Upcoming Deadlines

Due 2/7: Superconductor lab analysis
Due 2/14 or 2/21: $K_2S_2 O_8$ formal report

Exp. 3: Electrolytic Synthesis of $K_2S_2O_8$ (Text #9)

What does "electrolytic" mean?

There are two broad "types" of electrochemical cells, galvanic (also called voltaic) and electrolytic. . . .

A galvanic cell employs a spontaneous electrochemical reaction to generate electric current.

In an electrolytic cell, current is supplied to drive a non-spontaneous electrochemical reaction.

Intro

- Electrolysis is a very important process in industry. Nearly all pure metals are obtained from electrolytic reduction of **ores**.

- Electrolysis works by forcing current across an electrolyte solution. Reduction reactions occur at the **cathode**, and oxidation reactions occur at the **anode**.

- Ex. Aluminum (dissolve in molten cryolite, Na_3AlF_6)

$$2\,Al_2O_{3\,(in\ cryolite)} + 3\,C_{(s)} \rightarrow 4\,Al_{(l)} + 3\,CO_{2\,(g)}$$

anode (ox.): $6\,O^{2-} + 3\,C \rightarrow 3\,CO_2 + 12\,e^-$

cathode (red.): $4\,Al^{3+} + 12\,e^- \rightarrow 4\,Al$

Electrolytic Synthesis of $K_2S_2O_8$

- In this lab, you will:
  - prepare potassium persulfate via electrolysis of a solution of potassium bisulfate using an electrolysis cell, an external power supply, and platinum wire
  - calculate the %yield of the reaction
  - demonstrate the oxidizing power of the persulfate anion

Preparation of Electrolyte Solution

- For the synthesis of potassium persulfate, an electrolyte solution comprised of potassium bisulfate is generated by the reaction of potassium sulfate and sulfuric acid

$$K_2SO_4(aq) + H_2SO_4(aq) \rightarrow 2KHSO_4$$

- Your potassium bisulfate solutions will be prepared by Ms. Aiken prior to lab on Thursday.

Predicting Spontaneity of Electrochemical Reactions

We use cell potentials (E_{cell}) to predict spontaneity. What values of E_{cell} correspond to a spontaneous reaction?

$$\Delta G = -nFE_{cell}$$

$F = 9.6485 \times 10^4$ C/mol e-
n = moles of electrons

Spontaneous reactions have positive values of E_{cell} ($\Delta G < 0$).

We typically use $E°$ values, so that we can employ standard potentials for half-reactions.

T = 25 °C; P = 1 bar; Conc. = 1 M

anode (ox.): $2\,SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\,e^-$ $E° = -2.05$ V

cathode (red.): $2\,H^+ + 2\,e^- \rightarrow H_2$ $E° = 0.00$ V

$E°_{cell} =$ -2.05 V; Non-spont.

Notes for working with $E_{1/2}$ values:

- For reverse reaction (for oxidation), change sign of $E°$
- E° does **not** depend on amount. Do **not** change the magnitude of $E°$ if you change coefficients of the half-reaction.

A Potential Problem to Overcome . . .

Competing oxidation of water:

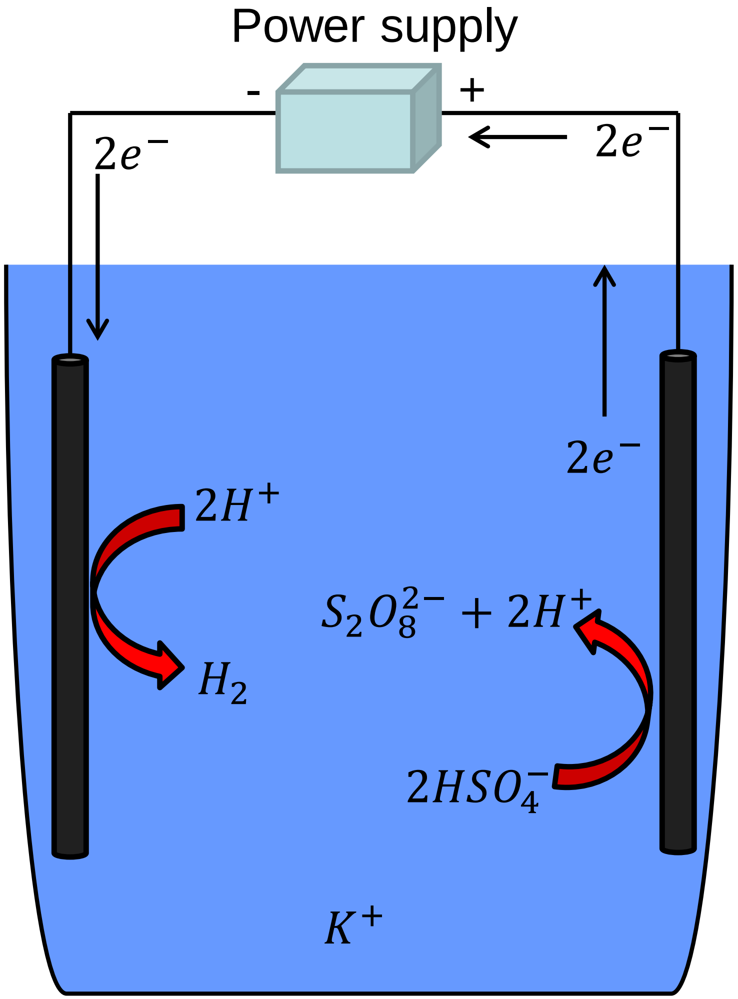
anode (ox.): $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ $E^\circ = -1.23$ V

Less negative than our desired oxidation (-2.05 V) → more favorable!

Fortunately, oxidation of water is very slow on Platinum electrode surfaces; much higher voltages are required to achieve reasonable reaction rates. We will use conditions that minimize the rate of water oxidation (maximizing the overvoltage required).

- Pt wire electrodes
- Cold temperature (ice bath)
- High concentration of reactant HSO_4^-
- High current density (1.0 A/cm^2)

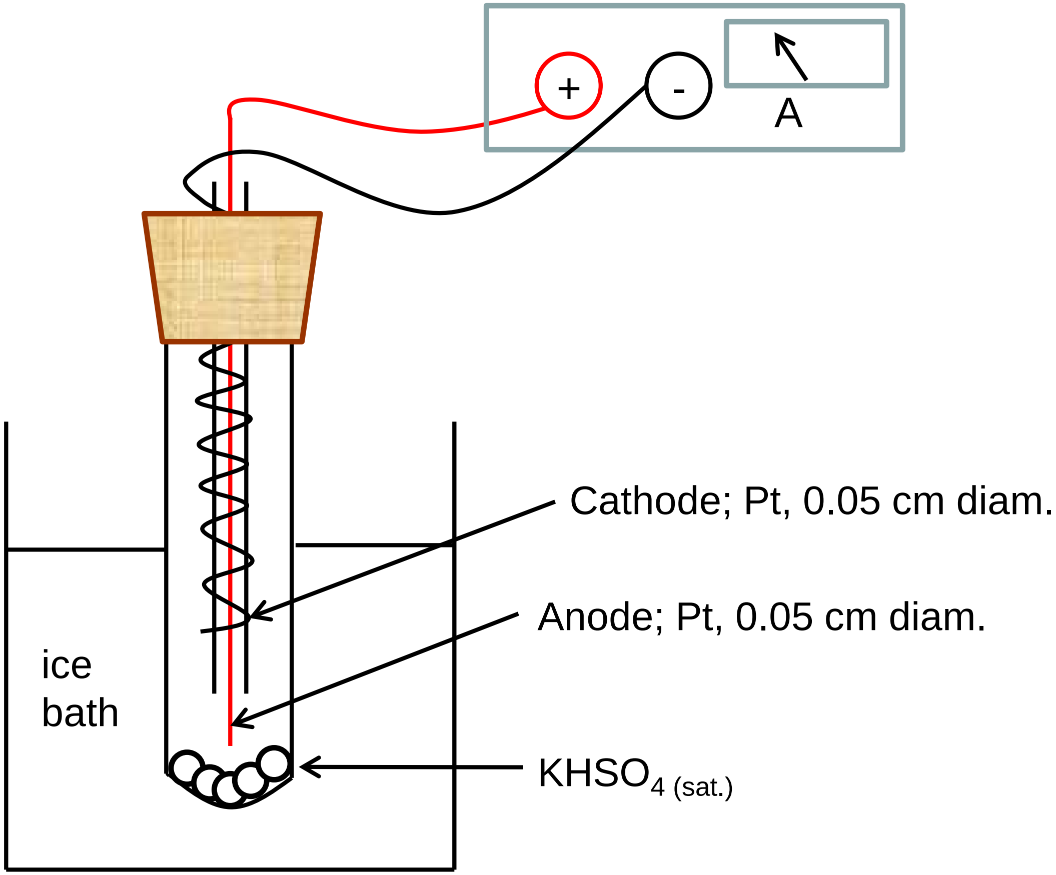
Schematic of Electrolysis



- **Bisulfate oxidized at the anode, loses two electrons. $S_2O_8^{2-}$ and H^+ are generated.**
- **The scavenged electrons conduct through the platinum wire, to the cathode.**
  - **H^+ diffuses to the cathode, where it is reduced to H_2.**
- **$S_2O_8^{2-}$ crashes out of solution as $K_2S_2O_8(s)$.**

The Electrolysis Cell

See Fig. 9-2, p. 98



Cathode; Pt, 0.05 cm diam.

Anode; Pt, 0.05 cm diam.

ice bath

$KHSO_{4\,(sat.)}$

- **Current density is the ratio of current to surface area. For this experiment, a current density of 1.0 A/cm^2 is required through the anode. The surface area of the exposed**

Calculating Theoretical Yield & %Efficiency

- You will pass a known current through the solution for a measured length of time. The number of moles of electrons passed through solution is calculated by:

$$e^{-} = \frac{current\left(\frac{C}{s}\right)\ x\ \ time\ (s)}{F\ \left(\frac{C}{mol\ e^{-}}\right)}$$

- According to our balanced reaction, one mole of persulfate is theoretically generated for every two moles of electrons transferred. Thus, you can calculate a theoretical yield of your product.

- Based on your actual yield (from experiment), you will calculate the efficiency of the reaction.

Testing the Oxidizing Ability of $K_2S_2O_8$

Once your synthesis is complete, you will complete two sets of reactions (10 total; 6 $S_2O_8^{2-}$ reactions, 4 H_2O_2 reactions) to compare the two oxidizing agents.

Reactants:
1) Acidified KI
2) $MnSO_4 \cdot H_2O$ in acid, with silver nitrate added*
3) $Cr_2(SO_4)_3 \cdot xH_2O$ in acid, with silver nitrate added*
4) $AgNO_3$

(*For #3 and #4, when reacting with persulfate, repeat these tests *without* silver nitrate. This is not necessary for peroxide)

For each reaction, you will:
a) Write the balanced overall reaction and predict whether it should be spontaneous.
b) Record your observations. Did you observe a spontaneous reaction?

Procedural Notes

1. Saturated $KHSO_4$ has been made. Keep it in the ice bath at all times.

2. Handle the electrodes **carefully**! Tape leads in place to avoid unnecessary strain/bending of Pt wire.

3. Be certain that your power supply can provide the current you calculate for your set up. You may have to adjust the length of anode in solution.

4. Get your set-up checked before turning on the power supply.

5. Be sure to **record the time when you begin and stop the electrolysis**. Maintain your ice bath during reaction and maintain constant current.

    a) Current will eventually drop when HSO_4^- is depleted.

6. Perform your reactions with $K_2S_2O_8$ and H_2O_2 in test tubes. Remember that "spontaneous" does not necessarily mean "fast."

Formal Report

Be sure to include:

- A sketch of the electrolysis cell showing connections to power supply
- Calculation of current required for ~1 amp/cm^2 current density
- Calculation of theoretical yield, actual yield, and current efficiency
- Half- and net reactions for each of 8 trials performed – include standard potentials and indicate whether the overall reaction should be spontaneous
    - Discuss whether your results are consistent with these calculations. Did you observe reactions in those cases where they were expected to occur? How were your observations different for $K_2S_2O_8$ and H_2O_2?
    - In your lab manual, the authors suggest that the oxidation of Ag^+ to Ag^{3+} assists in the oxidation of Mn^{2+} and Cr^{3+} by $S_2O_8^{2-}$ (pp. 96-97). Are your results consistent with this statement? (Can H_2O_2 oxidize Ag^+ to Ag^{3+}?)