Learning Objectives

The purpose of this experiment is to . . .

- to determine the rate of a chemical reaction.
- to determine the rate law for a chemical reaction.
- to propose a mechanism for the reaction under study.
- to determine the activation energy, the enthalpy and the entropy for the reaction.

Procedure Overview

- the kinetics of a series of reactions involving ferroin will be studied using the colorimeter.
- each student group will complete one of three possible reaction series, at two different concentrations and temperatures.
- data will be pooled so that each student has a complete set for all three reactions.
- the order of the reaction for ferroin and the non-ferroin reactant will be determined graphically.
- rate constants for each series at each temperature will be determined.
- the activation energy will be estimated by comparing the rates at the different temperatures.
- The enthalpy and entropy will be determined for the $P_2O_7^{4-}$ reactant from the Eyring equation.

NOTICE: THIS EXPERIMENT REQUIRES THE USE OF EXTERNAL TEMPERATURE CONTROLLED WATER BATHS SET AT THE DESIRED TEMPERATURES
### Summary report

<table>
<thead>
<tr>
<th>Item</th>
<th>T1</th>
<th>T2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental rate law</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate constant (k)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial rate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activation energy (Ea)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-exponential factor (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta H$ for the $P_2O_5^{4+}$ reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta S$ for the $P_2O_7^{4-}$ reaction</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
KINETIC STUDIES OF THE FERROIN COMPLEX

Mechanisms
Series A

Series B

Series C

Calculations
Complete this section for one series and summarize results of all series in the summary table.

1. Order of the reaction in ferroin (from attached graph).

2. Order of the reaction in non-ferroin reactant.
   a. slope of concentration 1 graph at 40 °C.

   b. slope of concentration 2 graph at 40 °C.

   c. order of reaction:

   d. explain:

   e. slope of concentration 1 graph at 50 °C.

   f. slope of concentration 2 graph at 50 °C.
3. Determine the activation energy for the reaction.

4. Calculate the Arrhenius pre-exponential factor (A) for the reaction.

5. Calculate the ΔH for the P₂O₇⁴⁻ reaction.

6. Calculate the ΔS for the P₂O₇⁴⁻ reaction.
1. The experimental rate law for the decomposition of nitrous oxide, $N_2O$, is

$$\frac{-d[N_2O]}{dt} \Rightarrow k[N_2O]^2$$

Which of the proposed mechanisms would agree with the observed rate law?

(a) $N_2O \Rightarrow N_2 + O$ (slow)
    $N_2O + O \Rightarrow N_2 + O_2$ (fast)

(b) $2 N_2O \Rightarrow N_2O_2$ (fast)
    $N_2O_2 \Rightarrow 2 N_2 + O_2$ (slow)

Develop the observed rate law from the mechanism chosen.
2. Chloroform and chlorine react to form carbon tetrachloride and hydrogen chloride:

\[
\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}
\]

The initial rate of reaction was determined for three mixtures of reactants.

<table>
<thead>
<tr>
<th>experiment</th>
<th>[CHCl₃]₀</th>
<th>[Cl₂]₀</th>
<th>( \text{rate (s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.94 x 10⁻²</td>
<td>4.32 x 10⁻²</td>
<td>8.19 x 10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>8.06 x 10⁻²</td>
<td>4.30 x 10⁻²</td>
<td>16.6 x 10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>4.02 x 10⁻²</td>
<td>2.10 x 10⁻²</td>
<td>5.82 x 10⁻⁴</td>
</tr>
</tbody>
</table>

a. What is the observed rate law for the reaction?

b. What is the value of the rate constant?

3. Concerning the hydrolysis of t-BuCl, would it be possible to distinguish between the associative and dissociative mechanism if the reaction was done with water as the solvent?
KINETIC STUDY OF THE FERROIN COMPLEX

Questions/Problems (page 3)

4. For a reaction that is second order in a given reactant, if one plots 1/conc vs. time for the reactant, the slope of the straight line is equal to the rate constant, but if one plots 1/(Absorbance) vs. time, the slope of the line is not equal to the rate constant.

a. Why?

b. How could you calculate the rate constant from the slope?

c. It does not make a difference in first order systems whether one plots ln(absorbance) or ln (concentration) data vs. time to determine the rate constant. Why?
KINETIC STUDIES OF THE FERROIN COMPLEX

Tips and Traps

1. Be sure to organize the groups and assignments in advance.

2. Controlling the temperature is a key factor. Students must use a beaker with controlled temperature water for carrying solutions to the computers.

3. **NOTICE:** This experiment requires the use of two external temperature controlled water baths, **set at 40 °C and 50 °C**.
The two water baths should be set up, one at 40 °C and the other at 50 °C, which are well stirred and large enough for the number of student beakers that will be done at each temperature. The chamber should have shelves such that the 50 ml beakers can be immersed to the level of the solution within and maintained stable.
KINETIC STUDIES OF THE FERROIN COMPLEX

Sample Data

Group Members

Series assignment

Summary report

<table>
<thead>
<tr>
<th>Item</th>
<th>T1</th>
<th>T2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental rate law</td>
<td>(- \frac{d[ferr]}{dt}) = 0.0232 min(^{-1})[ferr]</td>
<td></td>
</tr>
<tr>
<td>Rate constant (k)</td>
<td>0.0232 min(^{-1})</td>
<td>0.119 min(^{-1})</td>
</tr>
<tr>
<td>Initial rate</td>
<td>(2.5 \times 10^{-6}) min(^{-1})</td>
<td>(1.3 \times 10^{-5}) min(^{-1})</td>
</tr>
<tr>
<td>Activation energy (Ea)</td>
<td></td>
<td>110 kJ/mol</td>
</tr>
<tr>
<td>Pre-exponential factor (A)</td>
<td></td>
<td>(8.5 \times 10^{-21})</td>
</tr>
</tbody>
</table>

Mechanisms

Series C

The mechanism is dissociative. One ferroin ligand must dissociate for an incoming ligand to react with the iron.
KINETIC STUDIES OF THE FERROIN COMPLEX

Sample Data (page 2)

Calculations

1. Order of the reaction in ferroin.
   
   *first order since the graph of \( \ln[\text{ferr}] \) vs. \( t \) is a straight line*

2. Order of the reaction in non-ferroin reactant.
   (a) slope of concentration 1 graph at 40 °C.
   \[ [\text{H}^+] = 0.40 \, M \quad k = 0.235 \, \text{min}^{-1} \]
   (b) slope of concentration 2 graph at 40 °C.
   \[ [\text{H}^+] = 0.40 \, M \quad k = 0.235 \, \text{min}^{-1} \]
   (c) order of reaction: **zero**
   (d) explain: *The two \( k \) values are equal which means the non-ferroin reactant does not affect the rate.*
   (e) slope of concentration 1 graph at 50 °C.
   \[ [\text{H}^+] = 0.20 \, M \quad k = 0.119 \, \text{min}^{-1} \]

3. Determine the activation energy for the reaction.
   
   \[ \ln(k_2/k_1) = \frac{E_a}{R} \left( \frac{1}{1/T_1} - \frac{1}{1/T_2} \right) \]
   
   \[ \ln(0.119/0.0232) = \frac{E_a}{8.3145 \, \text{J/mol K}} \left( \frac{1}{312.2 \, \text{K}} - \frac{1}{324.7 \, \text{K}} \right) \]
   
   \[ 1.634 = \frac{E_a}{8.3145 \, \text{J/mol K}} \left( 1.233 \times 10^4 \, \text{K}^{-1} \right) \]
   
   \[ 110 \, \text{kJ/mol} = E_a \]
4. Calculate the Arrhenius pre-exponential factor (A) for the reaction.

\[ k = Ae^{(-E_a/RT)} \]

\[ \ln k = -\frac{E_a}{RT} + \ln A \]

\[ \ln(0.0232) = \frac{110200 \text{ J/mol}}{(8.3145 \text{ J/mol})(312.2 \text{ K})} + \ln A \]

3.764 = 42.45 + lnA

46.22 = lnA

A = 8.5 \times 10^{-21}
KINETIC STUDIES OF THE FERROIN COMPLEX

Sample Data (page 4)

A sample *MicroLAB* Spectrum Profile for the Ferroin complex.

![Spectrum Profile for Ferroin](image)
KINETIC STUDY OF THE FERROIN COMPLEX

Suggested Answers to Questions/Problems

1. The experimental rate law for the decomposition of nitrous oxide, N2O, is

$$\frac{d[N_2O]}{dt} \implies k[N_2O]^2$$

Which of the proposed mechanisms would agree with the observed rate law?

(a) \(N_2O \implies N_2 + O\) (slow)
\(N_2O + O \implies N_2 + O_2\) (fast)

(b) \(2N_2O \implies N_2O_2\) (fast)
\(N_2O_2 \implies 2N_2 + O_2\) (slow)

*mechanism b is the accepted*

Develop the observed rate law from the mechanism chosen.

**Rate** = \(k_2[N_2O_2]\)

\(k_1 \ [N_2O_2]^2 = k_3 \ [N_2O_2]\)

\([N_2O_2] = [N_2O]^2\)

**Rate** = \(k_2 \frac{k_1}{k_3} \ [N_2O]^2 = k \ [N_2O]^2\)


KINETIC STUDY OF THE FERROIN COMPLEX

Suggested Answers to Questions/Problems (page 2)

2. Chloroform and chlorine react to form carbon tetrachloride and hydrogen chloride:

\[ \text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl} \]

The initial rate of reaction was determined for three mixtures of reactants.

<table>
<thead>
<tr>
<th>experiment</th>
<th>[CHCl\textsubscript{3}]\textsubscript{0}</th>
<th>[Cl\textsubscript{2}]\textsubscript{0}</th>
<th>Rate \textsubscript{0}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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</table>

What is the observed rate law for the reaction?

\[ \text{Rate} = k [\text{CHCl}_3]^{1/2} [\text{Cl}_2] \]

What is the value of the rate constant?

\[ k = 0.100 \]

3. Concerning the hydrolysis of t-BuCl, would it be possible to distinguish between the associative and dissociative mechanism if the reaction was done with water as the solvent?

No
4. For a reaction that is second order in a given reactant, if one plots 1/conc vs. time for the reactant, the slope of the straight line is equal to the rate constant, but if one plots 1/(Absorbance) vs. time, the slope of the line is not equal to the rate constant. Why? How could you calculate the rate constant from the slope? It does not make a difference in first order systems whether one plots ln(absorbance) or ln (concentration) data vs. time to determine the rate constant. Why?

\[
\text{Since } C = \frac{A}{c_b}, \text{ the equation } \frac{1}{C} = \frac{kt}{C} + \frac{1}{C_0}
\]

becomes

\[
\frac{1}{\frac{A}{c_b}} = \frac{kt}{\frac{A}{c_b}} + \frac{1}{\frac{A}{c_b}}
\]

which can be rearranged to

\[
\frac{1}{A} = \frac{kt}{A_0} + \frac{1}{A_0}
\]

Thus for a plot of 1/A vs. t the slope is k/c_b.

For a first order reaction the conversion from A to C cancels out because of the first order rate law.

\[
\ln(C/C_0) = -kt = \ln\left(\frac{A/c_b}{A_0/c_b}\right) = \ln\left(\frac{A}{A_0}\right)
\]
KINETIC STUDIES OF THE FERROIN COMPLEX

Laboratory Preparation (per student station)

**Equipment**
- colorimeter and 2 cuvettes, 2.54 cm path length
- two water baths with Temperatures set for 40 °C and 50 °C.
- 6 - 13 x 100 test tubes
- 2 - 150 ml beakers
- Mohr pipets (10.0 and 1.0 mL)
- 2 - 50 ml beakers

**Supplies**
- Kimwipes
- paper towels

**Chemicals** (Prepare at least 50 percent more than listed here for wastage.)
- \(0.02 \, M \, Cu(NO_3)_2\) (10.0 mL)
- \(0.10 \, M \, Na_2P_2O_7\) (10.0 mL)
- \(1.0 \, M \, HNO_3\) (10.0 mL)
- ferroin solution (5.0 mL)
- purchase ferroin at 0.025 \(M\) from supply house and dilute to \(5.0 \times 10^{-14} \, M\) for student use

**Safety and Disposal**
- no special precautions necessary