

## Experiment

### ENTHALPY AND ENTROPY OF ZINC WITH COPPER SULFATE

The CCLI Initiative

Computers in Chemistry Laboratory Instruction

#### LEARNING OBJECTIVES

The learning objectives of this experiment are to . . .

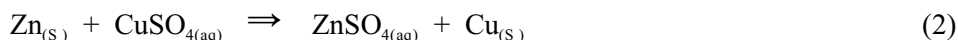
- determine changes in enthalpy and entropy of the reaction of zinc with copper sulfate using two methods: electrochemistry and calorimetry.
- compare the enthalpy values obtained by the two methods.

#### BACKGROUND

Thermodynamics is concerned with energy changes that occur in chemical and physical processes. The enthalpy and entropy changes of a system undergoing such processes are interrelated by the change in free energy,  $\Delta G$ , according to the equation

$$\Delta G = \Delta H - T \Delta S \quad (1)$$

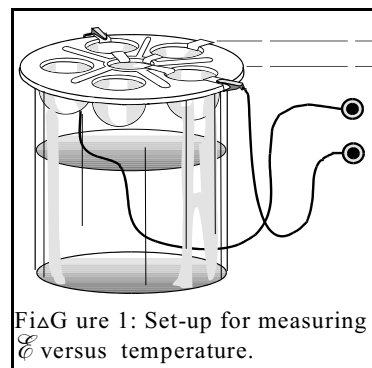
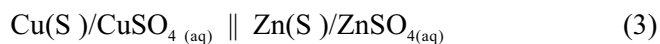
This investigation focuses on the reaction



$\Delta G$  will be calculated from the  $\Delta H$  and  $\Delta S$  values obtained electrochemically. The validity of Equation (1) will be tested by comparing the value of  $\Delta H$  obtained electrochemically with the value of  $\Delta H$  obtained calorimetrically for the same reaction.

#### The electrochemical method

The electrochemical method offers simple and accurate means for the determination of thermodynamic quantities. A simple electrochemical cell is constructed in a Chem-Carrou-Cell™ plate as shown in Figure 1.



The overall galvanic cell reaction is



and it is essentially the same as that taking place in the calorimeter.

The quantity of the electrical energy,  $\mathcal{F}$ , produced or consumed during the electrochemical reaction is a constant measured per mole of electrons, and can be accurately measured. The free energy change,  $\Delta G$ , of an electrochemical reaction is related to the voltage,  $\mathcal{E}$ , of the electrochemical cell by the equation

$$\Delta G = -n \mathcal{F} \mathcal{E} \quad (5)$$

where  $n$  = the number of moles of electrons transferred in a redox reaction.  
and  $\mathcal{F}$  = Faraday's constant of 96,500 C/mole of electrons .

Combining equations (1) and (5), and dividing both sides by the constant “n,” we obtain a linear relationship between the voltage change,  $\Delta \mathcal{E}$ , and the enthalpy and entropy changes at different temperatures

$$\mathcal{E} = -\frac{\Delta H}{n \mathcal{F}} + \frac{T \Delta \Delta S}{n \mathcal{F}} \quad (6)$$

or

$$\mathcal{E} = \frac{\Delta S}{n \mathcal{F}} (T) - \frac{\Delta H}{n \mathcal{F}} \quad (7)$$

By measuring the voltage  $\mathcal{E}$ , of our electrochemical cell, at several temperatures, we can obtain a plot of the voltage *versus* temperature. Assuming that  $\Delta H$  and  $\Delta S$  remain constant over a small temperature range, we can calculate the  $\Delta S$  and  $\Delta H$  from the slope and the intercept of the straight line respectively

$$\text{slope} = \frac{\Delta S}{n \mathcal{F}} \quad (8)$$

and

$$\text{Y-intercept} = -\frac{\Delta H}{n \mathcal{F}} \quad (9)$$

$\Delta G$  can now be calculated by means of Equation (1). We can verify its value using Equation (5).

Please note that in both cases,  $\Delta G$  must be calculated for the same temperature. If the calculations are done for 298 K (25 °C), we can also verify the experimental value of  $\mathcal{E}^\circ$  for this temperature by employing the Nernst equation (7)

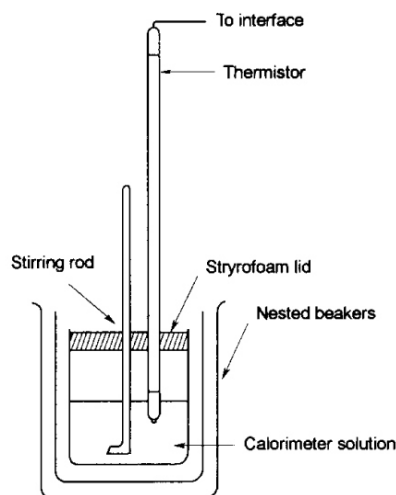
$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT \ln [\text{products}]}{n \mathcal{F} [\text{reactants}]} \quad (10)$$

where  $\mathcal{E}^\circ$  is the standard potential measured at 25 ° C and is 1.100V for the cell under consideration.

When the concentrations of the  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  solutions are equal, the log term of the Nernst equation becomes zero. Under these conditions, the standard voltage,  $\mathcal{E}^\circ$ , of the cell is equal to the measured voltage,  $\mathcal{E}$ .

### The calorimetric method

The ideal calorimeter is a perfectly insulated vessel which contains a large known weight of solution in perfect thermal contact with an accurate thermometer and a small reaction tube (Figure 2). When measured quantities of reactants are introduced into the reaction tube, the heat of reaction changes the temperature of the calorimeter solution.



**Figure 2.** Diagram of Calorimeter

The heat of the chemical reaction is given by the equation

$$\Delta H = \frac{(K + W)(T_i - T_f)}{n} \quad (11)$$

$H$  is the heat of reaction at constant pressure.

$n$  is the number of moles of a limiting reactant as expressed in the balanced equation.

$K$  is the heat capacity of the calorimeter solution.

$W$  is the heat capacity of the calorimeter.

$T_i$  is the initial temperature of the calorimeter solution.

$T_f$  is the final temperature of the calorimeter solution.

The heat capacity of the calorimeter solution is obtained by multiplying the specific heat of the solution ( $3.8 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$  for  $\text{CuSO}_4$ ) by the weight of the solution in the calorimeter.  $W$ , the estimated cup heat capacity, is  $30 \text{ J }^\circ\text{C}^{-1}$ .

## SAFETY PRECAUTIONS

Safety goggles must be worn in the lab at all times. Any skin contacted by chemicals should be washed immediately.

### BEFORE PERFORMING THIS EXPERIMENT . . .

... you will need a *MicroLAB* program capable of:

Part I - measuring voltages and temperatures and displaying them in the **Graphing**, **Digital Display** and **Spreadsheet** views. Use *delta.G.experiment* supplied by your instructor.

Part II - collecting temperature readings as a function of time and displaying them in the **Graphing**, **Digital Display** and **Spreadsheet** views. Use *heat of Solution* from the **Time and Temperature** tab in the *MicroLAB* opening window.

### EXPERIMENTAL PROCEDURES

#### Part I: Electrochemistry

1. Calibrate your Temperature probe at a minimum of three separate temperatures with ice-cold water and hot tap water.
2. Fill a 600 ml beaker three-quarters full of ice. Fill the rest of the beaker with cold tap water until the beaker is filled to one cm from the top. Stir the ice/water mixture to distribute the ice evenly.
3. Place the beaker on a hot plate -- **don't turn the heat on yet!** Rest the Chem-Carrou-Cell™ on top of the beaker so that the bottoms of the wells of the Cell are immersed in the ice/water mixture. Let the set-up stand for 15 minutes until the temperature stabilizes.
4. Pour about 5 ml of 0.1 M KNO<sub>3</sub> into the center well. Pour about 5 ml of 0.50 M ZnSO<sub>4</sub> into well #1 and about 5 ml of 0.50 M CuSO<sub>4</sub> into well #2.
5. With clean tweezers, take a strip of filter paper and dip one end into the central well (where immersion in the KNO<sub>3</sub> solution will hold one end); dip the other end into well #1. Repeat this procedure with another strip of filter paper, dipping the other end into well #2. This creates the salt bridge for your galvanic cell.
6. With clean tweezers take a zinc metal strip and sand it (**on a piece of paper so as not to scratch the table top**) to remove any oxide coating. Bend 2 cm of one end of the ΔS trip and immerse it in the ZnSO<sub>4</sub> solution (well #1). The rest of the metal strip (3cm) extends out to the edge of the cell and should be bent over the rim. Repeat the same procedure with the copper metal strip and place it in well #2. Later the electrical leads (alligator clips) from the interface will be attached to the metal strips.
7. Fasten your temperature probe to the ring stand with a clamp and adjust the temperature probe such that its tip can be immersed in the central well (KNO<sub>3</sub> solution) of the cell. It is assumed that the temperature of the ZnSO<sub>4</sub> solution and CuSO<sub>4</sub> solution will be very close to the temperature of the KNO<sub>3</sub> solution throughout the experiment.
8. Start the computer program to monitor the temperature.
9. Read and record the temperature. Attach the alligator clips to the metal strips and take the voltage reading. If a negative number appears on the screen, reverse the wires. Disconnect the wires immediately after the reading is recorded.
10. Turn the hot plate onto high, **Start the *MicroLAB* program**, then the program will pause every five °C to measure the voltage and temperature. When the **Message** window "**Attach probes, Press ENTER to take a reading, then detach probes**" appears on the screen, **connect the voltage leads to the**

**appropriate metal tabs, make sure the voltage is stable, then press ENTER, and disconnect the voltage leads** until the next reading is due. Prolonged connection of the wires will cause electric current to flow through the cell. This discharge will result in changes in concentrations of the solutions. Since the measured voltage depends on these concentrations, there will be an error in the voltage readings. **Stop** the program when the temperature reaches 40 °C.

## Part II: Calorimetry

1. Weigh a clean, dry 150 ml beaker on the top loading balance, then add 50 ml of 0.5 M CuSO<sub>4</sub> solution. Weigh the beaker a second time to determine the mass of the solution in the calorimeter. Nest the 150 ml beaker inside a 400 and 600 ml beaker, thread the stirring rod and temperature probe through the Styrofoam lid and position the lid on the inner beaker. The temperature probe should be as deep into the solution as possible but without strain. Let the apparatus stand  $\Delta$ so that the components attain the same temperature.
2. Using the top loading balance, tare the plastic weighing boat, then weigh 0.5 grams of zinc powder into a plastic weighing boat, noting the exact weight in your notes.
3. Start the program and plot temperature against time for several minutes.
4. Add the zinc powder to the copper solution. Save the boat and any Zn stuck to it for weighing at the end of the run. Stir thoroughly and watch the plot of temperature *versus* time until a well defined cooling trend is established. It is important that a rubber policeman be used continually to ensure that any residue produced (copper coated zinc powder) is broken up.
5. Weigh the weighing boat on the analytical balance and obtain the amount of Zn added by difference, noting the exact weight in your notes.
6. Print the graph of your data.
7. From your plot of temperature vs. time, determine the initial and final temperatures and calculate the heat of reaction per mole of zinc. Compare this value with  $\Delta H$  obtained in Part I.

## DATA ANALYSIS

### Part I: Electrochemistry

1. Column B of the **spreadsheet** displays voltage values of the cell in volts.
2. Column C displays temperature readings in degrees Celsius. Use the **Formula** tool to convert these temperatures into Kelvin, then “click-drag” the formula to the **D** column, then the **Y-2** Axis.
3. Using the **Analysis** functions, construct a linear curve fit through the data.
4. Using the linear curve fit equation, calculate  $\Delta S$  from the slope ( $\Delta S/n \mathcal{F}$ ) and  $\Delta H$  from the intercept ( $\Delta H/n \mathcal{F}$ ).

### Part II: Calorimetry

1. From your plot, determine the temperature of the copper sulphate solution before mixing ( $T_i$ ) and the maximum temperature of the mixture ( $T_f$ ).
2. Using Equation (11), determine the enthalpy change,  $\Delta H$ , per mole of zinc added.

