Enthalpy and Entropy of Zinc with Copper Sulfate

INSTRUCTOR RESOURCES

The CCLI Initiative

Learning Objectives

• 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.

Procedure Overview

• a simple electrochemical cell $\text{Cu(s)}/\text{CuSO}_4(\text{aq}) // \text{ZnSO}_4_{(aq)} / \text{Zn(s)}$ is constructed in a Chem-Carro-Cell™ and voltages are measured at different temperatures.

• a spreadsheet is used to plot a linear regression graph of voltage versus temperature, and the graph is used to calculate the enthalpy and entropy changes for the cell reaction.

• heat of reaction of zinc powder with 0.5 $M$ CuSO$_4$ solution is determined calorimetrically.
PART I: Electrochemical Procedure

1. From your graph of Voltage versus T, copy the straight line equation you have obtained.

2. From the slope of your equation, calculate $\Delta S$ for the cell reaction.

3. From the y-intercept, calculate $\Delta H$ for the cell reaction.

4. Using the entropy and enthalpy changes determined above, calculate $\Delta G$ at 25°C.

5. Calculate $\Delta G$ using Equation 2.

6. From your straight line equation, calculate the voltage, $\varepsilon^\circ$, at 25°C.
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Report Sheet (page 2)

Part I : Calorimetric Method

weight of beaker + solution
weight of empty beaker
mass of the solution
weight of boat + zinc
weight of empty boat
mass of zinc
initial temperature
final temperature

1. Write the equation for the reaction that took place in the calorimeter.

2. Calculate the heat of reaction per mole of zinc.

3. Compare the values of $\Delta H$ obtained by the two methods.
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Questions/Problems

1. Compare the calculated value of $\mathcal{E}$ at 25 °C to the value obtained from your graph at the same temperature.

   (a) Is it close to the theoretical value of 1.1 V?

   (b) What might be the reasons for any difference between the theoretical and experimental values of you obtained?

2. A student performs this experiment incorrectly, leaving the alligator clips hooked to the cell for the entire time. Assume that the concentration of Cu$^{2+}$ changes from 0.50 M to 0.40 M and that the Zn$^{2+}$ concentration changes from 0.50 M to 0.60 M. How much will these concentration changes affect the measured potential?

3. Why is it necessary in this experiment to assume that $\Delta H$ and $\Delta S$ for the reaction are independent of temperature?
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Suggested Answers to Questions/Problems

1. Compare the calculated value of \( \Delta H \) at 25 °C to the value obtained from your graph at the same temperature.

   \( \text{Answers will vary.} \)

   (a) Is it close to the theoretical value of 1.1 V?

   \( \text{Answers will vary.} \)

   (b) What might be the reasons for any difference between the theoretical and experimental values of you obtained?

   \( \text{The original concentrations of the solutions might be incorrect or the alligator clips might be left in place too long causing significant current flow in the solutions.} \)

2. A student performs this experiment incorrectly, leaving the alligator clips hooked to the cell for the entire time. Assume that the concentration of \( \text{Cu}^{2+} \) changes from 0.50 \( \text{M} \) to 0.40 \( \text{M} \) and that the \( \text{Zn}^{2+} \) concentration changes from 0.50 \( \text{M} \) to 0.60 \( \text{M} \). How much will these concentration changes affect the measured potential?

   \( \text{From the Nernst equation (at 25)} \)

   \[
   E = -(0.0592/n) \log Q
   \]

   \( \text{the concentration term is} \)

   \[
   (0.0592/2) \log [\text{Zn}^{2+}] / [\text{Cu}^{2+}]
   \]

   \( \text{This term is zero for} \ [\text{Zn}^{2+}] = [\text{Cu}^{2+}] = 0.50 \text{ M}. \text{ If the concentrations of} \ \text{Cu}^{2+} \text{ and} \ \text{Zn}^{2+} \text{ change to 0.40 M and 0.60 M, respectively, the potential changes by} \)

   \[
   (0.0592/2) \log (0.60/0.50) = 0.005 \text{ V}
   \]

3. Why is it necessary in this experiment to assume that \( \Delta H \) and \( \Delta S \) for the reaction are independent of temperature?

   \( \text{In order to use the equation} \)

   \[
   \frac{\Delta S (T)}{n \mathcal{F}} - \frac{\Delta H}{n \mathcal{F}}
   \]

   \( \text{to obtain values of} \ \Delta S \) and \( \Delta H \), we plot \( \varepsilon \) versus \( T \). In doing so, we assume that \( T \) is the only variable on the right side of the equation.
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Sample MicroLAB Program

Part I: Electrochemistry

Experiment name: \textit{delta G experiment}

Sensors: \textbf{Temperature probe}: X axis, Col. A, DD on top, units = °C; \textbf{Voltage}: Y1 axis, Col B, DD on bottom, units = volts.

Special program:
Read Sensors
Repeat every 0.5 seconds
\hspace{1cm} \textbf{If} Delta TempIC > +/- 5.00
\hspace{2cm} Read Sensors
\hspace{1cm} \textbf{Else}
\hspace{2cm} Read Sensors
\hspace{1cm} \textbf{End If}
Until \textbf{Stop Button} is pressed

Part II: Calorimetry

Experiment file name: \textit{heat of solution}

Sensors used: \textbf{Timer 1}: X axis, Col. A, DD on top, units = sec; \textbf{Temperature probe}: Y axis, Col. B, DD on bottom, units = °C;

Program
\hspace{1cm} \textit{Repeat every 0.5 seconds
\hspace{2cm} Read Sensors
\hspace{1cm} Until \textbf{Stop button} is clicked}
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Tips and Traps

1. For the electrochemical section of the experiment, the best results were obtained below 40 °C.

2. ΔS values are quite inconsistent. They depend on the slope reading of the voltage vs. a temperature graph. The slope is always a very small number; therefore, any variation in slope from one trial to another would change the entropy value greatly.

3. The experiment can be performed in a Styrofoam cup. The estimated heat capacity is 10 J °C⁻¹.

4. Any combination of small containers can be used in place of the Chem Carron-Cell™.

5. Chem Carron-Cell™ is available from Freeman, Cooper & Co., San Francisco, CA 94133.
Part I: Electrochemical Procedure

1. From your graph of Voltage versus T, copy the straight line equation you obtained

\[ V = 0.0003648 (T) + 0.9502 \]

2. From the slope of your equation, calculate \( S \) for the cell reaction.

\[ \Delta S = (2 \text{ mol e}) (96,500 \text{ C/mol e}) (0.0003648 \text{ V/K}) \]

\[ \Delta S = 70 \text{ J/K} \]

3. From the y-intercept, calculate \( H \) for the cell reaction.

\[ \Delta H = (2 \text{ mol e}) (96,500 \text{ C/mol e}) (0.9502 \text{ V}) \]

\[ \Delta H = 1.83 \times 10^5 \text{ J or 183 kJ} \]

4. Using of entropy and enthalpy changes determined above, calculate \( G \) at 25 C.

\[ \Delta G = (183 \text{ kJ}) (298 \text{ K}) (0.070 \text{ kJ/K}) \]

\[ \Delta G = 204 \text{ kJ} \]

5. Calculate \( \Delta G \) using Equation 2.

\[ \Delta G = (2 \text{ mol e}) (96,500 \text{ C/mol e}) (1.06 \text{ V}) \]

\[ \Delta G = 2.05 \times 10^5 \text{ J or 205 kJ} \]

6. From your straight line equation, calculate the voltage, \( \varepsilon \), at 25 C.

\[ \varepsilon = 0.0003648 (298) + 0.9502 \]

\[ \varepsilon = 1.06 \text{ V} \]
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Sample Data (page 2)

Part II: Calorimetric Method

- weight of beaker + solution = 119.8 g
- weight of empty beaker = 65.6 g
- mass of the solution = 54.2 g
- weight of boat + zinc = 0.8975 g
- weight of empty boat = 0.4043 g
- mass of zinc = 0.4932 g
- initial temperature = 24°C
- final temperature = 30°C

1. Write the equation for the reaction that took place in the calorimeter.

\[ \text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu} \]

2. Calculate the heat of reaction per mole of zinc.

\[ \Delta H = (3.8 \text{ J g}^{-1} \text{ C}^{-1} \times 54.2 \text{ g} + 30 \text{ J C}^{-1}) (24 \text{ C} - 30 \text{ C}) / (0.4932 \text{ g/65.38 g/mol}) \]

\[ \Delta H = 1.88 \times 10^5 \text{ J/mol} \text{ or } 188 \text{ kJ} \]

3. Compare the values of \( \Delta H \) obtained by the two methods.

*The electrochemical value of 183 kJ compares very well with the calorimetric value of 188 kJ.*
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Laboratory Preparation (per student station)

Part I: Electrochemistry

Equipment
- 600 ml beaker
- 50 ml beaker
- tweezers
- Chem-Carron-Cell™
- one pair of black and red alligator clip leads

Supplies
- filter paper strips (0.5 x 5 cm)
- sandpaper
- ceramic tile

Chemicals
Exact quantities needed are listed below. A minimum 50% excess is recommended.
- copper metal strip (0.5 x 5 cm)
- zinc metal strip (0.5 x 5 cm)
- 0.5 M CuSO₄ (5 ml)
- 0.5 M ZnSO₄ (5 ml)
- 0.1 M KNO₃ (5 ml)

Part II: Calorimetry

Equipment
- thermistor
- 600 ml beaker
- 400 ml beaker
- 150 ml beaker
- 50 ml graduated cylinder
- insulated cover (for 100 ml beaker)

Supplies
- towel

Chemicals
Exact quantities needed are listed below. A minimum 50% excess is recommended.
- 0.5 M CuSO₄ (50 ml)
- zinc powder (0.5 g)

Safety and Disposal
dispose of the wastes into specially marked containers.