Kinetics of Dye Bleaching

Objective:
To examine the kinetics of a reaction in which a dye is bleached

We write the reaction as

$$\text{MG}^+ + \text{OH}^- \rightarrow \text{MGOH}$$

Rate law for the reaction is

$$\frac{d[\text{MG}^+]}{dt} = - \frac{d[\text{MG}^+]}{dt} = k [\text{OH}^-]^n [\text{MG}^+]^m$$

The rate of disappearance of \text{MG}^+

$$k = \text{rate constant}$$ of the reaction

$$m = \text{order of the reaction with respect to \text{MG}^+}$$

$$n = \text{order of the reaction with respect to \text{OH}^-}$$

Our objective is to determine $k$, $n$ and $m$

Since the reactant, \text{MG}^+ is colored but neither \text{OH}^- nor the product, \text{MGOH}, is

(i.e., \text{OH}^- bleaches the dye)

We can follow the concentration of \text{MG}^+ as the reaction proceeds using the Absorbance of light and Beer's Law

$$A = s c$$

Where, as usual,

$s$ will be the slope of the Beer's Law plot for the dye. ($s = \varepsilon d$)

To keep things simple, in this exercise, we limit the possible values of both $m$ and $n$ to either 1 or 2

For these two cases, calculus provides an expression for the way in which $[\text{MG}^+]$ will vary with time, namely:

$$m = 1 \quad \frac{d[\text{MG}^+]}{dt} = q [\text{MG}^+]$$

$$m = 2 \quad \frac{1}{[\text{MG}^+]} \frac{d[\text{MG}^+]}{dt} = q [\text{MG}^+]$$

Where $[\text{MG}^+]_0$ is the $[\text{MG}^+]$ at $t = 0$. 

This exercise explores the time dependence of the reaction of the dye:

Malachite Green, \text{MG}^+

with \text{OH}^-

To form the corresponding alcohol, \text{MGOH} which is colorless.
If we measure \([\text{MG}^+]\) at a sequence of times, we should be able to tell the value of \(m\) by plotting the concentration vs time. It will be very difficult to tell these two curves apart!

But, we can produce linear plots of \([\text{MG}^+]\) vs time

For \(m = 1\)

\[
[MG^+] = [MG^+]_0 e^{-qt}
\]

taking the natural logarithm of each side produces:

\[
\ln [MG^+] = \ln [MG^+]_0 - qt
\]

Linear plots vs time with slopes \(q\) or \(-q\)

For \(m = 2\)

We have

\[
\frac{1}{[MG^+]} = \frac{1}{[MG^+]_0} + qt
\]

If the plot of \(-\ln [MG^+]\) is linear with time, the reaction is first order with respect to \(MG^+\)

If the plot of \((1 / [MG^+])\) is linear with time, the reaction is second order with respect to \(MG^+\)

\[
\text{rate} = -\frac{d[MG^+]}{dt} = k[OH^-]^n[MG^+]^2
\]

For \(m = 2\):

\[
\frac{1}{[MG^+]} = \frac{1}{[MG^+]_0} + q t
\]

Substitute in \([MG^+] = Abs/s\) and divide each term by \(s\)

\[
\frac{1}{Abs} = \frac{1}{Abs_0} + \left(\frac{q}{s}\right) t
\]

I.e., the slope of the second order plot is \(q/s\) rather than just \(q\) \((=k[OH^-]^n)!\)

But we actually measure absorbance, not concentration

From Beer's law: \(\text{Abs} = s[\text{MG}^+]\) where \(s = cd\)

So \([\text{MG}^+] = \text{Abs}/s\) and \([\text{MG}^+]_0 = \text{Abs}_0/s\)

For \(m = 1\)

\[
\ln [MG^+] = \ln [MG^+]_0 - qt
\]

\[
\ln (Abs) = \ln (Abs_0) - q t
\]

For this case, \(\ln (s)\) cancels out. We can just plot \(-\ln(Abs)\) verses time to find \(q\) (the slope).

Is the same true for \(m = 2\)?

Having determined \(m\), how do we determine \(n\), the order of the reaction with respect to \(OH^-\)?

Study reaction at two different, known, values of \([OH^-]\), \(c_1\) and \(c_2\), insuring that they are both in large excess over the concentration of \(MG^+\).

This gives us two slopes \(q_1\) and \(q_2\), whose different values depend on the two \(OH^-\) concentrations by

\[
q = k[OH^-]^n
\]

\[
q_1 = k_1[OH^-]_{c_1}^n = k c_1^n
\]

\[
q_2 = k_2[OH^-]_{c_2}^n = k c_2^n
\]

\[
q_1 / q_2 = c_1^n / c_2^n = (c_1 / c_2)^n
\]
This gives us two slopes \( q_1/s \) and \( q_2/s \), whose different values depend on the two OH\(^-\) concentrations by

\[
q = k \ [\ OH^-\ ]^n \\
q/s = k \ [\ OH^-\ ]^n/s
\]

\[
q_1/s = k \ [\ OH^-\ ]^n/s = k \ c_1^n/s \\
q_2/s = k \ [\ OH^-\ ]^n/s = k \ c_2^n/s
\]

\[
q_1 / q_2 = c_1^n / c_2^n = (c_1 / c_2)^n
\]

Having determined both \( m \) and \( n \), we can now go back and calculate \( k \), the specific rate.

**Again, \( c_1 \) and \( c_2 \) are known from the way we made up the solutions.**

If \( m = 1 \)

\[
q_1 = k \ [\ OH^-\ ]^n = k \ c_1^n \\
q_2 = k \ [\ OH^-\ ]^n = k \ c_2^n
\]

\[
k = q_1/c_1^n = q_2/c_2^n
\]

If \( m = 2 \)

\[
q_1/s = k \ [\ OH^-\ ]^n/s = k \ c_1^n/s \\
q_2/s = k \ [\ OH^-\ ]^n/s = k \ c_2^n/s
\]

\[
k = s (q_1/s) / c_1^n = s (q_2/s) / c_2^n
\]

where \( s \) is the Beer's Law constant for the dye.

**In either case, report the average of the two values.**

**This is how we determine \( k \)**

**PROCEDURE**

**WORK IN PAIRS**

1.) Prepare appropriate dilutions of Mg\(^2+\) and NaOH stock solutions

2.) Permit solutions to come to temperature of water bath

   **Do not** measure absorbance of the dye solution (procedure 3b) You will be given the Beer's Law slope in case you need it!

   Blank should be NaOH - use water instead

3.) Start timer, combine, and mix solutions

   **ALL AT THE SAME TIME (t=0)**

   **Don't stop the timer!**
PROCEDURE (cont'd)

4.) Make an absorbance measurement as soon as possible and then, again at appropriate time intervals as instructed (~60 sec, ~120 sec), Record absorbance & total elapsed time

5.) Plot data on lab computer and decide on m, the order of the reaction with respect to MG+

6.) From the slope of the plot, determine the apparent specific rate constant q

This slope includes the term [OH⁻]ⁿ

\[ q = k [OH^-]^n \]

\[ \text{Slope} = q/s \text{ if } m = 2 \]

7.) Repeat Steps 1-6 using different [OH⁻]

8.) Plot new data appropriately vs time, Use the same function (i.e., ln or 1/[MG⁺]) that produced linear plot in Run 1

9.) From the 2 sets of data, determine n, and the specific rate constant k

Note: The cuvettes may become slightly stained by the dye. If so, they can be cleaned by rinsing with 2-3 mL of 95% ethanol

Modifications to the procedure:

You will NOT do part 3b – Determination of the Beer's Law constant for Malachite Green.

• Should you need it, the Beer's Law constant is 4.03 x 10⁻⁴ L/mol.

You will not do part 8 – Determination of the rate constant for the bleaching of Crystal Violet.

It will be helpful to have a watch with a second hand for this exercise.

The Excel Workbook has two sheets – scaled properly for the time scales of the two runs.
Spreadsheets require exactly 8 entries in order of increasing time.

<table>
<thead>
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<th>Time (sec)</th>
<th>Abs</th>
<th>-ln(Abs)</th>
<th>1/Abs</th>
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<td>0.693</td>
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<td>0.200</td>
<td>1.609</td>
<td>5.000</td>
</tr>
<tr>
<td>1303</td>
<td>0.150</td>
<td>1.897</td>
<td>6.667</td>
</tr>
</tbody>
</table>

Note that times are the total elapsed seconds.

The relevant plot is the one that produces the largest value of $R^2$. The slopes and intercepts are as follows:

- **LOG PLOT**
  - slope: 9.290E-04
  - intercept: 6.090E-01
  - Rsq: 0.9712

- **RECIPROCAL PLOT**
  - slope: 3.408E-03
  - intercept: 1.425E+00
  - Rsq: 0.8875

An example - the logic and calculations - Bleaching of Congo Red (CR)

**Run1:**
- 20 mL of CR stock solution ($1.9x10^{-4}$ M) diluted to 100 mL
- 10 mL of NaOH stock solution ($2.2x10^{-1}$ M) diluted to 100 mL
- Let solutions come to bath temperature
- At $t=0$, two above solutions are mixed ($V=200$ mL)
- CR Absorbance is measured at 90 sec intervals (Beer’s Law constant = $1.2 \times 10^5$)

$[\text{OH}^-] = \frac{(10 \text{ mL})(2.2x10^{-1} \text{ mmol/mL})}{200 \text{ mL}} = 1.1x10^{-2}$ M

$[\text{CR}]_0 = \frac{(20 \text{ mL})(1.9x10^{-4} \text{ mmol/mL})}{200 \text{ mL}} = 1.9x10^{-5}$ M

**LOG PLOT**
- slope: 7.290E-04
- intercept: 6.090E-01
- Rsq: 0.833

**RECIPROCAL PLOT**
- slope: 7.302E-02
- intercept: 1.425E+00
- Rsq: 0.962

Conclusions:
- $R^2 = 0.833$
- Slope = $2.2x10^{-3}$ s$^{-1}$

- $R^2 = 0.962$
- Slope = $7.3x10^{-2}$ mol/Ls

**Conclusion:** rate is second order in CR
Run 2:
- 20 mL of CR stock solution diluted to 100 mL
- 20 mL of NaOH stock solution diluted to 100 mL
- at t=0, two above solutions are mixed
- CR Absorbance is measured at 60 sec intervals

\[ c_1 = 1.1 \times 10^{-2} \text{ M} \]
\[ c_2 = [\text{OH}^-] = \frac{(20 \text{ mL})(2.2 \times 10^{-4} \text{ mmol/mL})}{200 \text{ mL}} = 2.2 \times 10^{-2} \text{ M} \]

Run 2:
- 20 mL of CR stock solution diluted to 100 mL
- 20 mL of NaOH stock solution diluted to 100 mL
- at t=0, two above solutions are mixed
- CR Absorbance is measured at 60 sec intervals
- Reciprocal plot of CR absorbance gives

\[ \frac{q_1}{q_2} = 30.6 \times 10^{-2} \text{ mol/Ls} \]
\[ \frac{q_1}{q_2} = 7.3 \times 10^{-2} \text{ mol/Ls} \]

\[ \log \left( \frac{q_1}{q_2} \right) = \log \left( \frac{c_1}{c_2} \right) \]
\[ n = \frac{\log(7.3 \times 10^{-2})}{\log(1.1 \times 10^{-2})} \]
\[ n = \frac{\log(2.2 \times 10^{-2})}{\log(1.1 \times 2 \times 10^{-2})} \]

\[ k = \frac{(q_1/s) \text{ s} / c_1^2}{c_2^2} \]
\[ = \frac{7.3 \times 10^{-2} \times 1.2 \times 10^5}{(1.1 \times 10^{-2})^2} \]
\[ = 7.2 \times 10^7 \text{ L}^3/\text{mol}^3\text{-sec} \]
From 1st run

\[ k = \frac{(q_2/s) \text{ s} / c_2^2}{c_2^2} \]
\[ = \frac{30.6 \times 10^{-2} \times 1.2 \times 10^5}{(2.2 \times 10^{-2})^2} \]
\[ = 7.6 \times 10^7 \text{ L}^3/\text{mol}^3\text{-sec} \]
From 2nd run

Our rate law can now be written as:

\[ \text{rate} = 7.4 \times 10^7 [\text{CR}]^2[\text{OH}^-]^2 \text{ M/sec} \]

FOR NEXT WEEK
SYNTHESIS OF ASPIRIN
READ SUSB - 028
DO PRE-LAB
You will need your 125 mL Erlenmeyer to be clean and dry for the aspirin synthesis. You might wish to wash it at the end of the kinetics exercise.