

Thermodynamics of an Electrochemical Reaction

Goal: To determine the effect of temperature and concentration on the ΔG of an electrochemical reaction. To use the temperature dependence of ΔG to determine ΔH and ΔS for the reaction.

Introduction: When iron is immersed in salt water (your car in a Rochester winter) or it is “burned” in air, an electron-transfer reaction occurs with iron as the source of the electrons and molecular oxygen as the recipient of the electrons. You probably recognize this as an oxidation-reduction, or redox reaction. Iron rusts in the presence of molecular oxygen because the reaction



is thermodynamically spontaneous. When the temperature and pressure of a reaction mixture are held constant, or controlled, the spontaneity of a reaction can be predicted by the Gibbs free energy change for the reaction. If the change in Gibbs free energy is negative, $\Delta G < 0$, the reaction is thermodynamically favored (i.e., it’s spontaneous). Although Gibbs free energy is very useful conceptually, it is generally difficult to measure directly. If, however, the reaction can be carried out electrochemically, ΔG can be measured directly. The voltage of an electrochemical cell, E , can be directly related to the Gibbs free energy change for the cell reaction through the relationship

$$\Delta G = -n\mathfrak{F}E \quad (2)$$

Here n represents the moles of electrons transferred per mole of reactant, and $\mathfrak{F} = 96,485$ C/mol is Faraday’s constant.

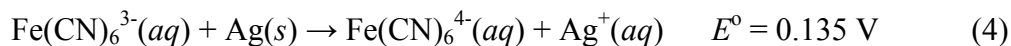
The Gibbs free energy change for the reaction is given by the Gibbs-Helmholtz equation, $\Delta G = \Delta H - T\Delta S$, in terms of the enthalpy change and entropy change of the reaction. These latter two thermodynamic functions are quite useful because they are only weakly dependent on temperature. Therefore, a plot of E vs. absolute temperature should be nearly linear, with a slope of $\Delta S/n\mathfrak{F}$ and an intercept of $-\Delta H/n\mathfrak{F}$.

Expression (2) is the operational equation to relate experimental cell voltages to ΔG values. However, it is very difficult to compare this value of ΔG to values found in the literature because it depends on the specific concentrations of the reactants and products that are present. To circumvent this problem, we define the standard $\Delta G = \Delta G^\circ$ of the reaction and, consequently, a standard cell voltage, E° . By definition the standard cell voltage is a function of temperature, yet independent of concentration. It is defined for the electrochemical cell where all species are at unit activity. To account for the variation of the actual cell voltage with concentration requires the use of the Nernst equation

$$E = E^\circ - (RT/n\mathfrak{F}) \ln Q \quad (3)$$

Here Q is called the activity quotient. To clarify the role of Q in expression (3) it would be best to consider a specific reaction. In this experiment you will consider the reduction

of potassium ferricyanide to potassium ferrocyanide in the presence of a standard electrode, Ag/AgCl or calomel. Let's focus on the reaction with silver.

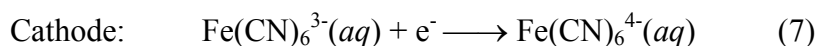
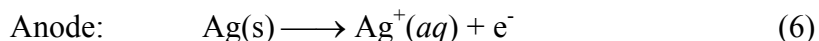


The activity quotient in this case is given by:

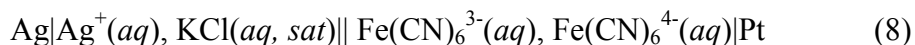
$$Q = \frac{a_{\text{Fe(CN)}_6^{4-}} a_{\text{Ag}^+}}{a_{\text{Fe(CN)}_6^{3-}}} \approx \frac{[\text{Fe(CN)}_6^{4-}][\text{Ag}^+]}{[\text{Fe(CN)}_6^{3-}]} \quad (5)$$

As you can see, if the activities are equal to 1 then $\ln Q = 0$, and $E = E^\circ$. If the activity quotient is equal to the equilibrium constant for the reaction, $\Delta G^\circ = -RT \ln K_{\text{eq}}$, then the cell voltage, $E = 0$. When $E = 0$ the reaction mixture is at equilibrium, and the concentrations won't change. We could measure the reactant and product concentrations spectrophotometrically. However, a simpler approach is to construct an electrochemical cell.

In an electrochemical cell the oxidation and reduction reactions can be physically separated into half-cells. The half cell reactions are:



If we connect the Ag/Ag⁺ half-cell and the ferricyanide/ferrocyanide half-cell by means of an electric circuit an electron current will flow from anode to cathode. The current through the circuit will be zero at equilibrium. If on the other hand, the resistance of the circuit is kept high, as in a voltmeter, we can get a good measure of the voltage, E , of the electrochemical cell. The electrochemical cell is schematically represented by:



Each vertical line represents an interface. The double vertical line at the center represents a porous barrier that enables the movement of potassium ions between the cells, while preventing the mixing of the solutions. This is necessary to complete the circuit, electrons move externally through the voltmeter, potassium counterions move internally through the barrier.

Experimental: To analyze the Ferricyanide/Ag cell, you will perform two sets of experiments. In the first set you will determine ΔH and ΔS for the electrochemical cell from a series of cell voltage measurements performed at different temperatures and at constant concentration. In the second set you will determine the effect of concentration on E at a constant temperature.

Reagents:

| | |
|--|-----------------------------|
| Potassium Ferricyanide | $\text{K}_3\text{Fe(CN)}_6$ |
| Potassium Ferrocyanide | $\text{K}_4\text{Fe(CN)}_6$ |
| Potassium Chloride | |
| Deionized Water | |
| Ag/AgCl electrode or Calomel Electrode | |
| 3.0 M Nitric Acid | |

Apparatus:

Electrochemical Cell with Pt-electrodes
Digital Multimeter
Volumetric Glassware
Temperature Controller & Recirculator
Thermometer
Aluminum Foil
Nitrogen Cylinder (as needed)

Solutions to Prepare:

- 1) Prepare 25 mL of a saturated aqueous KCl. This is required for the standard electrodes. (This may already be available.)
- 2) Prepare 100 mL of an aqueous solution containing 1.0 M KCl and 0.05 M $\text{K}_3\text{Fe}(\text{CN})_6$. Wrap the flask in aluminum foil.
- 3) Prepare 100 mL of an aqueous solution containing 1.0 M KCl and 0.05 M $\text{K}_4\text{Fe}(\text{CN})_6$. Wrap the flask in aluminum foil.

Temperature Series:

- 1) Connect the electrochemical cell to the temperature controller.
- 2) Thoroughly clean the platinum electrodes with 3.0 M nitric acid, followed by rinsing with deionized water and drying.
- 3) Fill the the standard electrode with the saturated KCl solution. Rinse the electrode with deionized water.
- 4) Add 25 mL of solution (2) and 25 mL of solution (3) to the clean electrochemical cell.
- 5) Place the Ag/AgCl and platinum electrodes in the cell.
- 6) Record the voltage and temperature of the electrochemical cell, making sure that both give stable readings. Disconnect the leads between readings.
- 7) Equilibrate the electrochemical cell at 10 °C and record the temperature and voltage for the cell. Disconnect the leads between readings.
- 8) Raise the temperature using the recirculator controls. As the temperature rises, record the temperature and voltage of the electrochemical cell. Stop at 50 °C.
- 9) Repeat steps 7-8, equilibrating at 50 °C, and going down in temperature to 10 °C.

Concentration Series:

- 1) Prepare fresh solutions as above.
- 2) Thoroughly clean the glassware, platinum electrodes and standard electrode with deionized water.

- 3) Add 45 mL of solution (3) to 5 mL of solution (2) in the electrochemical cell.
- 4) Set the constant temperature bath to 30 °C. Equilibrate the cell at the elevated temperature.
- 5) Place the Ag/AgCl and platinum electrodes in the cell.
- 6) Record the voltage and temperature of the electrochemical cell, making sure that both give stable readings. Disconnect the leads between readings.
- 7) Take two more readings of the cell voltage, stirring the solution between runs.
- 8) Add 5 more milliliters of solution (2) to the electrochemical cell and repeat steps 6 and 7.
- 9) Repeat step 8 until a total of 45 mL of solution 2 have been added.
- 10) Repeat steps 2 – 9, interchanging solution (2) and solution (3).
- 11) Discard all solutions in the inorganic waste.

Data Analysis:

- 1) The cell voltage of the Ag/AgCl electrode in $\text{KCl}(aq, sat.)$ vs. the normal hydrogen electrode (NHE) is given by $E(\text{mV}) = 199 - 1.01(T-25)$. The temperature is measured in °C.
- 2) Make a table of cell voltage vs. temperature based on your experimental data. Add the potential for the reference electrode to this data. You now have values for the reduction potential of ferricyanide vs. the normal hydrogen electrode (NHE). Place the data for increasing and decreasing temperature into separate columns.
- 3) Make a plot from the data to determine ΔH and ΔS for the ferricyanide half-cell. Place the heating and cooling experiments as separate data series on the same plot.
- 4) Give 95% confidence limits for the two sets of ΔH and ΔS values.
- 5) Determine whether the results for ΔH and ΔS for the heating and cooling experiments are statistically different.
- 6) Make a table of the cell voltage vs. volume ratio of ferrocyanide to ferricyanide solution. Adjust the cell voltage to be referenced to the NHE.
- 7) Using the adjusted data, make a plot of E vs $\ln([\text{Fe}(\text{CN})_6^{4-}]/[\text{Fe}(\text{CN})_6^{3-}])$. Determine the slope and intercept of this curve. Along with their 95% confidence limits.
- 8) Using an error analysis, establish whether the slope is statistically different from $-RT/\mathfrak{F}$.

Questions to Discuss:

- 1) What were the specific goals of your experiment?
- 2) How were the goals met, or not met? Be as quantitative as possible. Do the results make sense in the context of the processes that are occurring during this reaction?

- 3) Which condition(s) gave a cell voltage closest to the half-cell voltage found in the literature? What does this imply about the activities of the reacting species at this condition?
- 4) What is the significance of the intercept for the plot of E vs $\ln([\text{Fe}(\text{CN})_6^{4-}]/[\text{Fe}(\text{CN})_6^{3-}])$? How does it relate to literature-reported data.?
- 5) Describe the main sources of error in the experiment and what influence these errors had on your results. Be as specific and quantitative as possible.