Electrochemistry and the Nernst Equation

Goal and Overview

An electrochemical cell is used to study the relative reduction potentials of various metals. The dependence of voltage on concentration will be examined and used to find approximate solubility product constants, K_{sp}, for AgCl, AgBr, and AgI.

Objectives and Science Skills

Understand and explain the chemistry, components, function, and operation of electrochemical and concentration cells.

Construct electrochemical cells and measure E^0_{cell} for different pairs of metals and metal ion solutions; identify anode and cathode and explain what occurs at each (oxidation or reduction).

Construct concentration cells and measure E_{cell} values; use experimental values to calculate K_{sp} for slightly soluble silver halide salts.

Quantitatively and qualitatively compare experimental results with theoretical values. Identify and discuss factors or effects that may contribute to the uncertainties in values determined from experimental data.

Suggested Review and External Reading

Reference material and textbook sections on thermodynamics, free energy, electrochemistry, and equilibrium

Introduction

Electrochemistry studies the relationship between electrical energy and chemical change. Oxidation-reduction (redox) reactions involve the transfer of electrons from one species that is oxidized to another that is reduced. A voltaic cell can harness the electrical energy generated by the electron transfer that occurs during an oxidation-reduction (redox) reaction to perform useful electrical work. Gathering this energy requires that the oxidation and reduction half-reactions are separated in space but connected by an external circuit (through which the electrons flow) and an electrolyte (to maintain charge neutrality).

A voltmeter inserted into the circuit quantifies the "push" on the electrons from one half-cell to the other and reflects the potential energy difference ("potential") of the electrons in the different chemical environments.

The Nernst equation relates cell potentials measured in volts to the Gibbs free energy change associated with the redox reaction.

$$\Delta G = \Delta G^0 + RT \ln Q \xrightarrow{\div by\ nF} \frac{\Delta G}{nF} = \frac{\Delta G^0}{nF} + \frac{RT}{nF} \ln Q = E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln Q$$

$$\xrightarrow{at\ 298\ K} E_{cell} = E_{cell}^0 - \frac{0.0591\ V}{n} \log Q = E_{cell}^0 - \frac{0.0591\ V}{n} \log \frac{[species\ oxidized, ox]}{[species\ reduced, red]}$$

Nonstandard concentrations (or activities) of the species undergoing oxidation and reduction are specified in the reaction quotient, Q. The amount of transferred negative charge, based on the balanced equation for the redox reaction, is nF, with n being the number of moles of electrons transferred. F is Faraday's constant, the charge on one mole of electrons.

The Nernst equation shows that positive voltages are associated with spontaneous electron transfer and a decrease in Gibbs free energy. It should also be noted that the greater the difference in the concentrations of the species oxidized and the species reduced, the greater the cell potential. This makes electrochemical cells particularly useful in determining equilibrium constants for reactions involving very low equilibrium concentrations of ions.

Equipment List

Voltmeter, glass vials, forceps/tweezers, Chem-wipes, labeling tape
Ring stand, clamp
One piece of filter paper, scissors
Metal electrodes (*e.g.*, Cu, Pb, Ni, Zn, Mg, Ag)
0.10 *M* metal ion solutions, KNO_3 solution
0.20 *M* KCl, KBr, and KI

Procedure

Please do not throw electrodes away. Return them clean and dry to the correct container. Your TA may check out and in the silver electrodes.

Please read labels on reactant bottles carefully, and please keep the correct pipet and lid with their associated bottle to avoid contamination.

Ag$^+$ solutions can stain clothing and skin.

Wash your hands thoroughly when you have finished the experiment.

Liquid waste must go into the liquid waste container. **Used vials and salt bridges must go into the solid waste container (not the trash)**.

To make a voltaic cell:

1. Label two vials and fill them about 2/3 full with the metal ions solutions you will use. Use the correct dropper for each solution. Please keep the correct cap and dropper with the associated bottle. The liquid levels in the vials must be equal to prevent siphoning from one vial to another.

2. Put the two vials side-by-side on the base of a ring stand and carefully clamp them in place with a utility clamp.

3. Obtain the metal electrodes that match the ions in each vial. The electrode that will serve as the anode should be clamped into the black lead from the voltmeter; the cathode electrode should be clamped in the red lead.

To generate a positive cell potential, the metal/metal ion combination with the most positive reduction potential or at the higher concentration should serve as the cathode.

4. Obtain one piece of filter paper and a pair of scissors. Cut thin strips of filter paper and fold each strip in half. These will serve as salt bridges for your cells. **A new strip of filter paper must be used with each new cell**.

5. Obtain a very small volume of KNO$_3$ in a labeled beaker.

When you are ready to make a voltage measurement:

6. Using tweezers, moisten a strip of filter paper in the KNO$_3$ solution and gently blot the strip on a Kim-Wipe.

7. When you are ready to make your voltage measurement, turn the voltmeter to the direct current voltage setting (V$_{DC}$). The display should show 0.000 V.

8. Using tweezers, **quickly** put one end of the moist filter paper salt bridge into the solution in one half-cell and the other end of the bridge into the other half-cell. **Quickly** dip the electrodes into the solutions in the correct, corresponding half-cells. **Quickly** record the

voltage reading to three decimal places; it should be a positive value. **Quickly** remove the electrodes and the filter paper salt bridge.

It is very important that you complete step 8 quickly. Not only do you not want to contaminate the solutions in the half-cells, you also do not want the concentrations of the metal ions to change significantly from their initial 0.10 M concentrations.

#.###		
V_{DC}	M_{ox} salt bridge M_{red}	
voltmeter	M_{ox}^{n+}	M_{red}^{n+}
	Anode	Cathode
	Oxidation	Reduction
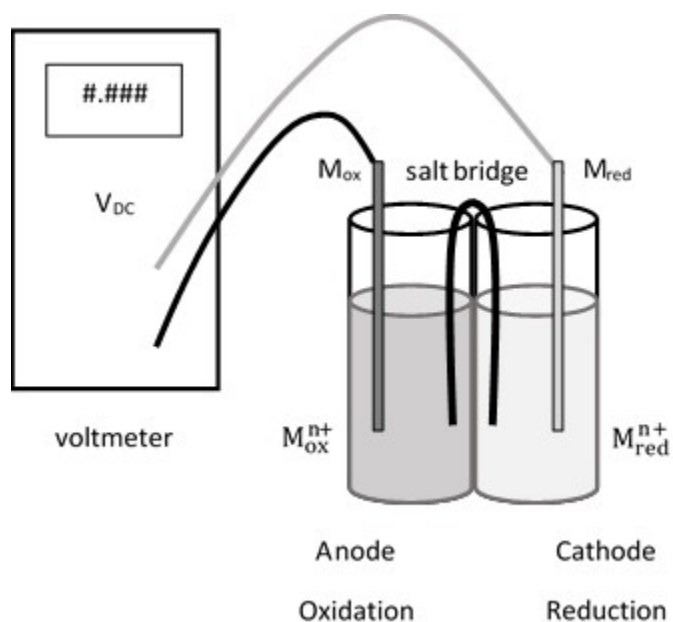
Part 1. Determination of E_{cell}^0 for Metals vs. Copper

Standard reduction potentials

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	$E^0 = -2.37$ V
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	$E^0 = -0.76$ V
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	$E^0 = -0.23$ V
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	$E^0 = -0.13$ V
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$E^0 = +0.34$ V
$Ag^+(aq) + e^- \rightarrow Ag(s)$	$E^0 = +0.80$ V

For $A(s) + B^{2+}(aq) \rightarrow A^{2+}(aq) + B(s)$, the Nernst equation is shown (assume $T = 298$ K). Because the metal ion solutions are both 0.10 M and $\log(1) = 0$, E_{cell} should equal E_{cell}^0.

$$E_{cell} = E_{cell}^0 - \frac{0.0591\ V}{n} \log \frac{[ox]}{[red]} = E_{cell}^0 - \frac{0.0591\ V}{2} \log \frac{[A^{2+}]}{[B^{2+}]} = "E_{cell}^0"$$

9. For the first set of measurements, use $Cu^{2+}(aq) | Cu(s)$ as the cathode and change out the anode side: (a) $Pb(s) | Pb^{2+}(aq)$; (b) $Ni(s) | Ni^{2+}(aq)$; (c) $Zn(s) | Zn^{2+}(aq)$; and, (d) $Mg(s) | Mg^{2+}(aq)$.

Make sure to use a new salt bridge for each cell. Follow your TA's instructions regarding replacing the $Cu^{2+}(aq)$ solution in each new cell.

10. Ask your TA if you should test other combinations of metals and metal ion solutions.

11. When you have finished, please return the electrodes clean and dry. Put each into the correct jar on the reagent counter. Dispose of the used vials and salt bridges into the appropriate solid waste container (not the trash). Return any other equipment borrowed clean. Wipe your lab bench down.

12. Calculate the theoretical E^0_{cell} values to two decimal places and compare them to your experimental "E^0_{cell}" readings. Find the % errors to three significant figures. What are possible reasons for any observed differences? What experimental factors could account for the % errors?

$$\% \ error = \left| \frac{theoretical - experimental}{theoretical} \right| \times 100\%s$$

Part 2. Dependence of E_{cell} on Ion Concentrations

You should read through this part of the procedure and make sure that you understand it, but please check with your TA to see if you will perform this part of the experiment.

You will make concentration cells using $Ag(s)$ electrodes and $Ag^+(aq)$ solutions. According to the Nernst equation, E^0_{cell} is zero because the oxidation and reduction half-reactions share the same standard reduction potential.

The cell potential is due to a concentration difference between the $Ag^+(aq)$ in the half-cells, with the spontaneous reaction occurring in an effort to equalize the ion concentration in the half-cells. $Ag^+_{conc}(aq)$ refers to the solution with the higher concentration of Ag^+ ions; $Ag^+_{dil}(aq)$, the lower concentration.
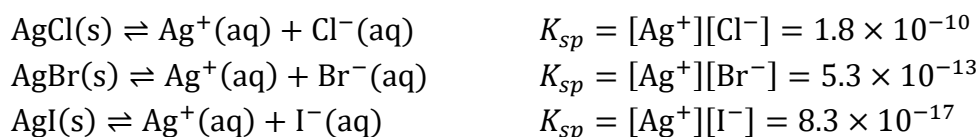
$$Ag(s) + Ag^+_{conc}(aq) \rightarrow Ag^+_{dil}(aq) + Ag(s)$$
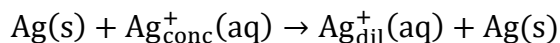
$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[Ag^+_{dil}]}{[Ag^+_{conc}]} \xrightarrow{\ at\ 298\ K\ } E_{cell} = -\frac{0.0591\ V}{1} \log \frac{[Ag^+_{dil}]}{[Ag^+_{conc}]}$$

13. Label six vials: two for $1.0 \times 10^{-1} M$ and one each for $1.0 \times 10^{-2} M$, $1.0 \times 10^{-3} M$, $1.0 \times 10^{-4} M$, and $1.0 \times 10^{-5} M$.

14. Make five salt bridges. Check out two silver electrodes from your TA. Record room temperature.

15. Use $1.0 \times 10^{-1} M$ Ag^+ solution in the cathode half-cell. Make a cell in which the anode half-cell solution is $1.0 \times 10^{-1} M$ Ag^+. Measure the voltage to three decimal places.

16. Repeat step 15 for the remaining Ag^+ solutions, replacing the anode solution and salt bridge in each cell.

17. When you have finished the entire experiment, plot E_{cell} vs. $\log \frac{[Ag^+_{dil}]}{[Ag^+_{conc}]}$. Determine the slope of the best-fit line and compare it to the theoretical value. Ask your TA if you should assume 298 K as the temperature or if you should use the value recorded in lab.

If you do not perform part 2 of the experiment, use the theoretical value at 298 K.

Part 3. K_{sp} of Sparingly Soluble Silver Halide Salts, AgX: AgCl, AgBr, and AgI

AgCl, AgBr, and AgI come to equilibrium with their aqueous ions at 298 K according to the following expressions. Reflecting their extremely low molar solubilities, their respective solubility product constants are very small.

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$
$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ $K_{sp} = [Ag^+][Br^-] = 5.3 \times 10^{-13}$
$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ $K_{sp} = [Ag^+][I^-] = 8.3 \times 10^{-17}$

Electrochemistry and concentration cells present an ideal way to find the Ag^+ concentration in saturated silver halide solutions because greater differences in Ag^+ concentrations in the half-cells produce larger voltage readings. This is in contrast with many other analytical methods where extremely small physical quantities lie below detection limits.

You will make three concentration cells, one for each silver halide salt. The cathode half-cell will contain $0.10\ M$ Ag^+ solution; this is $[Ag^+_{conc}]$. Ask your TA if you should replace this solution for each cell. Make sure to use a new salt bridge each time. If you have not checked out two Ag electrodes from your TA, do so.

18. To make the saturated AgCl solution which contains Ag^+ ions at $[Ag^+_{dil}]$, fill the anode vial to approximately the same level as the 0.10 M Ag^+ solution in the cathode vial with 0.20 M KCl solution. Add one drop of 0.10 M Ag^+; you should see some white cloudiness that indicates solid AgCl precipitate has formed. The level of the solutions in the half-cells should be equal.

19. Quickly insert the salt bridge and the Ag electrodes. Quickly record the voltage to three decimal places. Quickly remove the electrode and salt bridge.

20. Repeat steps 18 and 19, replacing the KCl solution with KBr solution (and a new salt bridge).

21. Repeat steps 18 and 19, replacing the KCl solution with KI solution (and a new salt bridge).

22. When you have finished, please return the electrodes clean and dry to your TA. Dispose of the used vials and salt bridges into the appropriate solid waste container (not the trash). Return any other equipment borrowed clean. Wipe your lab bench down.

23. Find the % error in each voltage measurement relative to the theoretical value to three significant figures. What are possible reasons why your experimental values differ from those predicted? How will these deviations affect your results?

24. Calculate $[Ag^+_{dil}]$, the Ag^+ concentration in each saturated AgX solution, to two significant figures. Assume the concentration of Ag^+ in the cathode half-cell remained roughly constant at 0.10 M. Find the % error in each concentration relative to the theoretical value to three significant figures. How might the assumption regarding $[Ag^+_{conc}]$ impact your results?

$$E_{cell} = -\frac{0.0591 \text{ V}}{1} \log \frac{[Ag^+_{dil}]}{[Ag^+_{conc}]} \quad \rightarrow \quad [Ag^+_{dil}] = [0.10 \text{ M}] \cdot 10^{-E_{cell}/0.0591 \text{ V}}$$

25. Calculate K_{sp} for each silver halide, AgX (AgCl, AgBr, and AgI; $X = Cl^-, Br^-,$ and I^-), to two significant figures. Assume $[X^-]$ remains roughly constant at 0.20 M. Find the % error in each experimental K_{sp} relative to the theoretical value to three significant figures. Do you think it was reasonable to assume that $[X^-]$ remain relatively unchanged? Would you expect a significant quantity to precipitate out of solution upon the addition of Ag^+ ions?

$$K_{sp} = [Ag^+][X^-] \approx [Ag^+_{dil}][0.20]$$

26. Calculate $\Delta G^0_{K_{sp}}$ in kJ/mol for each solubility equilibrium to three significant figures. Find the % error in each standard Gibbs free energy relative to the theoretical value to three significant figures. What do large, positive values of $\Delta G^0_{K_{sp}}$ suggest about the solubility equilibria of these silver halide salts under standard conditions?

$$\Delta G^0_{K_{sp}} = -RT \ln K_{sp}, \text{where } R = 0.008314 \frac{kJ}{K \cdot mol} \text{ and } T = 298\ K$$

Do not use $\Delta G = -nFE_{cell}$ because that does not reflect the solubility equilibrium expression.

Silver halide, AgX	Theoretical E_{cell}, V	Theoretical $[Ag^+_{dil}]$, M	Theoretical K_{sp}	Theoretical $\Delta G^0_{K_{sp}}$, kJ/mol
AgCl	0.476	9.0×10^{-10}	1.8×10^{-10}	55.6
AgBr	0.625	2.7×10^{-12}	5.3×10^{-13}	70.0
AgI	0.850	4.2×10^{-16}	8.3×10^{-17}	91.7

Results / Sample Calculations

Complete the online inlab or write a lab report as directed by your TA.

Part 1. "E^0_{cell}" and % error for each cell

Part 2. (if preformed) E_{cell} for each concentration cell; plot of E_{cell} vs. $\log \frac{[Ag^+_{dil}]}{[Ag^+_{conc}]}$; slope of best-fit line

Part 3. E_{cell}, $[Ag^+_{dil}]$, K_{sp}, $\Delta G^0_{K_{sp}}$ for each silver halide salt and % errors

Discussion Questions and Review Topics

What did you do and how did you do it?
What are reasons for differences between your experimentally-based data and results vs. the theoretically-predicted values? How might you reduce these sources of error?
If you did not perform part 2, do you think using the theoretical value for the proportionality between cell potential and concentration for part 3 was a major source of error? Why or why not?
Why are electrochemistry and cell potential measurements useful?
Are there limitations to the applications of electrochemistry and cell potential measurements? Does every reaction involve mobile charged particles that experience oxidation/reduction)?