



Lab 5: Electrochemistry

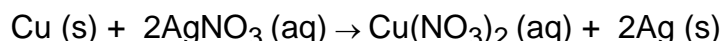
Introduction

Part I. Measurement of Standard Potentials (E°)

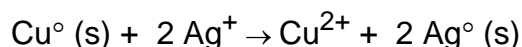
Redox Reactions

Chemical reactions that involve a change in the oxidation state of chemical species are called **redox reactions** (an abbreviation of **reduction-oxidation** reaction). Redox reactions can be identified, and the movement of electrons followed, by using a formal "bookkeeping" system for the number of electrons associated with each atom. This accounting scheme assigns an **oxidation number** to each atom, which indicates how many electrons it has gained or lost. **In a redox reaction, the oxidation numbers change.** Furthermore, every redox reaction can be divided into two **half-reactions**: one that involves a gain of electrons and one that involves a loss of electrons. Because electrons are negatively charged, a substance that gains electrons is said to be **reduced**, while one that loses electrons is said to be **oxidized**.

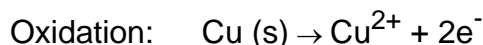
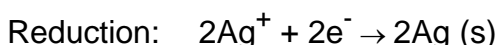
A beautiful demonstration of redox chemistry occurs when a copper coin is dropped into a dilute solution of silver nitrate (AgNO_3). Needles of metallic silver grow slowly on the copper surface, especially if the solution is not disturbed, giving the coin a mantle of 'grey hair'. The solution also slowly changes from colorless to pale blue, indicative of the presence of Cu^{2+} ions. The chemical equation is



for which the net ionic equation is



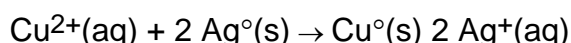
This reaction is a redox reaction because the oxidation number of copper changes from 0 to +2 (Cu is oxidized), while silver changes from +1 to 0 (Ag^+ is reduced). The NO_3^- ion remains unchanged (in this reaction), and is therefore just a *spectator ion*. The overall reaction can be divided into two half-reactions which explicitly show the electrons:



and which add together to give the net ionic reaction. As the reaction proceeds the concentration of Cu^{2+} increases, and the concentration of Ag^+ decreases. The equilibrium constant for the reaction is:

$$K = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

K is a very large number because the forward reaction (as written) is highly favored. The reverse reaction:

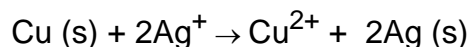




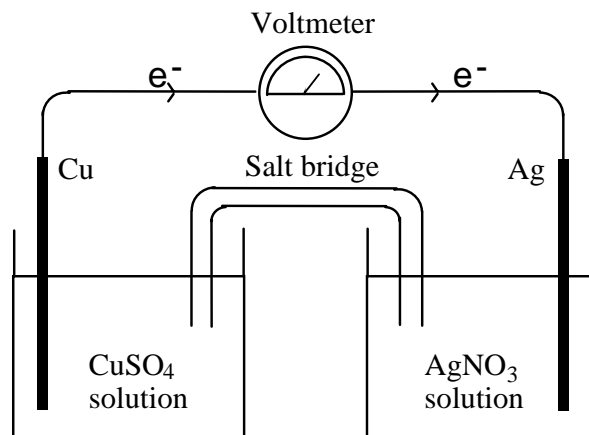
balances the forward reaction only when the silver ion concentration is very small. When this happens the reaction is at equilibrium and the free energy change $\Delta G = 0$. As long as the silver ion concentration is above the equilibrium value, ΔG is negative and the forward reaction is spontaneous.

Electrochemistry

Redox reactions in which electrons are completely lost by one species and completely gained by another are very useful because the two half-reactions can often be physically separated. The electrons that are transferred can then be directed to flow through an external wire in a circuit where they can do physical work. **Electrochemistry** is the study of redox reactions that either produce or consume electrical energy in an arrangement called an **electrochemical cell**. In the reaction:



the two half-reactions can actually be separated by placing the reactants in different compartments, partitioned by a barrier that prevents mixing, but not ion flow. Each compartment, called a **half-cell**, contains a metal electrode in contact with a solution containing its own metal ion, as shown in the figure below:



A Cu/Ag electrochemical cell

An external connection between the two electrodes completes the circuit, allowing electrons to flow from the copper electrode through the wire and meter and into the silver electrode. The copper electrode dissolves, forming Cu^{2+} ions in solution, while Ag^+ ions pick up electrons at the surface of the silver electrode and are deposited as silver atoms. The electrode at which oxidation takes place (the copper electrode) is called the **anode**, and the electrode at which reduction takes place (the silver electrode) is called the **cathode**. The combination of the two half-cells is called an **electrochemical cell**.

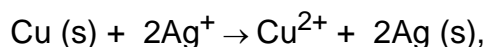
The voltage read on the meter is related to ΔG by $\Delta G = -nFE_{\text{cell}}$, where n is the number of moles of electrons in the redox reaction as written, and F is the faraday, 96485 coulombs per mol of electrons. If the ions are present in 1M solutions, the voltage (historically called the 'electromotive force' or 'emf') is called the 'standard emf' or E° . Over time, as $[\text{Cu}^{2+}]$ increases,



and $[\text{Ag}^+]$ decreases, the voltage decreases, eventually becoming zero when the concentrations reach their equilibrium values. Note that ΔG is also zero at this point. The equilibrium concentrations in this case are the same as those in a direct reaction between Cu and Ag^+ .

Standard Potentials

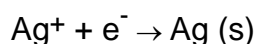
In the electrochemical cell given by the reaction:



the reaction that occurs at the Cu electrode is the oxidation reaction:

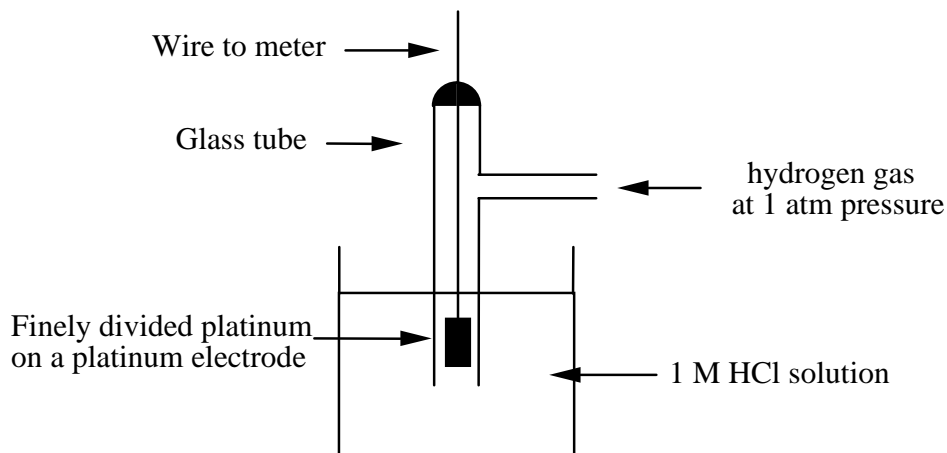


while the reduction reaction occurs at the silver electrode:



The relative tendency of a particular species to give up or accept electrons is manifested as a **potential**, measured in volts, between the two electrodes. This potential is the sum of two potentials called **half-cell potentials** or **single-electrode potentials**.

The tendency of a species to give up or accept electrons can only be judged by comparing it to another species. In order to have a consistent set of data, it is necessary to compare all single electrodes to a standard reference electrode. The universal reference electrode, chosen by international agreement, is the **standard hydrogen electrode**, shown below:



A Standard Hydrogen Electrode

The half-reaction at the standard hydrogen electrode (SHE),

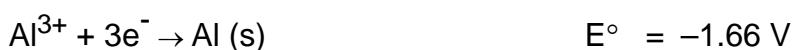


is usually written as a reduction. If reversed, the standard oxidation potential is also zero. By assigning a value of **zero** volts to the SHE, all other half-reactions can likewise be given values, based on the overall voltage of a cell made from a given half-reaction and the SHE. **It**



must be remembered that these half-cell potentials would all shift to some other set of values if a different 'reference electrode' was chosen. The magnitude of the shift would simply be the difference between the new 'standard' and the SHE. (This will be the case in this lab).

The half-cell potential depends on the concentration of the ions in solution as well as the temperature. Standard conditions of 1M concentration and 298 K (25°C) have been chosen, and by international agreement all standard electrode potentials (E°) are reported as **standard reduction potentials**. Some examples are shown below.



A useful way of thinking about E° values is to remember that the more **positive** the E° value, the further to the right that that reaction will go before reaching equilibrium. The E° values for half-reactions written as oxidations are simply the **negative** of the E° values for the reduction reaction, e.g.,

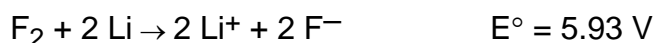


A larger table of standard reduction potentials is in Table 11.1 (Zumdahl text).

You will note that the values are arranged in decreasing order of the voltage. Thus Li, at the bottom of the table, is hard to reduce and (change sign) easy to oxidize. Exactly the opposite is true of F_2 at the top of the table. To find the voltage of a cell made of these two half-cells, we reverse one of them and change the sign so that the *sum is positive*:



The sum is +5.93. To balance the net ionic equation we must multiply the second half-reaction by two and add:



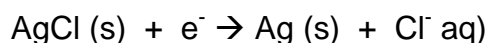
Note that you do NOT multiply E° for lithium by two. This is best seen from the formula $\Delta G^\circ = -nFE^\circ$. If you double the number of electrons ΔG° also doubles, therefore E° must stay the same.

Note that the voltage **of any complete cell will always be positive**; this is because any reaction which occurs by itself (without outside sources of energy) always has $\Delta G < 0$, and hence $E > 0$. A further bit of knowledge can be obtained from this fact: if the two half-reactions

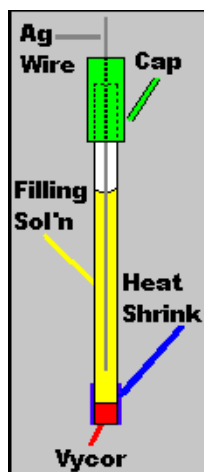


are written so that E° is positive, the positive electrode (as indicated by a voltmeter) is the half-reaction where electrons enter the cell (i.e. the reduction reaction) and the negative electrode is where electrons are produced (i.e. the oxidation reaction).

In this experiment, you will make measurements using a Ag/AgCl reference electrode. In this reference electrode, a silver wire is coated with silver chloride and this is in contact with a 3.0M NaCl filling solution (see figure below). The electrode potential is set by the following half reaction:



$E_{(\text{Ag/AgCl reference})} = 0.22 \text{ V}$ relative to standard hydrogen electrode. If you use the reference instead of the hydrogen electrode, all E° values would be 0.22 V lower. Thus if you make measurements using this reference electrode, you have to add 0.22 V before comparing your results with Table 11.1 (Zumdahl text).



Ag-AgCl Reference Electrode

Comparison of Electrode Potentials:

An important practical consideration in the measurement of cell potentials is that **the cell reaction must be carried out under standard conditions**. A simple wire connecting the two electrodes would allow the electrons to flow and the redox reaction to go to completion. In the process the ion concentrations in each half-cell would change until the forward and reverse reactions were balanced and the cell voltage reached zero. Cell potential measurements are therefore usually made with instruments that allow only a few electrons to pass through the circuit, i.e. they have a very high **resistance** – typically 10^7 ohms (10 megohms), which means a 1V difference will cause 10^{-7} coulombs per second (amps) to flow, or in chemical terms, about 10^{-12} moles of e^- per second. This rate is so low that no discernible change in concentration is noticeable.

Another important consideration is that **one must not only provide a path for the electrons to flow, but also one for the ions produced**. At first glance this may not be obvious, since it appears that the Cu^{2+} ions will just stay in the solution where they are formed. While this is true, unless there is a way to balance the charge carried by these ions, the reaction will quickly



cease as the solution builds up a net positive charge. The solution to this problem is to provide a pathway for the excess positive ions to escape, or conversely, for additional negative ions to enter the solution. This path is called a **salt bridge** because it contains a solution of some salt, such as KCl or KNO_3 , whose ions do not interfere with either of the half-cell reactions. In the cell where electrons leave (the oxidation half-reaction), either negative ions must come in, or positive ions must go out (or both). Similarly, in the reduction half-cell (where electrons come in), either negative ions must leave or positive ions must come in (or both). The salt bridge allows this to happen by providing an 'ionic wire' that can transport either + or - ions from one half-cell to the other.

Part II. Concentration Effects and Batteries

The concentration of the solution affects the half-cell potentials because it alters the relative stability of the ions. **Concentrated solutions** inhibit further ion formation, making **reduction more favorable**, and, therefore, increase the reduction potential of the half-reaction. Conversely, **dilute solutions (compared to the standard of 1M) favor oxidation processes** and, therefore, lower the value of the half-cell reduction potentials.

In a reaction in which both species lose or gain the same number of electrons the concentration effect ' **Cancels out**' if both solutions have the same concentration. If the half-reactions involve different numbers of e^- s, so that different numbers of ions are required to go into (or come out of) solution, then there will be a '**concentration effect**'.

The magnitude of this effect is given by the **Nernst equation** (Zumdahl, section 11.4), that basically provides a way to correct standard cell potentials for non-standard concentration conditions:

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

where Q is the Reaction Quotient (just like the equilibrium constant K, except you use the actual concentrations, not the equilibrium concentrations). $R = 8.314 \text{ J/mol}\cdot\text{K}$ and $F = 96485 \text{ C}$. T is in Kelvin, and $n = \#$ of electrons in the balanced reaction. E is the observed potential and E° is the standard reduction potential. At 25°C (298 K) and in log (base 10), the equation becomes:

$$E = E^\circ - \frac{0.05915}{n} \log(Q)$$

$$Q = [\text{Cu}^{2+}]/[\text{Ag}^+]^2 \text{ for the reaction: } \text{Cu (s)} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag (s)}$$

You might think that since 'n' depends on how you write the equation, that E will also depend on 'n'. 'Q', however, takes care of this problem: if you multiply the equation by two, for example, all the concentrations that appear in Q are squared, which means that the ln (or log) term is just 2x its previous value. This factor of two exactly cancels the increased value of 'n' in the denominator; thus E remains independent of how the equation is written. Note that if all the concentrations equal 1.0 M, then $Q = 1$, hence $\ln(Q)$ (or $\log(Q)$) = 0, so $E = E^\circ$.



The prelab assignment on WebAssign addresses the following:

- Calculating E_{cell} for several electrochemical cells, using $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$ for standard (E°) conditions and $E_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$ and the Nernst equation for non-standard conditions (E).
- Using the Nernst equation to figure out the Reaction Quotient (Q) for an electrochemical cell that will have a potential of exactly +0.50 V. (From Q , you will know what the ratio of the concentrations of the metal-ion solutions needs to be so that you will know how to dilute the 1 M solutions in lab in order to make this cell.)

Helpful information

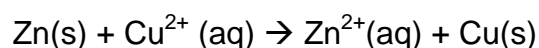
- Review sections 4.10 and 4.11 in Zumdahl for an introduction to Oxidation-Reduction reactions: definitions, characteristics, and how to balance them (Zumdahl's first discussion of half-reactions).
- A galvanic cell (section 11.1) is one in which chemical energy is changed to electrical energy – the spontaneous redox reaction produces current that can do work.
- *Oxidation occurs at the anode.* Tips to help you remember: "**OIL RIG**" - **O**xidation **I**s **L**oss of electrons, "**LEO says GER**" – **L**oss of **E**lectrons is **O**xidation, "**Oxidation/Anode**" – keep the words starting with vowels together.
- *Reduction occurs at the cathode.* Tips to help you remember: "**OIL RIG**" - **R**eduction **I**s **G**ain of electrons, "**LEO says GER**" – **G**ain of **E**lectrons is **R**eduction, "**Reduction/Cathode**" – keep the words starting with consonants together.
- Standard reduction potentials are explained in Zumdahl, section 11.2, cell potential and free energy in section 11.3, and the dependence of cell potential on concentration and the Nernst equation are covered in section 11.4.
- The Nernst equation is used for calculating potentials when some or all of the cell components are not in standard states.
- E°_{cell} is the standard potential (for standard conditions: 1 M, 25°C and 1 atm) and E_{cell} is the observed potential (for non-standard conditions).
- Cell notation: Anode | Anode Soln || Cathode Soln | Cathode

The single vertical lines represent physical interfaces between the metal-ion solution and the double vertical lines represent the salt bridge.

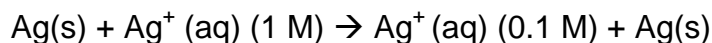
Example: $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) = 1 \text{ M} || \text{Cu}^{2+}(\text{aq}) = 1 \text{ M} | \text{Cu(s)}$



- When writing the spontaneous chemical reaction for any electrochemical cell, you first have to figure out in which direction each half-cell reaction is proceeding. Since the standard reduction potential for Cu/Cu^{2+} (0.34 V) is greater than the standard reduction potential for Zn/Zn^{2+} (-0.76 V), the Cu/Cu^{2+} cell will be the cathode (reduction half-cell) and run in the forward direction as written in the Table of Standard Reduction Potentials (Table 11.1). If the Cu reaction is $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ (electrons gained), then the Zn reaction must be the anode (oxidation half-cell) and the reaction must proceed in the opposite direction: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (electrons lost). When you combine these two reactions for the complete electrochemical cell, the result is:



The same approach applies to concentration cells when the two electrodes contain the same metal but different concentrations of metal-ion solution. You need to figure out which half-cell is the anode and which is the cathode so that you are sure each half-cell reaction is written in the correct direction (see the discussion on page 479 in Zumdahl, 5th Ed.). For this type of electrochemical cell, also note the concentration for each metal-ion solution:



- In order to compare the observed E°_{cell} relative to the Ag/AgCl reference electrode with the values presented in Table 11.1, you need to account for the standard potential of the non-SHE reference electrode. Consider the equation: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. When using the standard hydrogen electrode (SHE), $E^\circ_{\text{anode}} = E^\circ_{\text{H}^+/\text{H}_2} = 0.00 \text{ V}$. For Cu/Cu^{2+} as the cathode, E°_{cell} (observed) = 0.34 V, as seen on the standard reduction potential table. When using Ag/AgCl for the reference electrode, the E°_{cell} (observed) = 0.12 V. In order to compare your experimental values for the half-cell potentials with those in Table 11.1, calculate the $E^\circ_{\text{cathode}} \rightarrow E^\circ_{\text{cathode}} = E^\circ_{\text{cell}}$ (observed) + $E^\circ_{\text{anode}} = 0.12 \text{ V} + 0.22 \text{ V} = 0.34 \text{ V}$.

Safety Considerations

- Silver nitrate, AgNO_3 , will stain your hands brown, but is not harmful. The staining will take a week or so to wear away, so be careful when using the solution and clean up any spills immediately.
- The metal-ion solutions and salt bridge solution must be disposed of according to established hazardous waste disposal protocols. Be sure to follow the instructions for cleaning up from this lab so that all of the reagents and materials are taken care of appropriately.