# Applications of Galvanic Cell Reactions

Background

  The exchange of electrons during a redox process makes this type of reaction potentially useful in a variety of ways. One of the more familiar applications of redox chemistry is the *galvanic* or *voltaic* cell in the form of a dry-cell *battery* (a group of galvanic cells in series). At the simplest level, a galvanic cell acts as a kind of electron "pump" which causes electron flow from one point to another through the difference in electric potential created by the redox reaction inside. This flow of electrons can be harnessed for a variety of practical tasks and is related to the free energy expended by the chemical system in the cell as the reaction proceeds to equilibrium.

  A single galvanic cell consists of an oxidizing agent and reducing agent which are physically separated by one or more electrolytes. In a dry-cell battery, the electrolyte is usually in the form of a moist paste but it can also be liquid (as in an automobile battery). If the agents are allowed to come in direct contact then no electrical work is done and the energy of the reaction is released solely as heat. For this reason cells generally contain some kind of porous barrier which permits ion movement within the cell but retards general mixing of the agents. This barrier can take many forms including a glass tube filled with an electrolyte solution or gel, a strip of filter paper soaked in an electrolyte, or unglazed porcelain separating the cell electrolytes. A typical laboratory cell is diagrammed below:


porous barrier
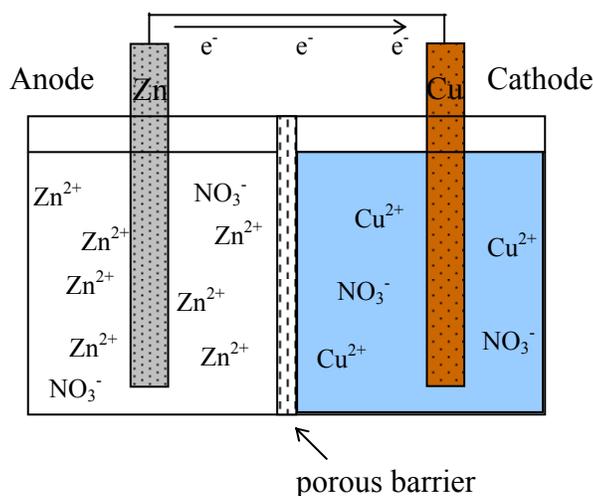
  In the example shown above the oxidation of zinc metal occurs spontaneously at the zinc electrode [anode] when the two pieces of metal are connected by a wire. This oxidation releases electrons which flow through the wire to the copper electrode [cathode] to enable the reduction of copper ions there. The direction of electron flow in a cell is determined partly by the relative ease of oxidation of the electrode materials. Because zinc is a more active metal than copper, a greater electric potential accumulates on the zinc strip when it is placed in the zinc solution, i.e., some of the zinc atoms from the metal enter the zinc solution spontaneously, resulting in a small surplus of electrons in the metal piece.

This process can be thought of as an equilibrium:

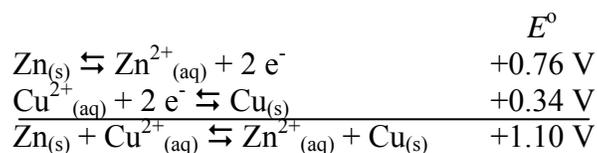$$Zn_{(s)} \leftrightarrows Zn^{2+}_{(aq)} + 2\ e^-$$
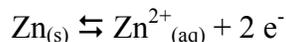
The equilibrium constant for this process is very small (or the zinc would simply dissolve). A similar equilibrium exists at the copper strip prior to connection:

$$Cu_{(s)} \leftrightarrows Cu^{2+}_{(aq)} + 2\ e^-$$
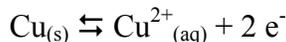
but since copper is a much less active metal than zinc the equilibrium constant for this process is even smaller than that for the zinc. We say the two metals have different *potentials* in this cell, comparing the tendency to release electrons. Thus when the two strips are connected with a wire, electrons will flow spontaneously from the zinc strip to the copper until the potential for electron release is the same at both strips. At that point equilibrium exists and there is no net flow of electrons between the metals. In common terms we describe such a cell as "dead". Thermodynamically speaking, its ability to do work is exhausted (i.e., $\Delta G = 0$).

The two *half-reactions* in this and other similar cells are kept physically separate but ion migration is permitted through the porous barrier. The movement of ions within the cell is part of the charge circulation which is needed to engender electron flow. If ions cannot move from one half of the cell to the other, there is a build-up of charge around each electrode. For example, as zinc atoms are spontaneously oxidized, zinc ions enter the solution at the electrode surface. This creates a greater concentration of these ions at that location and will cause the equilibrium at the electrode to shift even more to the left (i.e., zinc metal). Ion migration helps prevent this electrode *polarization* as well as moving charge through the internal part of the cell.

The potential for electrons to flow spontaneously in cells like this is measured as *voltage*. Each half-reaction has associated with it a standard potential which has been measured relative to the reduction of hydrogen ions in 1 M acid solution at standard thermodynamic conditions. The standard potentials are known as E^o values and represent electrical work that may be done by the half-reaction in combination with another. In the copper-zinc example presented earlier, the overall E^o value may be determined as:

$$
\begin{array}{ll}
 & E^o \\
Zn_{(s)} \leftrightarrows Zn^{2+}_{(aq)} + 2\ e^- & +0.76\ V \\
Cu^{2+}_{(aq)} + 2\ e^- \leftrightarrows Cu_{(s)} & +0.34\ V \\
\hline
Zn_{(s)} + Cu^{2+}_{(aq)} \leftrightarrows Zn^{2+}_{(aq)} + Cu_{(s)} & +1.10\ V
\end{array}
$$

E^o values in tables are typically given as reduction potentials. In the example above the zinc half-reaction has been written as an oxidation since zinc has a greater tendency to lose electrons than copper. Therefore the original table value of -0.76 V for the E^o of this process has been changed to +0.76 V.

The maximum free energy available from a galvanic cell can be calculated from standard thermodynamic values but because of the transfer of electrons through an external circuit (and therefore through devices) with the potential to do work, the free energy is also obtainable from the standard electric potential value for the cell.

The relationship is:

$$\Delta G^o = -nFE^o$$

where **n** represents the moles of electrons transferred as seen in the overall balanced chemical equation and *F* is a constant called the **faraday**, 96500 coulombs/mole e⁻ [a *coulomb* (C) is a unit of electric charge equivalent to 1 joule/volt].

This expression can be extended to great analytical advantage by recalling that there is also a relationship between the maximum free energy change for a reaction and the equilibrium constant, K_c:

$$\Delta G^o = -RT \ln K_c$$

Since reactions seldom begin with substances at standard states, an amended relationship allows the calculation of the free energy available at a given point in a reaction:

$$\Delta G = \Delta G^o + RT \ln Q_c$$

where Q_c is the reaction quotient with the same form as K_c, but initial or current concentrations rather than equilibrium concentrations. When $Q_c = K_c$, $\Delta G = 0$, i.e., the system is at equilibrium.

Combining the relationship between the standard free energy and the standard cell potential with that between the standard free energy and the equilibrium constant we have:

$$-nFE^o = \Delta G^o = -RT \ln K_c$$

This gives a relationship between the standard cell potential and the equilibrium constant for the reaction. An even more useful relationship can be derived following the substitution process shown earlier which relates the actual cell potential, *E*, with the ambient concentrations:

$$-nFE = -nFE^o + RT \ln Q_c$$

This is the basic relationship that is today known as the Nernst Equation and is generally given as:

$$E = E^o - \frac{RT}{nF} \ln Q_c$$

In practice this relationship can only be used accurately at 298 K because of the presence of the standard potential value. Other temperatures require an estimation of "E^o" for those conditions (this can be done experimentally or by calculating an approximate "ΔG^o" from the Gibbs-Helmholtz equation using a non-standard value for T). Because of the restricted nature of the relationship, the constants (including T as 298 K) are traditionally combined along with a conversion from the natural log to $\log_{10}$ and the expression is often written as:

$$E = E^o - \frac{0.0592}{n} \log Q_c$$

The power hidden in this expression may not be immediately evident on casual inspection. At face value it appears useful for determining the voltage output of a galvanic cell at non-standard concentrations. However, its real utility lies in doing just the opposite: <u>determining an unknown concentration based on a measured voltage</u>.

In the laboratory, many reactions involve ions which are part of standard galvanic cell combinations. The Nernst equation thus provides a tool for determining the concentration of these ions in equilibrium systems.

For example, the complexation of copper(II) by ammonia is a reaction you have seen in the lab:

$$Cu^{2+}_{(aq)} + 4\ NH_{3(aq)} \leftrightarrows Cu(NH_3)_4^{2+}_{(aq)}$$
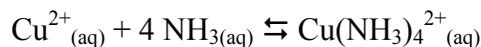
We know that this process, while strongly favoring the formation of tetraamminecopper(II) ion, is an equilibrium process. The K_f value for the formation of the complex ion can be found in many references. If a known amount of excess ammonia is added to the copper half of the Cu-Zn galvanic cell used as an example earlier:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \leftrightarrows Zn^{2+}_{(aq)} + Cu_{(s)} \qquad E^o = +1.10\ v$$
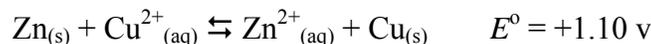
the concentration of $Cu^{2+}_{(aq)}$ will drop dramatically. The measured cell voltage, E, will change from the standard value, E^o, based on this decrease. The new equilibrium $[Cu^{2+}]$ will thus be the only unknown left in the following expression (assuming original standard conditions):

$$E = E^o - \frac{0.0592}{n}\ \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

If the equilibrium $[Cu^{2+}]$ can be found in this way and the initial $[NH_3]$ is also known, it is possible to calculate K_f for the complexation process. The same technique can often be applied to solubility product constants.

It is even possible to determine the concentration of an ion in one half of a cell with the same anode and cathode! The measured E for a standard cell of that description should be 0.00 V (since $Q_c = 1$). But such "concentration cells" can generate small potentials based on the slightly different equilibria that exist at each electrode by virtue of the fact that there are more or fewer ions present in the electrolyte around one of the electrodes. An important application of this behavior is found in every chemistry laboratory around the world in the form of a pH electrode.

In addition to their analytical uses in the laboratory, galvanic cells are good systems for examining relationships among thermodynamic quantities. The determination of standard free energy values for reactions is generally an indirect process. If the equilibrium constant for such reactions can be determined then ΔG^o can be calculated from that value. We have seen in the previous discussion that there is also a relationship between the standard potential for a cell reaction and the standard free energy change:

$$\Delta G^o = -nFE^o$$

Moreover, we know that standard free energy changes can be calculated from standard enthalpy and standard entropy changes:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Combining these expressions we might write:

$$-nFE^o = \Delta H^o - T\Delta S^o$$

or

$$E^o = \frac{\Delta S^o}{nF} T - \frac{\Delta H^o}{nF}$$

This expression, of course, is in the form of the equation of a straight line and suggests that careful measurements of the cell voltage over a range of temperatures can yield a much more difficult quantity to determine: the standard entropy change for the reaction, ΔS^o. This expression, like the Nernst equation, suffers from an important limitation: it is strictly correct only at 298 K. However, the values of ΔS and ΔH typically change only a little over a small temperature range and careful measurements in the vicinity of room temperature can give results which agree well with other methods.

The Experiment

There are three parts to this experiment:

- determine the apparent E^o value for the following cell:
    Cu|Cu^{2+}(1.0 M)|| Ag$^+$(1.0 M)|Ag

- determine the following ion concentrations:
    1) Cu^{2+}$_{(aq)}$ in an unknown solution [reference half-cell: Cu|Cu^{2+}(1.0 M)]
    2) Ag$^+$$_{(aq)}$ in a saturated AgCl solution [reference half-cell: Cu|Cu^{2+}(1.0 M)]
    3) Cu^{2+}$_{(aq)}$ in excess NO$_2$$^-$$_{(aq)}$ solution [reference half-cell: Ag|Ag$^+$(1.0 M)]

- determine the temperature dependence of the voltage for the cell:
    Cu|Cu^{2+}(1.0 M)||Ag$^+$(1.0 M)|Ag

The following non-locker materials will be provided:

- solutions of 1.0 M Cu(NO$_3$)$_2$, 1.0 M AgNO$_3$, 1.0 M NaNO$_2$, 1.0 M KCl,
    "x" M Cu(NO$_3$)$_2$, 0.10 M Cu(NO$_3$)$_2$
- metal electrodes: Cu, Ag
- glass tubing, cotton string and septum stopper (see **Technique** section)
- CBL thermometer probe
- CBL voltage probe
- forceps
- beral pipets
- micropipettor and tips
- multimeter and leads

The Chemicals

Copper(II) nitrate is the source of the Cu^{2+} ion in this experiment. Commonly available in several hydrates, the blue-green solid is deliquescent and very soluble in water.

It is used in light-sensitive reproductive papers and as a colorant in ceramics. The compound is also an ingredient in a solution for producing an antique black finish on copper. It is employed in a variety of electroplating baths. The solid material is irritating to the skin.

Silver nitrate (the source of Ag^+ in this experiment) forms colorless, transparent crystals. It is stable and not darkened by light in pure air but darkens in the presence of organic matter and H_2S. It decomposes at low red heat into metallic silver. It is used in photography and the manufacture of mirrors, silver plating, indelible inks, hair dyes, etching ivory and as an important reagent in analytical chemistry. It has been used as a topical antiseptic in a 0.1 to 10% solution. However, it is caustic and irritating to skin. Silver nitrate stains skin and clothing. These stains will wear off skin in a few days to a week but clothing is generally ruined. Swallowing silver nitrate can cause severe gastroenteritis that may end fatally.

Potassium chloride is a white, crystalline solid or powder. One gram will dissolve in as little as 2.8 mL of water. The compound occurs in nature as the mineral *sylvine*. It is used in photography, buffer solutions and electrodes. Large doses by mouth can cause gastrointestinal irritation, purging and circulatory disturbances. In this experiment it is the source of Cl^- used to saturate a solution with AgCl.

Silver is one of the few metals that can be found native and is also found associated with copper, gold, or lead. It constitutes 1×10^{-5} % of the earth's crust. It is more malleable and ductile than any metal except gold and when pure is perhaps the best electrical conductor. It is insoluble in acids except nitric or hot concentrated sulfuric. Most silver salts are light sensitive (they darken on exposure to light) and this property makes them useful in the manufacture of photographic film. Small crystals of silver chloride are used in some photochromic eyeglasses. Absorption of light causes the AgCl to dissociate into Ag and Cl. The finely dispersed silver atoms tint the glass gray. The reverse reaction occurs in subdued light.

Copper makes up about 0.01% of the earth's crust. It is one of the earliest known metals and is known for its unique reddish color when pure. However it becomes dull when exposed to air, forming oxides of copper, and in moist air becomes coated with green copper carbonate (this is part of the patina that appears on old copper or copper alloy exposed to the elements--like the Statue of Liberty). It is very slowly attacked by dilute hydrochloric acid and sulfuric acid, while nitric acid can readily dissolve it. It also slowly dissolves in aqueous ammonia.

Copper is used in the manufacture of bronzes (copper + tin) and brasses (copper + zinc), and is used extensively in electrical conductors (wires, printed circuits, etc.). Of course copper also makes up a percentage of nearly all U.S. coins minted today.

Copper itself probably has little or no toxicity, but some of its compounds can be quite hazardous.

Technique Discussion

Electrode preparation is always very important for good results in electrochemical experiments. Electrodes should be cleaned with an abrasive pad of some kind, then wiped clean. Contamination of the electrode solutions can also contribute to inaccurate results. For this reason, only the solutions within the two standard half-cells should be reused. The standard copper and silver half-cells used in the first part of the experiment may be retained for later parts, but all other solutions must be discarded at the end of each measurement and new, clean test tubes should be used for each solution.

The standard half-cells are constructed from pieces of glass tubing. A short length of cotton string is inserted into one end of the tubing and is held in place by firmly inserting a rubber septum stopper. When the collar of the septum stopper is folded over there should be a small length of the string exposed (and a small length visible in the tube as well):
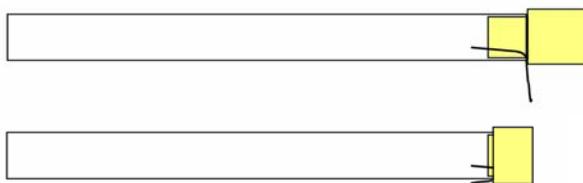
The cotton string acts as a salt bridge but prevents solution from dripping out (or diffusing in) at an observable rate. Two half-cells should be made in this way. One holds a copper electrode in 1.0 M $Cu(NO_3)_2$, the other has a silver electrode in 1.0 M $AgNO_3$. The half-cells only need to be filled about ½ to ⅔ of the way with solution. During the experiment the half-cells are inserted into (clean) locker test tubes which are used for the other half of the cell. In these test tubes the electrolyte is filled to about the same level as the solution in the tube and a second electrode is inserted. Both electrode strips can be folded over gently to keep them from falling into the tubes and to aid in connecting to electrical leads.

Because the standard half-cells will be used in several parts of the experiment it is important to rinse the outside of the cell thoroughly with distilled water between parts, paying special attention to the protruding cotton string. The outside of the tube should then be dried before reuse. Care should be exercised with the silver half-cell as some silver nitrate will have diffused into the string. Gloves may be helpful.

The multimeters have several scales for displaying small voltages. In general more significant digits are better. Two digits are the absolute minimum and you should always try to adjust the meter to display three by using the millivolt settings. It is important to note the polarity of the cell (i.e., which electrode is the anode and which is the cathode). This will enable you to establish the spontaneous direction of the reaction. When a positive reading is displayed on the multimeter, the electrode connected to the black lead (marked COM on the meter) is the anode.

For the initial measurement of the standard cell voltage, 1.0 M solutions of Cu^{2+} and Ag^+ are used. For ease of clean-up and conservation of expensive silver solution it is best to use the silver half-cell as the inner tube.

In the second part of the experiment the solution volumes in the outer half-cell (in the test tube) are critical only in the determination of $[Cu^{2+}]$ for the Cu^{2+}-NO_2^- mixture. To ensure that the maximum amount of complex is formed, a **0.10 M** $Cu(NO_3)_2$ solution should be used with excess 1.0 M ligand solution (suggested volume ratio: 300:2700 μL).

For the determination of $[Ag^+]$ in a saturated AgCl solution, only one drop of 1.0 M silver ion should be added to the 1.0 M KCl to sustain a visible precipitate. Be sure to mix thoroughly.

A 250 mL beaker can be used as a stirred water bath for temperature control in part 3. The silver/copper cell should be clamped so that all of the solution is below the water bath level. A second test tube filled with room temperature water should also be clamped in place and a thermometer probe suspended in it. This should give a better indication of the temperature in the actual galvanic cell.

Care should be exercised in heating the water bath so that there is time for temperature equilibration. The hotplate setting of "2" seems to work well. The CBL should be set up for two probes, voltage (0 to +5) on channel 1 and temperature on channel 2. Record data every 5 minutes (300 s) for 60 minutes. A temperature range of 5^oC to about 60^oC should be sufficient. Pre-chilled water will be available.

The Report

Your initial calculations should include:

1. The half-cell potential of $Cu^{2+}|Cu$, taking the reduction half-cell potential of the silver system to be +0.80 v [relative error]

2. The K_{sp} of AgCl based on the concentration of $Ag^+_{(aq)}$ after precipitation with 1.0 M KCl [relative error]

3. The concentration of the unknown $Cu^{2+}_{(aq)}$ solution

4. The K_f for $CuNO_2(H_2O)_3^+$ based on the equilibrium concentration of free $Cu^{2+}_{(aq)}$ remaining after addition of 1.0 M $NaNO_2$

5. A graph of E vs. T for the Cu-Ag cell

6. Estimates of ΔG^o, ΔS^o, ΔH^o, and E^o for the Cu-Ag cell [relative error]

You should include a comparison of your calculated half-cell potentials and constants with literature values as well as a discussion of possible sources of error if your values do not agree well. Can you suggest experimental conditions under which you might obtain better results?

Why is the silver half-cell chosen in this experiment as the "standard" (i.e., it's potential is assumed to be +0.80 v)?

In a previous experiment you ranked the nitrite ligand among several others for its ability to displace the others from a copper(II) complex ion. Does the K_f determined in this experiment agree with your ranking? If not, attempt to account for the discrepancy.

Finally, the entropy change in the Cu-Ag cell is negative. For the cell $Pb|Pb^{2+}$(1.0 M)$||Cu^{2+}$(1.0 M|Cu the entropy change is found to be positive. What effect would this have on the temperature dependence of E for this cell? Attempt to account for the different signs of the entropy changes.