ELEMENTS OF ELECTROCHEMISTRY

I. Introduction

   A. A number of analytical techniques are based upon oxidation-reduction reactions.

   B. Examples of these techniques would include:

      1. Determinations of K_{eq} and oxidation-reduction midpoint potentials.
      2. Determination of analytes by oxidation-reductions titrations.
      3. Ion-specific electrodes (e.g., pH electrodes, etc.)
      4. Gas-sensing probes.
      5. Electrogravimetric analysis: oxidizing or reducing analytes to a known product and weighing the amount produced
   6. Coulometric analysis: measuring the quantity of electrons required to reduce/oxidize an analyte

II. Terminology

   A. Reduction: the gaining of electrons

   B. Oxidation: the loss of electrons

   C. Reducing agent (reductant): species that donates electrons to reduce another reagent. (The reducing agent get oxidized.)

   D. Oxidizing agent (oxidant): species that accepts electrons to oxidize another species. (The oxidizing agent gets reduced.)

   E. Oxidation-reduction reaction (redox reaction): a reaction in which electrons are transferred from one reactant to another.
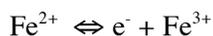
      1. For example, the reduction of cerium(IV) by iron(II):

$$Ce^{4+} + Fe^{2+} \Leftrightarrow Ce^{3+} + Fe^{3+}$$
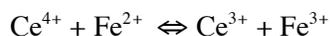
         a. The reduction half-reaction is given by:

$$Ce^{4+} + e^- \Leftrightarrow Ce^{3+}$$
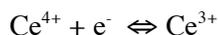
         b. The oxidation half-reaction is given by:

$$Fe^{2+} \Leftrightarrow e^- + Fe^{3+}$$

      2. The half-reactions are the overall reaction broken down into oxidation and reduction steps.

      3. Half-reactions cannot occur independently, but are used *conceptually* to simplify understanding and balancing the equations.

III. Rules for Balancing Oxidation-Reduction Reactions

   A. Write out half-reaction "skeletons."

B. Balance the half-reactions by adding H^+, OH^- or H_2O as needed, maintaining electrical neutrality.

C. Combine the two half-reactions such that the number of electrons transferred in each cancels out when combined.

D. For example, consider the following reaction of the peroxydisulfate ion with manganese ion:
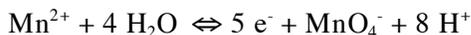
$$S_2O_8^{2-} + Mn^{2+} \Leftrightarrow SO_4^{2-} + MnO_4^-$$

1. The reduction step is:

$$S_2O_8^{2-} + 2 \, e^- \Leftrightarrow 2 \, SO_4^{2-}$$
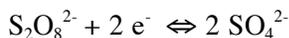
(Each sulfur atoms goes from +7 to +6 oxidation state.)

2. The oxidation step is:

$$Mn^{2+} + 4 \, H_2O \Leftrightarrow 5 \, e^- + MnO_4^- + 8 \, H^+$$

(Manganese(II) loses 5 electrons, going from +2 to +7.)

3. In combining the two equations, the oxidation step must be multiplied by "2," and the reduction step must be multiplied by "5" to cancel out the electrons:
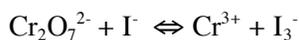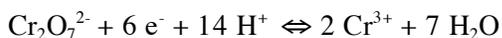
$$2x[Mn^{2+} + 4 \, H_2O \Leftrightarrow 5 \, e^- + MnO_4^- + 8 \, H^+]$$

$$5x[S_2O_8^{2-} + 2 \, e^- \Leftrightarrow 2 \, SO_4^{2-}]$$
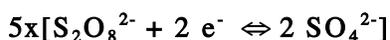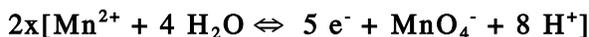
Adding these two equations together:

$$5 \, S_2O_8^{2-} + 2 \, Mn^{2+} + 8 \, H_2O \Leftrightarrow 10 \, SO_4^{2-} + 2 \, MnO_4^- + 16 \, H^+$$

6. Note that the half-reactions are charge-balanced before adding them together.

E. Consider the next example:

$$Cr_2O_7^{2-} + I^- \Leftrightarrow Cr^{3+} + I_3^-$$

1. The reduction step is given by:

$$Cr_2O_7^{2-} + 6 \, e^- + 14 \, H^+ \Leftrightarrow 2 \, Cr^{3+} + 7 \, H_2O$$

(Cr(IV) in the dichromate on is reduced to Cr(III).)

2. The oxidation step is give by:

$$3 \, I^- \Leftrightarrow 2 \, e^- + I_3^-$$

3. Multiplying the oxidation half-reaction by 3x and adding the two half-reactions together:

$$Cr_2O_7^{2-} + 9 \, I^- + 14 \, H^+ \Leftrightarrow 2 \, Cr^{3+} + 3 \, I_3^- + 7 \, H_2O$$
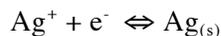
IV. Oxidation-Reduction Reactions in Electrochemical Cells

A. It is possible to separate the half-reactions of an oxidation-reduction reaction in an electrochemical cell.
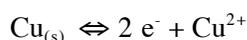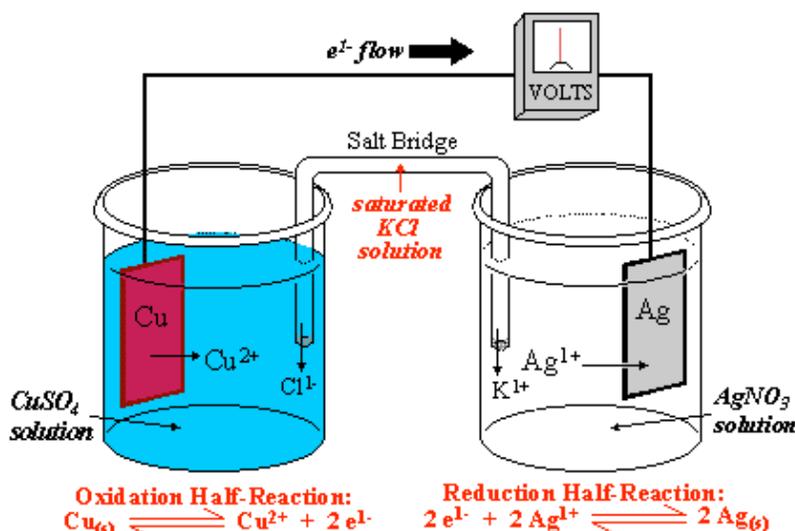
B. Consider the following reaction:

$$2 \ Ag^{1+} + Cu_{(s)} \ 2 \ Ag_{(s)} + Cu^{2+}$$
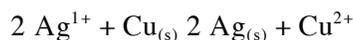
  1. The reduction half-reaction is given by:

$$Ag^+ + e^- \Leftrightarrow Ag_{(s)}$$

  2. The oxidation half-reaction is given by:

$$Cu_{(s)} \Leftrightarrow 2 \ e^- + Cu^{2+}$$

C. These reactions can be "separated" in a galvanic cell (also called a voltaic cell or battery):

D. Description of the battery above:

  1. The left container contains of 0.020 M $CuSO_4$. The right cell contains 0.0200 M $AgNO_3$.

  2. A Cu electrode is immersed in the $CuSO_4$ solution. An Ag electrode in immersed in the $AgNO_3$ solution.

  3. The two solutions "communicate" via a salt bridge which consists of a saturated KCl solution in a tube with glass frits in both ends.

  4. At the **anode, oxidation** takes place:

$$Cu_{(s)} \Leftrightarrow 2 \ e^- + Cu^{2+}$$

  5. At the **cathode, reduction** takes place:

$$2 \ Ag^+ + 2 \ e^- \Leftrightarrow 2 \ Ag_{(s)}$$

  6. Chloride ions move into the $CuSO_4$ solution to maintain electrical neutrality.

  7. Potassium ions move into the $AgNO_3$ solution to maintain electrical neutrality.

8. The volt meter reads 0.412 V at the instant the connection is made between the two electrodes. (This represents the difference is voltage (E_{cell}) between the two electrodes.

> a. The copper electrode has an initial voltage of 0.2867 V.
> b. The silver electrode has an initial voltage of 0.6984 V.
>
> c. Voltage Difference = Voltage$_{cathode}$ - Voltage$_{anode}$
>
> Voltage Difference = 0.6984 - 0.2867 = + 0.412 V

9. This initial voltage drops as the reaction proceeds toward equilibrium as soon as connection is made. At equilibrium, the voltage read zero volts.

10. The potential difference (voltage) between the anode and cathode is a measure of the tendency of the reaction to proceed from nonequilibrium to equilibrium.

E. Operation of an electrolytic cell

1. An external voltage source with a voltage larger than that of the battery is connected to the galvanic cell - positive pole to the silver electrode; negative pole to the copper electrode.

2. The external voltage source reversed the direction of electron flow (and reverses the direction of the reactions at each electrode):

> a. The silver electrode switches from the cathode to the anode (the site of oxidation).
> b. The copper electrode switches from the anode to the cathode (the site of reduction.
> c. The voltage meter will read "negative" if still connected in the original fashion.
> d. The battery will "recharge."

V. Schematic Representation of Cells

A. The copper(II) sulfate/silver nitrate systems described above would be symbolized:

$$Cu|CuSO_4 \ (0.02 \ M)||AgNO_3 \ (0.02 \ M)|Ag$$

1. Each vertical line ("|") represents a phase boundary or interface where a potential develops.
2. Each double vertical line ("||") represents two phase boundaries (e.g., the salt bridge).
3. The direction of electron flow is from left to right: Cu--->Ag.

B. The equilibrium expression for this galvanic cell would be:

$$2 \ Ag^+ + Cu_{(s)} \Leftrightarrow 2 \ Ag_{(s)} + Cu^{2+}$$

a. If the battery, initially with 0.0200 M copper ion and 0.0200 M silver ion, is allowed to react to equilibrium, the final concentrations of these ions at equilibrium is determined experimentally to be 0.0300 M copper ion and 2.7 x 10^{-9} M silver ion.

$$K_{eq} = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{0.03}{(2.7 \cdot 10^{-9})^2} = 4.14 \cdot 10^{15}$$

b. Note that the calculation above requires that the cell voltage be zero (i.e., at equilibrium) and that the concentrations be determined by analysis.

C. The original, *initial* voltage for the cell is given by:

$E_{cell} = E_{right} - E_{left} = E_{cathode} - E_{anode} = E_{Ag} - E_{Cu}$

1. The potentials (absolute voltages) at the two electrodes cannot be determined experimentally.

2. Only the differences between electrodes (via a voltmeter) can be measured.

3. Potentials at electrodes are assigned relative values, based upon comparison to a standard.

4. By convention, the standard hydrogen electrode (SHE) is used as the "agreed upon" reference half-cell against which all others are compared.

5. The voltage or cell potential is related to the free energy of the reaction driving the cell:

$$G = -nF \; E_{cell} = -2.303RTlog(K_{eq})$$

VI. Standard Hydrogen Electrode (SHE)

A. The SHE (standard hydrogen electrode) is the reference point for determining relative electrode potentials.

B. The SHE is symbolized:

Pt, H_2 ($p_{hydrogen}$ = 1.00 atm)|H^+ (a_{H+} = 1.00)||Ag^+ (a_{Ag+} = 1.00)|Ag)
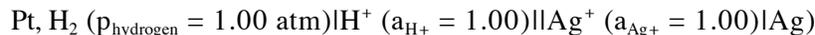
1. The platinum electrode is a platinized platinum electrode (platinum coated with finely divided platinum called platinum black).
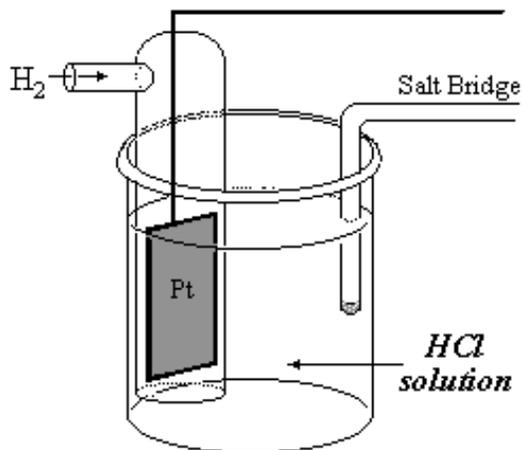
2. The aqueous acid solution has an activity of 1.00 (i.e., approximately 1.00 M hydrogen ion) and is saturated with hydrogen gas, bubbled in at 1.00 atmosphere.

3. The SHE is connected via the salt bridge and connecting wire to the other half-cell of the battery.

C. The half-cell reaction is given by:
$$2 \ H^+ + 2 \ e^- \Leftrightarrow H_{2(g)}$$
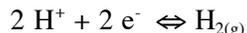
1. The SHE acts as either the anode or cathode, depending upon whether electrons are given up to the other half-cell or taken in.

2. By convention, the SHE is **assigned** an absolute potential (voltage) = 0.00 volts at **ALL temperatures**.

3. All other half-cells (and half-reactions) are measured relative to the SHE. By definition, the electrode potential is the potential of a cell with the standard hydrogen electrode acting as the anode and the other half-cell acting as the cathode.

a. For example, consider the cell formed with the SHE as one half-cell and an Ag/Ag^+ half-cell on the other side consisting of a silver electrode and an $a_{Ag+} = 1.00$ silver nitrate solution.

1) At the anode (oxidation): SHE

$$2 \ H^+ + 2 \ e^- \Leftrightarrow H_{2(g)}$$
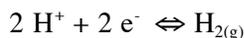
2) At the cathode (reduction): Ag/Ag^+
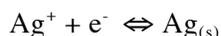
$$Ag^+ + e^- \Leftrightarrow Ag_{(s)}$$

3) At the instant the connection between half-cells is made, the experimentally observed difference in potential between the two electrodes measured by the voltmeter (i.e., the battery voltage) is +0.799 V.

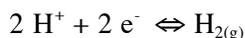4) Electrons flow **from** the SHE **to** the Ag electrode.

5) By convention, the sign of the voltage is positive if electrons leaves the SHE; negative if electrons are taken in.

b. Consider what happens if the Ag/Ag^+ half-cell is replaced with a Cd/Cd^{2+} half-cell ($a_{Cd2+} = 1.00$) attached to an SHE.

1) At the anode (oxidation): Cd/Cd^{2+}

$$Cd \Leftrightarrow Cd^{2+} + 2 \ e^-$$

2) At the cathode (reduction): SHE

$$2 \ H^+ + 2 \ e^- \Leftrightarrow H_{2(g)}$$

3) At the instant the connection between half-cells is made, the experimentally observed difference in potential between the two electrodes measured by the volt meter (i.e., the battery voltage) is a **negative voltage** (-0.403 V).

4) Electrons flow *to* the SHE *from* the Cd electrode.

5) By convention, the sign of the voltage is negative if electrons are taken in by the SHE. This means that the half-cell reaction opposite the SHE is more reducing than the SHE.

6) A voltage greater than 0.403 V would have to be applied to reverse the flow of electrons.

VII. Accepted IUPAC Conventions and Electrode Potentials

A. Half-reactions are always written as reductions (i.e., electrodes potentials are by definitions reduction potentials).

B. The sign of the electrode potential is determined relative to the SHE.

 1. Positive (+) means electrons flow out of the SHE to the other electrode (i.e., the SHE acts an the anode).
 2. Negative (-) means electrons flow to the SHE from the other electrode (i.e., the SHE becomes the cathode).

C. The sign of the electrode potential signifies whether the net reaction of the battery is spontaneous "to the right" or "to the left." For example:

 1. The Ag/Ag^+ half-reaction has an electrode potential of +0.799 V, meaning electrons flow to the Ag electrode.
 2. The Cd/Cd^{2+} half-reaction has an electrode potential of -0.403 V, meaning electrons flow to the SHE (and the reactions occur *opposite* to the directions written above).

D. The effect of species concentration of electrode potentials is described by the Nernst equation. For the reversible half-reaction:

$$aA + bB + ... ne^- \Leftrightarrow cC + dD$$
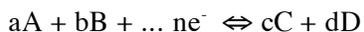
$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where,
  E = the electrode potential
  E° = the standard electrode potential (i.e., the potential observed when species in the half-cell are at a = 1.00 or pressure = 1.00 atm)
  R = the gas constant ($8.314 \ JK^{-1}mol^{-1}$)
  T = Kelvin temperature
  n = number of moles of electrons in balanced half reaction
  F = Faraday's constant (96,485 coulombs/mole; the charge on a mole of electrons).

 1. Note that the standard electrode potential (E°) is measured under standard conditions (a = 1, pressure = 1 atm).
 2. The Nernst equation corrects for nonstandard concentrations.
 3. 2.303RT/nF simplifies to 0.0592/n.
 4. E = E° if all species are at a = 1 and pressure = 1 atm.

VII. Calculating battery voltages: differences in potentials between electrodes

A. The battery voltage is given by:

$$E_{cell} = E_{right} - E_{left} = E_{cathode} - E_{anode}$$

B. Each half-cell electrode potential is calculated, and the difference between electrode determined.