(\text{NO}_3)_2$ solution in the other. *When you add solutions to the test tubes as follows, be VERY careful not to cross-contaminate the tubes with any of the wrong solution!* Half-fill (~ 3 mL) the test tube labeled A with the silver solution, and half-fill the test tube labeled Z with the zinc solution. The amounts are not critical, but the liquid levels should be the same, and no more than 2/3 of the volume of the test tubes. *If you happen to mix the liquids, discard them in the waste container, thoroughly rinse the tubes with distilled water and try again.*
3. To the third bundled test tube, add distilled water to the height of the other liquids. Put the thermometer through the rubber stopper and insert into the test tube with distilled water. Mount the test tube assembly in the pinch clamp, *gripping the assembly as close to the top of the test tube bundle as possible (Figure 1).*
4. Obtain a sponge salt bridge that has been soaking in 1.5 M NaNO_3 solution. Do NOT wring it out – it must stay very wet! Insert the two "legs" into the test tubes with one leg in the Ag^+ solution and the other in the Zn^{2+} solution. Push the legs into the test tubes such that they reach into the silver and zinc solutions. (The sponge should be rigid enough to push it into the tube, but you can use a spatula or stir rod if necessary. Be sure not to cross-contaminate the zinc and silver solutions, though.) Wash off your fingers after handling the sponge salt bridge – contact is not harmful but can dry your skin like any salt solution.
5. Use a small piece of steel wool to clean the entire silver wire electrode until it is shiny. Thoroughly rinse off the cleaned Ag electrode with distilled water, dry it, and insert it into the AgNO_3 solution in the test tube bundle.
6. Use a small piece of steel wool to clean the entire zinc wire electrode until it is shiny. Thoroughly rinse off the cleaned Zn electrode with distilled water. Next, dip one end of the cleaned Zn electrode into a vial of 3M HCl, leave it there for ~ 15 second, and then remove it. Quickly rinse off the dipped end with distilled water, dry the electrode, and insert the cleaned, dipped end into the $\text{Zn}(\text{NO}_3)_2$ solution in the test tube bundle. You now have a completed electrochemical cell (Figure 2).
7. Attach the red (positive) multimeter wire to the Ag metal electrode of your cell, and the black (negative) wire to the Zn electrode. Make sure that the metal parts of the wires and electrodes do not touch the pinch clamp, thermometer or each other. Turn on the multimeter to the 2 V DC scale. The meter should read between ~ 0.8 V and ~1.0 V, and should show a positive value. If not, check the assembly again; consult your Instructor if you still have a problem.
8. Make a heating bath by filling a 150 mL beaker about to the 140 mL mark with tap water (i.e., nearly full). Dry off the bottom (if wet) and place the beaker on the hot plate. Arrange the beaker, hot plate and ring stand with mounted cell in such a way that you can lower the cell into the center of the bath just by adjusting the height of the pinch clamp on the ring stand (Figure 3).
9. Lower the cell into the center of the bath, as far as it will go. Record the initial temperature and voltage reading. Let stand about three minutes. During that time, again make sure that you can read the thermometer at all times, that the wires and electrodes do not touch other metals, and also that the multimeter wires are not contacting the top of the hot plate. (The wire insulation cannot tolerate the hot plate surface temperature.) Once satisfied that there are no inadvertent contacts or shorts, you are ready to begin. FROM THIS POINT TO THE END OF THE HEATING RUN, DO NOT TOUCH CELL, WIRES, THERMOMETER – ANYTHING! (The voltages are very sensitive to contact and we are looking for small trends that might be lost if there is a sudden change in voltage.)



10. Turn on the hot plate to about the middle heat setting. Watch the temperature of the cell and the voltage readings. They should change very slowly at first, and then begin to change more quickly as the bath heats up. Begin recording temperature and voltage readings as you heat, collecting data every 5°C between 30°C and 65°C.
11. When the cell reaches ~ 68°-70°C, turn off the hot plate. Carefully raise the cell assembly out of the water bath, trying not to disturb the wires. The cell will start cooling rapidly. Begin recording cell temperature and voltage readings as the cell cools, at the same temperature points as you collected while heating (65°, 60°, 55°C, etc.).

Repeat Run (optional)

Your Instructor may have you perform a second trial with the same cell, or with a new cell.

- Second trial with same cell: Use a plastic dropper to add a few drops of 1.5 M NaNO₃ to the sponge salt bridge in the cell. Carefully replace the hot water bath with fresh cool tap water and repeat steps 8 through 11.

- Second trial with new cell: Dismantle the cell. Pour the liquids into the waste container. Thoroughly rinse the sponge salt bridge in flowing distilled water, squeeze the pure water out as much as possible, and return it to the lab supply of sponges immersed in 1.5 M NaNO₃ electrolyte. Repeat steps 2 through 11.

Clean-Up

1. Disconnect the multimeter and turn it off. Remove the wire electrodes from the cell and rinse them with distilled water.
2. Remove the sponge salt bridge from the cell, and thoroughly rinse it with flowing distilled water – this is really important for your classmates! Squeeze out as much pure water as possible, and place in the beaker of 1.5 M NaNO₃ electrolyte solution for reuse. Wash off your fingers after handling the sponge salt bridge – contact is not harmful but can dry your skin like any salt solution.
3. Empty the solutions from the test tube bundle into the waste container in the small hood. (Do not pour these metal solutions down the drain.) Rinse the test tubes with distilled water and leave them to drain on the pegs of the test tube rack.
4. Empty any metal ion solutions remaining in the graduated cylinders into the waste container. Rinse the glassware with distilled water
5. Empty the water bath and rinse the beaker. Turn off the thermometer.

Name _____

Section _____

Partner _____

Date _____

DATA SECTION
Exp. 42B

Trial 1**Trial 2 (instructor option)****Initial readings****Initial readings**

Temperature _____ °C

Temperature _____ °C

Voltage _____ V

Voltage _____ V

Heating			Cooling	
Temp. (°C)	Voltage (V)		Temp. (°C)	Voltage (V)
30.0			30.0	
35.0			35.0	
40.0			40.0	
45.0			45.0	
50.0			50.0	
55.0			55.0	
60.0			60.0	
65.0			65.0	

Heating			Cooling	
Temp. (°C)	Voltage (V)		Temp. (°C)	Voltage (V)
30.0			30.0	
35.0			35.0	
40.0			40.0	
45.0			45.0	
50.0			50.0	
55.0			55.0	
60.0			60.0	
65.0			65.0	

DATA ANALYSIS:

1. Enter your temperature and voltage data into an Excel spreadsheet. Place the heating data and cooling data in adjacent columns such that the voltages for the same temperature appear in the same row. Create a new column and find the average voltage value at each temperature. (If your Instructor had you repeat the run, average all voltage values corresponding to the same temperature together.) Create another column for the Kelvin (absolute) temperatures corresponding to your data.
2. Create a plot of average cell voltage vs. absolute temperature. Insert a Trendline for the data. Change the numeric format of the trendline label to Scientific notation. (Right-click on the trendline equation label and choose "Format Trendline Label". Change the Number Category to Scientific, showing two decimal places.) Report the values of the slope and intercept, with units, and the R^2 value.

slope _____ intercept _____ R^2 _____

3. For the chemical reaction of the cell, equation (2), how many moles of electrons are transferred for each mole of reaction? This is the value of n to use in your calculations.

$n =$ _____ mole e^-

4. Use the equation of your trendline to calculate the value of the cell potential E_{298} at 298 K. Show your work.

E_{298} _____ V

5. Use the slope of your trendline to calculate the value of entropy change for the reaction, $\Delta_r S$, based on equation (5)? Express the result in J/K·mol. Show your work.

$\Delta_r S$ _____ J/mol·K

6. Use the y-intercept of your trendline to calculate the value of the enthalpy change for the reaction, $\Delta_r H$, based on equation (6). Express the result in kJ/mol. Show your work.

$\Delta_r H$ _____ kJ/mol

7. Use the definition of $\Delta_r G$ and your calculated values of $\Delta_r H$ and $\Delta_r S$ to calculate the Gibbs free energy change at 298 K. Express the value in kJ/mol. Show your work.

$\Delta_r G$ _____ kJ/mol

8. Do the signs of E and $\Delta_r G$ agree with your expectations for this system? Explain your answer.

9. What is the maximum electrical work available from this cell, based on your results?

_____ kJ/mol

10. A test circuit for the cell such as used in this experiment showed a power delivery of 0.103 W. If the cell ran the circuit at this level for 12 hours, what was the total energy output of the cell, in joules?

_____ J

Name _____

Section _____

Date _____

PRE-LAB QUESTIONS
Experiment 42B

1. Selected thermodynamic values associated with the reaction for this experiment are:

Species	$\Delta_r H^\circ$ (298K), kJ/mol	S° (298K), J/ K·mol	$\Delta_r G^\circ$ (298K), kJ/mol
Ag⁺ (aq)	105.58	72.68	77.11
Zn²⁺ (aq)	-153.89	-112.1	-147.06
Ag(s)	0	42.55	0
Zn(s)	0	41.63	0

Data from R. Chang and K.A. Goldsby, *Chemistry, 11th Ed*, Mc-Graw-Hill, New York, 2013, p. A8.

*Values of S° for aqueous ions are not really absolute entropies, but rather standard entropies measured relative to H^+ (aq). However, they can be used like absolute entropies for computation of $\Delta_r S$.

Use the data to calculate the following for: $2 \text{Ag}^+(\text{aq}) + \text{Zn}(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2 \text{Ag}(\text{s})$

- $\Delta_r H^\circ$ at 298K
 - $\Delta_r S^\circ$ at 298K
 - $\Delta_r G^\circ$ at 298K
2. Based on your calculation, what is the maximum work available from this reaction, if run under standard conditions at 298 K?
3. Based on your answer to question 2, what cell voltage E° might be expected if the reaction were run reversibly under standard conditions at 298K?