Resources

1. Prof. Posey (questions related to course content)
2. General Chemistry Office (administrative issues and technical problems with Connect)
3. Lecture
4. Recitations (beginning Tuesday, September 4)
5. Help Room (81/83 Chemistry). The staffing schedule will be posted online and outside the room.
6. Tutoring sessions offered by the Learning Resource Center in Bessey Hall and at other campus locations. Schedules can be found at http://www.lrc.msu.edu/
7. Mock exams (Learning Resource Center)
   - Exam #1-Wednesday, October 3, 2012, 5–8:30 PM, B119 Wells
   - Exam #2-Wednesday, November 7, 2012, 5–8:30 PM, B119 Wells
8. Study groups

Tips for Success

1. Schedule some time every day to work on CEM 142. Do not wait until the last minute to prepare for tests. There are only two of them! Work on the Connect© problems as the material is covered in lecture. It is important to stay current with the material in the course.
2. Do the reading assignment before lecture.
3. Take notes in class and review them the same day.
4. Take doing the Connect© problems seriously. They count for 16% of the semester grade, and learning how to do these problems will help to prepare you for exams. Collaboration with your peers on solving these problems is encouraged; however, you are responsible for submitting your own answers before Saturday 8 AM.
5. Come to recitation prepared to put in your best effort on the recitation problem sets. Participate in the discussion of the problems and presentation of solutions.
6. Practice working problems from old exams.
7. Take advantage of the available resources.
8. *If you have questions, don’t wait to seek help!*
Today’s Topics—Chemical Kinetics II

- Integrated rate laws for first-, second-, and zeroth-order kinetics
- Half lives

Related Problems from Spring 2008 Exam 1: 3, 4, 8 & Spring 2009 Exam 1: 2, 5
Corresponding Connect Problems: Set 1: 11–14

Learning Objectives (Lecture 2)

You should:

1. understand that integration of rate laws yields expressions for reactant concentrations as a function of time for zeroth-, first-, and second-order reactions.

2. be able to apply integrated rate law equations to determine the rate constant for a reaction from the time dependence of reactant or product concentrations and to predict the concentration of reactant remaining or product formed at specified times using a rate constant.

3. be able to apply graphical methods to determine the reaction order and rate constant from concentration data collected as a function of time.

4. know how to find half-life ($t_{1/2}$) expressions for zeroth-, first-, and second-order reactions.

5. know what the half-life ($t_{1/2}$) for a first-order reaction represents, how $t_{1/2}$ is related to the first-order rate constant $k$, and how $t_{1/2}$ can be determined graphically from a plot of reactant concentration vs. time.

6. be able to use half-life behavior to infer reaction order.
Relationship Between Concentration and Time

- Rate law equations provide a relationship between reactant concentrations and reaction rates.
  \[ \text{Rate} = k[A]^m[B]^n \]
- But how do the concentrations of reactants and products change over time?
- The answer (a mathematical relationship between concentration and time) can be found by integrating the rate law equations.
- The form of the resulting mathematical expressions that provide the relationship between reactant or product concentration and time will depend on the reaction order.

Integrated Rate Equations: First-order Reactions

The rate law equation for the first-order reaction $R \rightarrow \text{products}$ is

\[ \text{Rate} = k[R]^1 \text{ or } \frac{d[R]}{dt} = k[R]^1 \]

After rearranging this expression

\[ -\frac{d[R]}{[R]} = kd \]

and integrating from $t = 0$ to $t = t$, the following integrated rate equation expressing the relationship between reactant concentration and time is obtained:

\[ \int_{[R]_0}^{[R]_t} \frac{1}{[R]} \, d[R] = -\int_0^t k \, dt \]

\[ \ln \frac{[R]_t}{[R]_0} = -kt \text{ or } [R]_t = [R]_0 e^{-kt} \]

where $[R]_0$ is the concentration at $t = 0$ and $[R]_t$ is the concentration at time $t$. 
A convenient way to determine if a reaction follows first-order kinetics is to rearrange the integrated rate law into slope-intercept form \( y = mx + b \)

\[
\ln[R]_t = -kt + \ln[R]_0
\]

If a linear plot is obtained when \( \ln[R]_t \) is plotted as a function of \( t \), the reaction is first-order in \( R \) and first-order overall. The slope of the plot corresponds to the rate constant \( k \) and the y-intercept is \( \ln[R]_0 \). (Figure-McMurray & Fay)

**First-order Reactions and the Reaction Half-life**

The half-life of a reaction is the time required for the concentration of a reactant to decrease to one half of its initial value, i.e. \( [R]_t = \frac{1}{2}[R]_0 \).

The relationship between the half-life \( t_{1/2} \) and rate constant \( k \) for a first-order reaction can be found by substituting for \( [R]_t = \frac{1}{2}[R]_0 \) in the integrated rate law expression

\[
\ln \frac{[R]_t}{[R]_0} = -kt
\]

\[
\ln \frac{\frac{1}{2}[R]_0}{[R]_0} = -kt_{1/2}
\]

\[
\ln \frac{1}{2} = -kt_{1/2}
\]

\[
t_{1/2} = -\frac{\ln \frac{1}{2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}
\]

Notice that the half-life for a first-order reaction is *independent* of the initial concentration of the reactant.
Problem-Radioactive (First-order) Decay

Gold-198 (^{198}\text{Au}) is radioactive (first-order decay). It has a half-life of 2.7 days. If there is 10 mg at the beginning of the week, how much is left at the end of the week?
Problem-Half-life of First-Order Reaction

The decomposition of formic acid (HCO$_2$H) at 550°C obeys the rate law: Rate = k[HCO$_2$H]. If a 5.00 atm sample of formic acid decays to 1.25 atm in 72 seconds, what is the half-life $t_{1/2}$ for the reaction?

Problem-First-order Decomposition of Acetaldehyde

The first-order decomposition of acetaldehyde CH$_3$CHO to methane CH$_4$ has a rate constant of 0.029 min$^{-1}$. How long does it take for a concentration of 0.050 mol L$^{-1}$ to reach 0.040 mol L$^{-1}$?
Integrated Rate Equations: Second-order Reactions

• A reaction that is second-order in a single reactant follows the rate law equation
  \[
  \text{Rate} = k[R]^2
  \]

• The integrated rate equation for such a reaction is
  \[
  \frac{1}{[R]_t} - \frac{1}{[R]_0} = kt
  \]

• Rearranged to slope-intercept \((y = mx + b)\) form, this equation becomes
  \[
  \frac{1}{[R]_t} = kt + \frac{1}{[R]_0}
  \]
  where the \textit{slope} = \(k\) and \textit{y–intercept} = \(1/[R]_0\). Plot \(1/[R]_t\) vs. \(t\). If the resulting plot is linear, the reaction is second-order with respect to \(R\) and second-order overall.

• The half-life \(t_{1/2}\) for a second-order reaction corresponds to the time at which
  \[
  [R]_t = \frac{1}{2}[R]_0.
  \]
  \[
  \frac{1}{\frac{1}{2}[R]_0} - \frac{1}{[R]_0} = k t_{1/2}
  \]
  \[
  \frac{2}{[R]_0} - \frac{1}{[R]_0} = k t_{1/2}
  \]
  \[
  t_{1/2} = \frac{1}{k[R]_0}
  \]
  The half-life in a second-order reaction depends on the initial concentration of the reactant \([R]_0\) and increases as the reaction proceeds and the concentration of the reactant decreases.
Plotting Experimental Data to Determine the Reaction Order

Is this reaction first- or second-order with respect to the reactant NO₂?

(Figure-McMurray & Fay)

Problem-Second-order Decomposition of HI

Decomposition of HI into H₂ and I₂ follows the second-order rate law Rate = k[HI]² where \( k = 0.080 \text{ L mol}^{-1} \text{ s}^{-1} \). If the initial concentration of HI is 0.050 M, what is the half-life? What is the second half-life?
Integrated Rate Equations: Zero-order Reactions

- In a zeroth-order reaction
  \[ \text{Rate} = k \]
  which means that the rate is independent of reactant concentration.

- The corresponding integrated rate equation is
  \[ [R]_0 - [R]_t = kt \]

- Slope-intercept form
  \[ [R]_t = -kt + [R]_0 \]

(Figure-McMurray & Fay)

Problem-Zero-order Kinetics

The decomposition of ammonia on a hot tungsten wire is a zero-order reaction. In one experiment the partial pressure of ammonia $P_{NH_3}$ decreased from 21 kPa to 10 kPa in 770 seconds.

1. What is the rate?

2. What is the rate constant?
3. How long does it take for all of the ammonia to disappear (estimate and calculate)?

Problem—Determination of Reaction Order

The concentration of a reactant in the reaction

\[ A + B \rightarrow 2C \]

changes as reported below as the reaction proceeds.

- At time zero (initial concentration) \(144 \text{ mol L}^{-1}\)
- After 12 minutes \(36 \text{ mol L}^{-1}\)
- After another 16 minutes \(18 \text{ mol L}^{-1}\)
- One hour after the start \(9 \text{ mol L}^{-1}\)

1. What is the order of the reaction with respect to this reactant?
2. What is the concentration of the product C in mol L\(^{-1}\) one hour after the start of the reaction? Assume that the volume does not change

Problem-Rate Constant Determination for a Second-order Reaction

A second-order gas-phase reaction has the following reactant concentrations:

\[
[R]_0 = 220 \text{ mmol} / L \\
[R]_t = 56 \text{ mmol} / L \text{ at } t = 1.22 \times 10^4 s
\]

What is the rate constant for the reaction?