

## Upcoming Deadlines

**Due 2/13:** Superconductor lab analysis

**Due 2/20:**  $K_2S_2O_8$  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. . . .

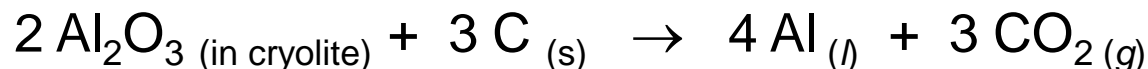
A **galvanic cell** employs a **spontaneous** electrochemical reaction to generate electric current.

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

# An Important Industrial Electrolysis: The Hall-Heroult Process

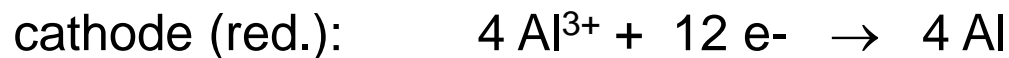
Aluminum is recovered from aluminum ore ( $\text{Al}_2\text{O}_3$ , alumina) in this electrolytic process, the only industrial method for Al smelting.

Prior to its development (1886), Al was thought of as a precious metal due to the difficulty and cost of its recovery.



What is oxidized and what is reduced in this process?

Write the half-reactions occurring at the anode and cathode.



# Electrolytic Synthesis of $\text{K}_2\text{S}_2\text{O}_8$



S is oxidized      anode (ox.):       $2 \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2 \text{e}^-$

$\text{H}^+$  is reduced      cathode (red.):       $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$

How can we theoretically predict the (non)spontaneity of this process?

# Predicting Spontaneity of Electrochemical Reactions

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

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

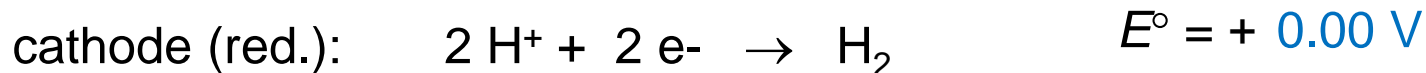
$$F = 9.6485 \times 10^4 \text{ C/mol e}^-$$

$n$  = moles of electrons

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

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

$$T = 25 \text{ }^\circ\text{C}; P = 1 \text{ bar}; \text{Conc.} = 1 \text{ M}$$



$$E_{\text{cell}}^\circ = \frac{\quad}{\quad} \\ -2.05 \text{ V}; \text{ Non-spont.}$$

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

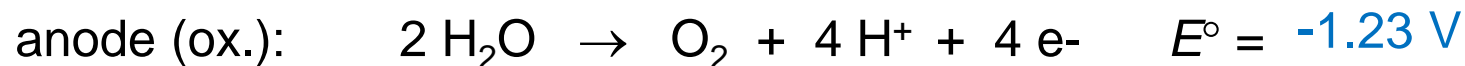
- When you change reaction direction (for oxidation), change sign of  $E^\circ$
- $E^\circ$  does **not** depend on amount. Do **not** change the magnitude of  $E^\circ$  if you change coefficients of the half-reaction.

## A Potential Problem to Overcome . . .

The standard cell potential for our desired reaction is a rather large negative value, indicating that this process is significantly unfavorable.

What challenge does this cause for completion of this **aqueous** reaction?

### Competing oxidation of water:



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

Fortunately, oxidation of water is very slow; 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).

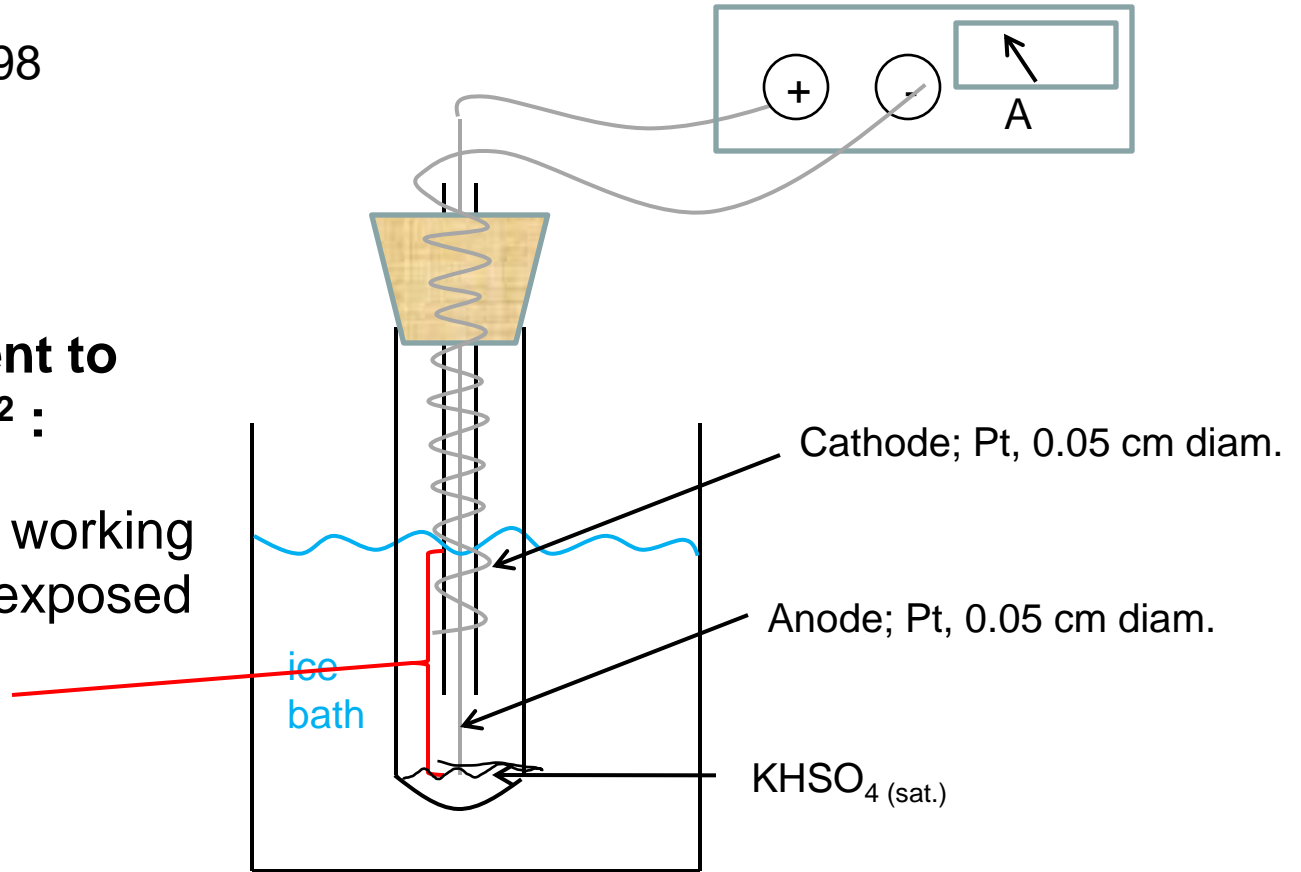
- Pt wire electrodes
- Cold temperature (ice bath)
- High concentration of reactant  $\text{HSO}_4^-$
- High current density ( $1.0 \text{ A/cm}^2$ )

# The Electrolysis Cell

See Fig. 9-2, p. 98

**Calculating current to achieve  $1.0 \text{ A/cm}^2$  :**

Need area of the working electrode that is exposed to solution



## Calculating Theoretical Yield (Current Efficiency)

**You will pass a known current through the solution for a measured length of time.** How can you determine the theoretical yield from this information?

$$\begin{aligned} \text{Theor. Yield} &= \left( \begin{array}{c} \mathbf{\text{Current}} \\ \text{A=C/s} \end{array} \right) \times \left( \begin{array}{c} \mathbf{\text{Time}} \\ \text{s} \end{array} \right) \div \left( \begin{array}{c} 96\,485 \\ \text{C/mol e}^- \end{array} \right) \times \left( \begin{array}{c} 1 \text{ mol K}_2\text{S}_2\text{O}_8 \\ 2 \text{ mol e}^- \end{array} \right) \\ &\quad \times \left( \begin{array}{c} 270.3118 \text{ g} \\ 1 \text{ mol K}_2\text{S}_2\text{O}_8 \end{array} \right) = \text{g K}_2\text{S}_2\text{O}_8 \end{aligned}$$

## Testing the Oxidizing Ability of $\text{K}_2\text{S}_2\text{O}_8$

Once your synthesis is complete, you will complete two sets of four reactions (8 total) to compare the oxidizing agent  $\text{K}_2\text{S}_2\text{O}_8$  to the more common oxidizer  $\text{H}_2\text{O}_2$ .

Reactants:

- 1) Acidified KI
- 2)  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in acid, with silver nitrate added
- 3)  $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  in acid, with silver nitrate added
- 4)  $\text{AgNO}_3$

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  $\text{KHSO}_4$  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  $\text{HSO}_4^-$  is depleted.
6. Perform your reactions with  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{O}_2$  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  $\sim 1$  amp/cm<sup>2</sup> 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  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{O}_2$ ?
  - In your lab manual, the authors suggest that the oxidation of  $\text{Ag}^+$  to  $\text{Ag}^{3+}$  assists in the oxidation of  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  by  $\text{S}_2\text{O}_8^{2-}$  (pp. 96-97). Are your results consistent with this statement? (Can  $\text{H}_2\text{O}_2$  oxidize  $\text{Ag}^+$  to  $\text{Ag}^{3+}$ ?)