

Electrochemistry and the Nernst Equation

GOAL AND OVERVIEW

A voltmeter is used to study the relative reduction potential of various metals and the concentration dependence of voltage in concentration cells. The solubility of silver halides will be determined by measuring the voltage of a saturated solution against a standard solution of Ag^+ ions. From the solubility, the values of K_{sp} for AgCl , AgBr , and AgI will be calculated.

Objectives of the Data Analysis

- work experimentally with concepts of electrochemistry
- understand redox reactions
- compare theoretical and experimental results

SUGGESTED REVIEW AND EXTERNAL READING

- relevant reference information and/or textbook information on thermodynamics, electrochemistry, equilibrium, and free energy

BACKGROUND

The primary measurement in electrochemistry is the *voltage* (V) of an electrochemical cell. The voltage describes the relative energies of electrons on different atoms and/or ions. The energy difference, or potential difference, between two electrons is measured in volts (joules/coulomb). The electrons may be on two ends of a wire, on two atoms, or on the cathode and anode of a battery having a potential difference. An *oxidation-reduction* or *redox reaction* is a chemical reaction in which one or more electrons from one molecule or atom are transferred to another. Thermodynamics can predict if electrons would prefer to be transferred from one species to another based on the free energy change of the system.

For example, electrons are more stable on copper than zinc, so if a piece of zinc is placed in a copper ion solution, the electrons will spontaneously transfer from Zn to Cu^{2+} , where they are more stable.



It is possible for a redox reaction to occur in such a way that the electrons cannot jump directly from one particle to another. Instead, the electrons are forced to flow through an external electrical circuit. This type of device is called a *voltaic cell*.

Consider the zinc-copper cell shown below. Zn atoms spontaneously give up 2 electrons and enter the solution as Zn^{2+} ions. The electrons flow through the external circuit into the Cu electrode. At the surface of the electrode, Cu^{2+} ions pick up the electrons and are reduced to Cu atoms. There

is a ‘push’ on the electrons from the Zn side of the cell to the Cu side. A salt bridge keeps charges from accumulating on one side or the other, thus maintaining charge neutrality.

If the external circuit is open so electrons cannot flow freely through it, electrons pile up on the left-hand side of the broken circuit and are depleted on the right-hand side, which results in the *potential difference or cell potential* (measured in volts).

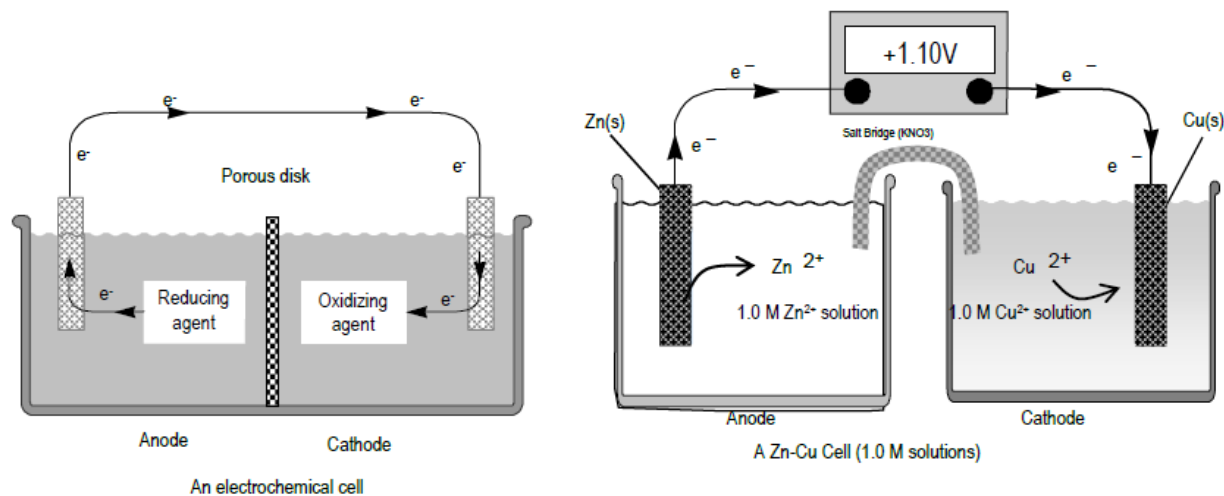


Figure 1

The cell voltage is proportional to ΔG , the change in Gibbs free energy. The ΔG of the reaction could be harnessed to do useful electrical work. The value of ΔG is given by this thermodynamic equation.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (2)$$

ΔG° is the change in Gibbs free energy for the process when all the reactants and products are in their standard states. For gases, the standard state is the pure gas at 1 atm pressure; for ions in solution, 1 mol/L (1 M). The standard state of solids and liquid solvents are the pure solids or liquids.

Q is the *reaction quotient* for the reaction. Q has the same form as the equilibrium constant, K , but the concentrations and/or gas pressures in Q are the instantaneous values in the non-equilibrium reaction vessel, rather than a set of values that characterize equilibrium.

The relationship between cell voltage, E , and ΔG for the cell reaction is given by the following equation.

$$\Delta G = -nFE, \text{ or } E = -\Delta G/nF \quad (3)$$

The nF term is related to the coulombs of negative charge transferred in the balanced redox

reaction. The number of moles of electrons transferred is given by n . F is Faraday's constant, which is the total charge (in coulombs) of a mole of electrons.

$$F = 96,485 \left(\frac{\text{coulomb}}{\text{mole } e^-} \right) = 96,485 \left(\frac{\text{Joule}}{\text{mole} \cdot \text{volt}} \right) \quad (4)$$

A process will spontaneously occur if there is a decrease in free energy, G , or $\Delta G < 0$. From Eq. 3, this implies spontaneity is associated with a positive E .

If Eqs. 3 and 4 are used in Eq. 2, the result is the Nernst equation. The Nernst equation includes a term that reflects the potential difference between products and reactants under standard conditions (E°) and a term to account for non-standard conditions ($RT/nF \times \ln Q$).

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (5)$$

This simplifies for the special case of a cell at 25°C (and using $2.303 \log_{10} x = \log_e x = \ln x$).

$$E = E^\circ - \frac{(0.0591 \text{ volts})}{n} \log_{10} Q \quad (6)$$

E is the voltage measured for the cell. E° is the voltage measured when $Q = 1$. The value 0.0591 is the same for all cells at 25°C.

E° is also related to the electron energy differences of the oxidation and reduction reaction.

$$\begin{aligned} E^\circ(\text{cell}) &= E^\circ_{1/2}(\text{reduction}) - E^\circ_{1/2}(\text{oxidation}) \\ &= E^\circ_{1/2}(\text{cathode}) - E^\circ_{1/2}(\text{anode}) \end{aligned} \quad (7)$$

$E^\circ_{1/2}(\text{reduction})$ is the standard reduction half potential of the reduction reaction, and $E^\circ_{1/2}(\text{oxidation})$ is the reduction half potential of the oxidation reaction. For a spontaneous reaction, the species with the most positive value of $E^\circ_{1/2}$ will be reduced and the other species will be oxidized.

If the concentrations of reactants and products are those characteristic of chemical equilibrium, then it is not possible to get any useful electrical work out of the cell. E equals zero. Setting $E = 0$ in Eq. 6 results in the equation below.

$$E^\circ = \frac{(0.0591 \text{ volts})}{n} \log_{10} K_{eq} \quad (8)$$

Here, K_{eq} is the equilibrium constant for the reaction as written. K_{eq} can be determined directly from a measured E° under standard conditions.

PROCEDURE

Please use small volumes of solution to reduce the cost of buying chemicals and the problems with waste disposal.

Dispose of all waste as instructed.

Waste solutions must be segregated according to type. **Read the labels on the waste bottles carefully.**

Clean up all spills.

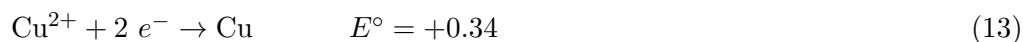
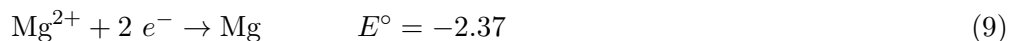
DO NOT THROW ELECTRODES AWAY. Please return them CLEAN.

Please dispose of the **used vials and salt bridges in the solid waste container in the back hood.**

Wash your hands thoroughly and carefully when done.

If you do not dispose of waste correctly, you may lose points.

Standard Reduction Potentials



Part 1: Determinations of E° for Metals vs. Copper

For the redox reaction $\text{A}(s) + \text{B}^{2+} \rightleftharpoons \text{A}^{2+} + \text{B}(s)$ the Nernst equation is shown below.

$$E = E^{\circ} - \frac{(0.0591 \text{ volts})}{n} \log_{10} Q = E^{\circ} - \frac{(0.0591 \text{ volts})}{n} \log_{10} \left(\frac{[\text{A}^{2+}]}{[\text{B}^{2+}]} \right) \quad (15)$$

The metal ion solutions are 0.10 M. Because the concentrations of both solutions are equal (0.10 M), Q will be 1, $\log Q$ will be 0, and the measured E will equal E° . The value of n is two because A loses 2 electrons and B gains two as written in the redox reaction. You are experimentally finding the relative ‘push’ on electrons from one species to another.

To create a voltaic cell:

- 1 Fill two vials about 2/3 full of the solutions you will use, labeling each one before you fill it. Dry the outside of the vials if needed. **Use only the dropper provided for filling your vials.**
- 2 Put the two vials on the base of a ring stand, side by side in the jaws of a utility clamp, so they are held together.
- 3 The two liquid levels should be exactly the same to prevent siphoning of liquid from the higher level vessel into the lower. Arrange the vials in the clamp to level them if they are slightly different.

To create the salt bridge:

- 4 Use a strip of filter paper as instructed by your TA.
- 5 Fold the paper in half.
- 6 Holding the paper in tweezers, soak it in a small beaker containing 1.0 M KNO_3 .
- 7 Gently blot the strip on a Chem-Wipe. You don’t want the concentrations of your solutions to be contaminated by solution from the salt bridge.
- 8 Put one end of the strip into the solution in one vial and the other end in the solution in the other vial.

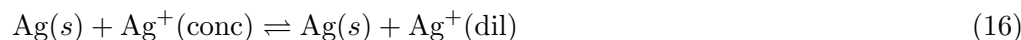
Do not let the tweezers touch the liquid in either vial.

- 9 Clip one Cu wire electrode to one lead of the voltmeter; clip the other to other lead of the voltmeter.
- 10 Insert the electrodes into the solution of their own ion carefully so they do not touch the salt bridge above the surface of the solution. You can use the electrodes to push the filter paper strip out of the way.
- 11 Measure the voltage difference and the cell polarity with the digital voltmeter.
- 12 Read the voltmeter to 3 figures but assign uncertainty based on the apparent reproducibility of readings.
- 13 Test Cu with each of different metals provided.
- 14 Compare your calculated theoretical E° values with your measured values. Find the percent error to three significant figures.

Part 2: Dependence of E on Ion Concentrations

In part 1 you measured E° values. In part 2, you will read about how E depends on concentration of ions in a concentration cell.

In a concentration cell, both electrodes are made of the same metal and the solutions in the cells are of the same ion as the electrodes. The difference between the cells lies in the metal ion concentration. In this case, the chemical reaction is given below.



E° is zero for a concentration cell because the half reactions are identical in both directions. The Nernst equation becomes the following.

$$E = -\frac{(0.0591 \text{ volts})}{n} \log_{10} \frac{\text{Ag}_{\text{dil}}^+}{\text{Ag}_{\text{conc}}^+} \quad (17)$$

The spontaneous direction for the reaction is from left to right when $\text{Ag}_{\text{conc}}^+ (c_1)$ is greater than $\text{Ag}_{\text{dil}}^+ (c_2)$.

- In cell 1, ions accept electrons from the metal, plate out on the electrode, and lower the concentration of the ions.
- In cell 2, atoms in the metal leave electrons behind and enter the solution, thus raising the ion concentration.
- The reaction occurs in such a direction as to equalize the concentrations of the two solutions.

Your TA will tell you if you need to perform this part of the experiment. IF YOU DO NOT PERFORM PART 2, use the slope of the given Nernst plot for the K_{sp} determinations in part 3.

- 1 Your data table from this part should have columns for E , c_2 , and c_1 .
- 2 Label six vials as follows: two of 10^{-1} M, and one each of 10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5} M. There are Ag^+ solutions with which to fill these vials, 2/3 full as before.
- 3 Use two Ag wire electrodes.
- 4 Set up concentration cells in which c_1 is 10^{-1} M.
- 5 Use all five of the other solutions for c_2 .
- 6 Measure each voltage and polarity.
- 7 Measure the temperature of the lab to determine if this might cause error due to temperature difference from 25°C (assumed in calculation of slope). Also, the temperature is needed in part 3 for the calculation of ΔG of solubility from K_{sp} .

- 8 Add another column in your data table for $\log (c_2/c_1)$.
- 9 In accordance with Eq. 17, prepare a plot of voltage E against $\log (c_2/c_1)$.
- 10 Fit the best straight line to your data points. Determine the slope of the best fit line.
- 11 Compare your experimental slope with that given in Eq. 17 (-0.0591 V/n).
- 12 The concentration dependence of the voltage (the slope) is used in part 3 to determine the Ag^+ concentration in saturated $\text{AgX}(s)$ solutions. And, part 2 can be considered a calibration for part 3 because the experimental Nernst slope found in part 2 may be used in determining K_{sp} values.

NOTE:

Depending on the lab schedule, part 2 might be omitted. Your TA will inform you in lab.

If part 2 is not performed, use the plot that would be obtained ideally (theoretical) from plotting E vs. $\log([\text{Ag}^+_{\text{dil}}]/[\text{Ag}^+_{\text{conc}}])$.

$$E = -\frac{(0.0591 \text{ V})}{n} \cdot \log_{10} \frac{\text{Ag}^+_{\text{dil}}}{\text{Ag}^+_{\text{conc}}} \quad (18)$$

$$y = m \cdot x$$

Theoretical slope = -0.0591 V .

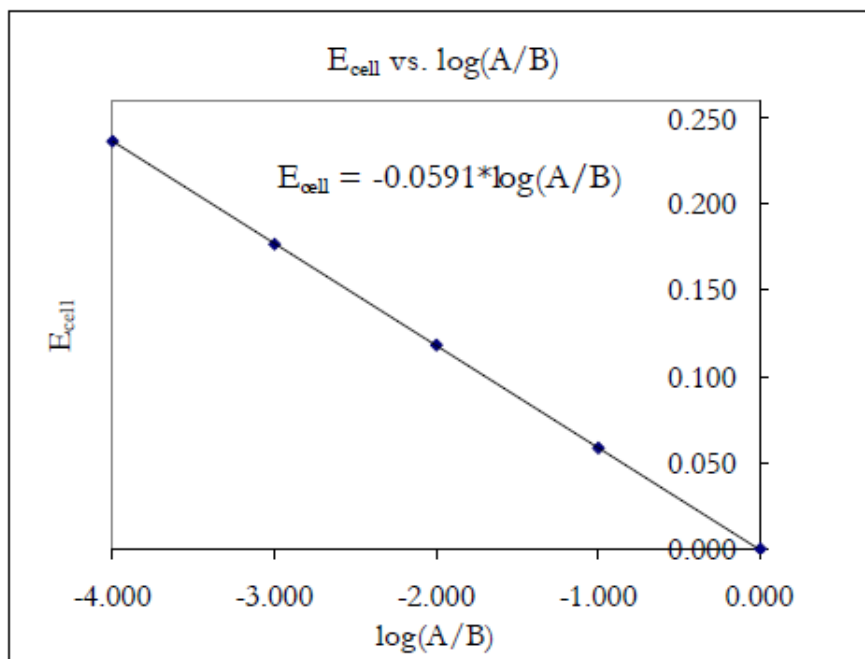


Figure 2

Part 3: Determination of K_{sp} of Very Insoluble Silver Halides

In this step you will determine the concentration of Ag^+ ion in a saturated solution of silver halides (AgCl, AgBr, and AgI) by measuring the voltage of a concentration cell in which the silver halide solution is paired with 0.10 M Ag^+ . There are 0.20 M stock solutions of KCl, KBr, and KI.

To measure K_{sp} for AgCl:

- 1 Put KCl solution into one of your vials and 0.10 M Ag^+ in the other.
- 2 To the vial containing KCl add 1 drop of 0.10 M AgNO_3 . You should observe the formation of a small amount of the white precipitate AgCl. If you don't, add another drop. The fact that solid AgCl precipitated in your vial means that $\text{AgCl}(s)$ is in equilibrium with Ag^+ and Cl^- ions, so the solubility product condition is satisfied in your vial: $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$.
- 3 Clamp the vials together and insert the salt bridge.
- 4 Since this is a concentration cell, use silver electrodes in both vials.
- 5 Measure the voltage and polarity of this cell.
- 6 Do the same experiment with KBr to study the solubility of AgBr.
- 7 Use KI to study the solubility of AgI.

Waste Disposal: Dispose of all waste as instructed. Clean up your work area. Wash your hands.

- 8 You have obtained enough information to determine the value of K_{sp} . The same applies to $[\text{Br}^-]$ or $[\text{I}^-]$ for AgBr or AgI.

K_{sp} for the three silver halides are $[\text{Ag}^+]_{\text{dil}}[\text{Cl}^-]$ or $[\text{Ag}^+]_{\text{dil}}[\text{Br}^-]$ or $[\text{Ag}^+]_{\text{dil}}[\text{I}^-]$.

The concentration of the halide ion is ~ 0.20 M, its initial molarity. Very little Ag^+ ion was added, so very little Cl^- reacted to form AgCl. Thus, the value of $[\text{Cl}^-]$ is essentially unchanged from its initial.

$[\text{Ag}^+]_{\text{dil}}$ is determined from the cell voltage and from Eq. 17: $[\text{Ag}^+]_{\text{conc}}$ is assumed to be 0.10 M (relatively unchanged from its initial value). E is the measured cell potential in volts.

- 9 Calculate all three values of K_{sp} to two significant figures.
- 10 Compare the experimental values of K_{sp} with the literature values.

Literature value of K_{sp} for AgBr = 5.3×10^{-13}

Literature value of K_{sp} for AgCl = 1.8×10^{-10}

Literature value of K_{sp} for AgI = 8.3×10^{-17}

11 Calculate ΔG° for the reaction, $\text{AgX} \rightleftharpoons \text{Ag}^+ + \text{X}^-$, using $\Delta G^\circ = -RT \ln K_{\text{sp}}$, to three significant figures.

Do not use $\Delta G^\circ = -nFE_{\text{measured}}$ to determine your ΔG° .

The measured voltage is due to using a 0.10 M reference cell of silver and would have been different if you used another concentration. Therefore it cannot be a measure of the solubility of $\text{AgX}(s)$.

Waste Disposal: Dispose of all waste as instructed. Clean up your work area. Wash your hands.

RESULTS

Complete your lab summary or write a report (as instructed).

Abstract

Results

Part 1. Data and Results table

E_{measured} for various metals relative to Cu (i.e. Cu-M₁),
 $E^\circ(\text{cell})$ predicted using metals other than copper

Part 2. Data and Results Table if *done*

$c_1(0.10 \text{ M})$, c_2 , E_{measured} , and $\log(c_2/c_1)$
graph E versus $\log(c_2/c_1)$, and determine the slope

Part 3. Data and Results

E_{measured} , c_{Ag^+} , K_{sp} for AgCl, AgBr, AgI, and ΔG°

Sample Calculations

Part 1. Predicted E° for cells with metals vs. Cu

Part 2. $\log(c_2/c_1)$ if *done*

Part 3. $[\text{Ag}^+]$, $K_{\text{sp}}(\text{AgCl})$, $\Delta G^\circ(\text{AgCl solubility})$, $K_{\text{sp}}(\text{AgBr})$, $\Delta G^\circ(\text{AgBr solubility})$, $K_{\text{sp}}(\text{AgI})$, $\Delta G^\circ(\text{AgI solubility})$

Discussion/Conclusions

Part 1: Does E_{measured} agree with $E_{\text{predicted}}$ for the various metals?

Part 2: Does the slope agree with the slope predicted by the Nernst equation?

Part 1 and 2:

Even though cell potentials are affected by both concentration differences and voltage differences between different metals, you were able to determine the dependence on each factor (RT/nF and $E_{1/2}^\circ$). How were the individual dependencies separated out and determined individually?

Part 3: How does part 3 depend on part 2?

Review