DIFFERENT METHODS TO DETERMINE RATE LAW (i.e., find the order(s) and k)

I. Initial rates method (see Help Sheet #6)

II. Description (see Help Sheet #6)

III. Integrated Rate Laws – Graphs (see below: this Help Sheet)

IV. Half-life, $t_{1/2}$: $[A]$ versus time – Graphs (see below: this Help Sheet)

V. Rate versus Concentration – Graphs (see below: this Help Sheet)

VI. Mechanisms (see Help Sheet #8)

III. Integrated Rate Laws – Graphs and Equations

Integrated Rate Law: function of time; when a question involves time (e.g., How much $[A]$ is left after 2 hours?) use the Integrated Rate Law equations

<table>
<thead>
<tr>
<th>Order</th>
<th>Rate Law</th>
<th>Integrated Rate Law</th>
<th>y-axis vs x-axis</th>
<th>Slope</th>
<th>y-intercept</th>
<th>$t_{1/2}$ (half-life)</th>
<th>Units of k</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$rate = k[A]^0 = k$</td>
<td>$[A]_t = -kt + [A]_0$</td>
<td>$[A]_t$ vs $t$</td>
<td>m = -k</td>
<td>$[A]_0$</td>
<td>$t_{1/2} = \frac{[A]_0}{2k}$</td>
<td>$M/time$</td>
</tr>
<tr>
<td>1</td>
<td>$rate = k[A]^1$</td>
<td>$\ln[A]_t = -kt + \ln[A]_0$</td>
<td>$\ln[A]_t$ vs $t$</td>
<td>m = -k</td>
<td>$\ln[A]_0$</td>
<td>$t_{1/2} = \frac{0.693}{k}$</td>
<td>$1/time$</td>
</tr>
<tr>
<td>2</td>
<td>$rate = k[A]^2$</td>
<td>$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$</td>
<td>$\frac{1}{[A]_t}$ vs $t$</td>
<td>m = k</td>
<td>$\frac{1}{[A]_0}$</td>
<td>$t_{1/2} = \frac{1}{k[A]_0}$</td>
<td>$\frac{1}{[(M)(time)]}$</td>
</tr>
</tbody>
</table>

Summary of the integrated rate law graphs (see next page for more detailed plots):

1st order rate law: $\ln[A]_t = -kt + \ln[A]_0$ can also be written: $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$

this rearranged equation is useful when given % remaining questions; the % remaining (not % consumed) is substituted for $\left(\frac{[A]_t}{[A]_0}\right): \ln(%remaining) = -kt$

KINETICS TECHNIQUE: “Flooding” – see the pages at the end of this Help Sheet for a description and example; understanding this technique and interpreting the data is aligned with the lab and is often asked
**Integrated Rate Law – Graphs (more details)**

Create 3 plots: [A] versus time, ln[A] versus time, and 1/[A] versus time; the plot that yields a line will then determine the order, k, and [A]₀ of the reaction; the other plots will be curves and are ignored.

**Zero order:**

\[ \text{Rate} = k[A]₀ \]

- Plotted in 3 ways; choose [A] vs time → linear (ignore other plots); slope = -k; y-intercept = [A]₀

**1st order:**

\[ \text{Rate} = k[A] \]

- Plotted in 3 ways; choose ln[A] vs time → linear (ignore other plots); slope = -k; y-intercept = ln[A]₀

**2nd order:**

\[ \text{Rate} = k[A]² \]

- Plotted in 3 ways; choose 1/[A] vs time → linear (ignore other plots); slope = k; y-intercept = 1/[A]₀
Why are successive half-lives not always constant? 

<table>
<thead>
<tr>
<th>Order</th>
<th>( t_{1/2} )</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( t_{1/2} = \frac{[A]_0}{2k} )</td>
<td>( t_{1/2} ) decreases with each successive ( t_{1/2} )</td>
</tr>
</tbody>
</table>
|       |                 | Let \( k = 0.01 \text{M/s} \) and \( [A]_0 = 1.0 \text{M} \); from integrated rates laws: \( t_{1/2} = \frac{[A]_0}{2k} \); calculate 3 half-lives:  
|       |                 | \( t_{1/2} \) (first half-life) = 1.0/M(2.001) = 50s (note: the new \([A]_0\) for the next half-life is now 0.50M) |  
|       |                 | \( t_{1/2} \) (second half-life) = 0.50/[2(0.01)] = 25s (note: \( t_{1/2} \) is smaller and \([A]_0\) for the next half-life is now 0.25M) |  
|       |                 | \( t_{1/2} \) (third half-life) = 0.25/[2(0.01)] = 12.5s (note: \( t_{1/2} \) is smaller and \([A]_0\) for the next half-life is now 0.125M) |  
|       |                 | On graph of \([A]\) versus time: If \( t_{1/2} \) decreases in size \( \rightarrow \) 0 order! |  
|       | 1.00M \( \rightarrow \) 0.50M \( \rightarrow \) 0.25M \( \rightarrow \) 0.125M \( (t_{1/2} \) decreasing) | | |
| 1     | \( t_{1/2} = \frac{0.693}{k} \) | \( t_{1/2} \) is constant |
|       |                 | Let \( k = 0.01 \text{M/s} \) and \( [A]_0 = 1.0 \text{M} \); from integrated rates laws: \( t_{1/2} = \frac{0.693}{k} \); calculate 3 half-lives:  
|       |                 | \( t_{1/2} \) (first half-life) = 0.693/[0.01] = 69.3s (note: the new \([A]_0\) for the next half-life is now 0.5M) |  
|       |                 | \( t_{1/2} \) (second half-life) = 0.693/[0.01] = 69.3s (note: \( t_{1/2} \) is constant and \([A]_0\) for the next half-life is now 0.25M) |  
|       |                 | \( t_{1/2} \) (third half-life) = 0.693/[0.01] = 69.3s (note: \( t_{1/2} \) is constant and \([A]_0\) for the next half-life is now 0.125M) |  
|       |                 | On graph of \([A]\) versus time: If \( t_{1/2} \) stays constant \( \rightarrow \) 1st order! |  
|       | 1.00M \( \rightarrow \) 0.50M \( \rightarrow \) 0.25M \( \rightarrow \) 0.125M \( (t_{1/2} \) constant) | | |
| 2     | \( t_{1/2} = \frac{1}{k[A]_0} \) | \( t_{1/2} \) increases with each successive \( t_{1/2} \) |
|       |                 | Let \( k = 0.01 \text{M/s} \) and \( [A]_0 = 1.0 \text{M} \); from integrated rates laws: \( t_{1/2} = \frac{1}{k[A]_0} \); calculate 3 half-lives:  
|       |                 | \( t_{1/2} \) (first half-life) = \( [1/0.01(1.0)] = 100s \) (note: the new \([A]_0\) for the next half-life is now 0.5M) |  
|       |                 | \( t_{1/2} \) (second half-life) = \( [1/0.01(0.5)] = 200s \) (note: \( t_{1/2} \) increased and \([A]_0\) for the next half-life is now 0.25M) |  
|       |                 | \( t_{1/2} \) (third half-life) = \( [1/0.01(0.25)] = 400s \) (note: \( t_{1/2} \) increased and \([A]_0\) for the next half-life is now 0.125M) |  
|       |                 | On graph of \([A]\) versus time: If \( t_{1/2} \) increases in size \( \rightarrow \) 2nd order! |  
|       | 1.00M \( \rightarrow \) 0.50M \( \rightarrow \) 0.25M \( \rightarrow \) 0.125M \( (t_{1/2} \) increasing) | | |
V. Rates versus \([A]\) – Graphs

**Zero Order**

Rate versus \([A]\) and Rate yields a horizontal line;
From Rate versus \([A]\) plot:

\[ k = \text{y-intercept} = \text{0.005} \]

- \([A]_0\): find largest \([A]\) value (right side of line)

**1st Order**

Rate versus \([A]\) yields a non-horizontal line;
From Rate versus \([A]\) plot:

\[ k = \text{slope} \]

- \([A]_0\): find largest \([A]\) value (right side of line)

**2nd Order**

Rate versus \([A]\) yields a curve
- \([A]_0\): find largest \([A]\) value (right side of curve)

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**MATH REVIEW – USING LOG OR LN:**

\[
\ln\left(\frac{x^a}{y^a}\right) = \ln\left(\frac{x}{y}\right)^a
\]

\[
\ln(a^x) = x\ln(a)
\]

\[
\ln(xy) = \ln(x) + \ln(y)
\]

\[
\ln\left(\frac{x}{y}\right) = \ln(x) - \ln(y)
\]

1. A reaction \(A + B \rightarrow C\) has a first order rate law rate = \(-\Delta[A]/\Delta t = k[A]\) with \(k = 1.50 \times 10^{-4} \text{ s}^{-1}\).
   a. If \([A]_0 = 1.55 \text{ M}\), what is the concentration of \([A]\) after 10.0 minutes?
   b. How long (in seconds) will it take to use up 99.9% of \(A\)?

2. Given the following reaction, \(A \rightarrow 2C\) has a rate law of \(-\Delta[A]/\Delta t = k[A]^1\)
   After 21.75 hours, the concentration of \(A\) has decreased from \(0.157 \text{ M}\) to \(0.0966 \text{ M}\). What is the rate constant?

3. The following reaction, \(2A \rightarrow B\), has a rate law that is first-order with respect to reactants, and has a rate constant of \(1.50 \times 10^{-2} \text{ s}^{-1}\). How long will it take for 35.0% of \(A\) to be consumed?

4. One of the reactions in a breeder reactor involves the first order conversion of \(^{239}\text{U}\) to \(^{239}\text{Np}\)
   \[ ^{239}\text{U} \rightarrow ^{239}\text{Np} + e^- \]
   The half-life of \(^{239}\text{U}\) is 23.5 minutes. How long does it take for 35% of the \(^{239}\text{U}\) to be consumed?

5. The reaction, \(A \rightarrow B\), is first order with a half-life of 2.75 days. What fraction of \(A\) remains after 13.75 days?
   a. \(\frac{1}{4}\)  b. \(\frac{1}{5}\)  c. \(\frac{1}{16}\)  d. \(\frac{1}{8}\)  e. \(\frac{1}{32}\)

6. What factors that can change the rate of a reaction?

7. The break down of \(\text{SO}_2\text{Cl}_2\) is a first-order reaction, \(\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2\)
   If the rate constant is \(2.80 \times 10^{-3} \text{ min}^{-1}\), and the initial concentration of \(\text{SO}_2\text{Cl}_2\) is \(4.75 \times 10^{-5} \text{ M}\), how long in minutes will it take for the concentration to drop to \(1.25 \times 10^{-5} \text{ M}\)?
8. When heated, tetrafluoroethylene dimerizes to form octafluorocyclobutane: \[ 2\text{C}_2\text{F}_4 \rightarrow \text{C}_4\text{F}_8 \]

Data from a kinetics experiment was collected and plotted below.

a. What is the rate law for this reaction?
b. What is the value of the rate constant?
c. What was the initial concentration of \( \text{C}_2\text{F}_4 \)?
d. What is the concentration of \( \text{C}_2\text{F}_4 \) at 600s?

9. The reaction, \( 2\text{HOF} \rightarrow 2\text{HF} + \text{O}_2 \) was analyzed and kinetic data was plotted below.

a. What is the rate law for this reaction?
b. What is the value of the rate constant?
c. What was the initial concentration of HOF?
d. What is the concentration of HOF after 120s?
10. The reaction: $\text{D}_2 + \text{E} \rightarrow \text{DDE}$ was analyzed using the “flooding” technique similar to your lab. In Experiment 1, $[\text{D}_2]_0 = 0.0025\text{M}$ and $[\text{E}]_0 = 1.00\text{M}$ ($T = 298\text{K}$). Concentration data of $\text{D}_2$ versus time was plotted below. In Experiment 2, $[\text{D}_2]_0 = 0.0050\text{M}$ and $[\text{E}]_0 = 2.00\text{M}$ ($T = 298\text{K}$), and again the concentration data of $\text{D}_2$ was plotted.

**Experiment 1**

| Run#1: $[\text{D}_2]$ versus time(s) at 298K |
| $[\text{D}_2]_0 = 0.0025\text{M}; [\text{E}]_0 = 1.00\text{M}$ |
| $\text{D}_2$ | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
| $\text{time (s)}$ | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
| $\ln[\text{D}_2]$ | -7.50 | -7.30 | -7.10 | -6.90 | -6.70 | -6.50 | -6.30 | -6.10 | -5.90 |
| $\text{y} = 0.45x + 400$ |

| Run#1: $\ln[\text{D}_2]$ versus time(s) at 298K |
| $[\text{D}_2]_0 = 0.0025\text{M}; [\text{E}]_0 = 1.00\text{M}$ |
| $\text{D}_2$ | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
| $\text{time (s)}$ | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
| $\ln[\text{D}_2]$ | -7.50 | -7.30 | -7.10 | -6.90 | -6.70 | -6.50 | -6.30 | -6.10 | -5.90 |
| $\text{y} = 0.45x + 400$ |

| Run#1: $1/[\text{D}_2]$ versus time(s) at 298K |
| $[\text{D}_2]_0 = 0.0025\text{M}; [\text{E}]_0 = 1.00\text{M}$ |
| $\text{D}_2$ | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
| $\text{time (s)}$ | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
| $1/[\text{D}_2]$ | -2.00 | -2.25 | -2.50 | -2.75 | -3.00 | -3.25 | -3.50 | -3.75 | -4.00 |
| $\text{y} = 0.05x + 100$ |

**Experiment 2**

| Run#2: $1/[\text{D}_2]$ versus time(s) at 298K |
| $[\text{D}_2]_0 = 0.0025\text{M}; [\text{E}]_0 = 2.00\text{M}$ |
| $\text{D}_2$ | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
| $\text{time (s)}$ | 0 | 400 | 800 | 1200 | 1600 | 2000 | 2400 | 2800 | 3200 |
| $1/[\text{D}_2]$ | -0.05 | -0.10 | -0.15 | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 |
| $\text{y} = 0.05x + 100$ |

a. What does the high concentration of $\text{E}$ do in terms of changing the rate law? Write the new general rate law using $k_{\text{obs}}$.
b. From Experiment 1, what is the order with respect to $\text{D}_2$?
c. What is the value of the observed rate constant, $k_{\text{obs}1}$, from Experiment 1?
d. What is the value of the observed rate constant, $k_{\text{obs}2}$, from Experiment 2?
e. What is the order with respect to $\text{E}$? (Hint: Recall: $\ln(k_{\text{obs}1}/k_{\text{obs}2})/\ln([\text{E}]_1/[\text{E}]_2)$)
f. What is the value of the rate constant $k$; include units?
g. Write the rate law for this reaction.

11. The reaction: $\text{D} + \text{E} \rightarrow \text{DE}$ was analyzed. In the first experiment, $[\text{E}]_0 = 0.010\text{M}$ and $[\text{B}]_0 = 1.0\text{M}$; in the second experiment, $[\text{E}]_0 = 0.010\text{M}$ and $[\text{D}]_0 = 2.0\text{M}$. Plots of $1/[\text{E}]_t$ versus time were plotted.

| 1/[E] versus time |
| $[\text{E}]_0 = 0.010\text{M}$ |
| $[\text{B}]_0 = 1.0\text{M}$ |
| $\text{y} = 0.3x + 100$ |
| 2/[E] versus time |
| $[\text{E}]_0 = 0.010\text{M}$ |
| $[\text{D}]_0 = 2.0\text{M}$ |
| $\text{y} = 0.05x + 100$ |

a. Determine the order with respect to $\text{E}$.
b. What is the order with respect to $\text{D}$?
c. What is the value of the rate constant $k$; include units?
12. a. Given the graph and the reaction $A \rightarrow 2B$, write the rate law and include the order of $A$.
b. What is the value of $k$? Include units.
c. What is the initial rate of the reaction?

![Graph of [A] versus time](image)

13. Given the graph and the reaction $A \rightarrow B$, write the rate law with the order of $A$.

![Graph of Rate versus [A]](image)
14. The reaction $B + C \rightarrow BC$ was run and the kinetics were studied. Two experiments were conducted during which chemical B was flooded in the reaction vessel. In the first experiment, $[B]_0 = 1.0\text{M}$ and in the second experiment $[B]_0 = 2.0\text{M}$. The resulting data of the concentration of C versus time is shown below in the graph.

a. Write the general rate law.

b. Since B was flooding the reaction, write a new simplified rate law. Clearly note any substitutions you made and what the dy represent.

c. Determine the order of C.

d. Determine the order of B.

e. Determine the rate constant.

ANSWERS

1. a. $1.42\text{ M}$ \[\ln[A]_t = -kt + \ln[A]_0 = -(1.5 \times 10^{-4}\text{s}^{-1})(10\text{min})(60\text{s}/1\text{min}) + \ln(1.55) = 0.3483; [A] = e^{0.3483} = 1.416\text{M}\]

b. $4.61 \times 10^4\text{ s}$ \{with %remaining use: \[\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \text{ where } \frac{[A]_t}{[A]_0} = \%\text{remaining}; \ln(0.001) = -(1.5 \times 10^{-4})t; t = 46052\text{s}\}

2. $k = 0.0223\text{hr}^{-1}$ \{\ln[A]_t = -kt + \ln[A]_0; \ln(0.0966) = -(k)((21.75) + \ln(0.157)); solve for k; k = 0.0223hr^{-1}\}

3. $28.7\text{s}$ \{with %remaining use: \[\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \text{ where } \frac{[A]_t}{[A]_0} = \%\text{remaining}; \ln(0.65) = -(1.5 \times 10^{-2})t; t = 28.72\text{s}\}

4. $14.6\text{ minutes}$ \{\[A]_t \text{ is the amount that is left over;} \]

\[
\frac{[A]_t}{[A]_0} = 65\% = 0.65; \ln(0.65) = -(0.0295)t; \text{solve for t}\]

5. e \{13.75/2.75 = 5.0 \text{ half-lives; } [A]_t = (1/2)^5 = 1/32 \text{ of the original amount remains}\}

6. Temperature, catalysts, concentration, surface area
7. \[ 477 \text{ min} \quad \ln[\text{SO}_2\text{Cl}_2] = -kt + \ln[\text{SO}_2\text{Cl}_2]_0; \quad \ln(1.25 \times 10^{-5}) = -(2.8 \times 10^{-3} \text{ min}^{-1})(t) + \ln(4.75 \times 10^{-5}); \text{ solve for } t; \quad t = 476.8\text{ min} \]

8. a. \[ \text{rate} = k[\text{C}_2\text{F}_4]^2 \quad \{\text{Since a linear plot occurs when } /1/ \text{ concentration vs time is plotted } \rightarrow 2\text{nd order}\} \]
   b. \[ k = 0.0449 \text{ M}^{-1}\text{s}^{-1} \quad \{\text{the slope of the equation of the line for } 2\text{nd order} = k; \text{ the slope} = 0.0449 \Rightarrow k; \text{ if the equation of the line was not given, } k \text{ can be calculated by determining the slope; } \text{slope} = k = \frac{\Delta y}{\Delta x} = \frac{(32 - 10)}{(500 - 0)} = 4.4 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}; \text{ note: if this question were on a quiz/exam, typically a range of values for } k \text{ would be acceptable because of how graph are read differently}\} \]
   c. \[ 0.100 \text{M} \quad \{y \text{-intercept} = \frac{1}{[\text{C}_2\text{F}_4]_0} = \frac{1}{10.000} = 0.100 \text{M} \} \]
   d. \[ 0.0271 \text{M} \quad \{\text{can try to extend the line; easier to use:} \quad \frac{1}{[\text{C}_2\text{F}_4]_t} = kt + \frac{1}{[\text{C}_2\text{F}_4]_0}; \quad \frac{1}{[\text{C}_2\text{F}_4]_t} = (4.49 \times 10^{-2})(600) + \frac{1}{0.100} \}
   \]

9. a. \[ \text{rate} = k[\text{HOF}] \quad \{\text{Since a linear plot occurs when } \ln[\text{I}] \text{ vs time is plotted } \rightarrow 1\text{st order}\} \]
   b. \[ 2.5 \times 10^{-2} \text{ }\text{s}^{-1} \quad \{\text{slope} = -k; \text{ slope} = -0.025; k = 0.025 \text{min}^{-1}\} \]
   c. \[ 0.86M \quad \{y \text{-intercept} = \ln[\text{HOF}]_0; \ln[\text{HOF}]_0 = -0.15; [\text{HOF}]_0 = e^{-0.15} = 0.861\text{M} \} \]
   d. \[ 0.043M \quad \{\ln[\text{HOF}]_t = -kt + \ln[\text{HOF}]_0 = -(0.025)(120) + \ln(0.86) = -3.151; [\text{HOF}] = e^{-3.151} = 0.0428\text{M} \} \]

10. a. Since the concentration of E is much larger than the concentration of D\(_2\), the concentration of E can be considered constant. This therefore simplifies the rate law from: \[ \text{rate} = k[\text{D}_2]^y[\text{E}]^y \] to:
   \[ \text{rate} = k_{\text{obs}}[\text{D}_2]^x \text{ where } k_{\text{obs}} = k[\text{E}]^y \]
   b. order for D\(_2\) = 2 \quad \{\text{since a plot of } 1/[\text{D}_2] \text{ versus time yielded a line } \rightarrow 2\text{nd order; } x = 2\} \]
   c. \[ k_{\text{obs}1} = 0.45 \quad \{k_{\text{obs}1} = \text{slope from Experiment 1}; k_{\text{obs}1} = 0.45\} \]
   d. \[ k_{\text{obs}2} = 0.90 \quad \{k_{\text{obs}2} = \text{slope from Experiment 2}; k_{\text{obs}2} = 0.90\} \]
   e. order for E = 1 \quad \{\text{When } [\text{E}] \text{ doubled going from } 1.00M \text{ to } 2.00M, k_{\text{obs}} \text{ doubled going from } 0.45 \text{ to } 0.90. \text{ Since } k_{\text{obs}} = k[\text{E}]^y \text{ and } k \text{ is constant, then if } [\text{E}] \text{ doubles and } k_{\text{obs}} \text{ doubles } \rightarrow y = 1; \text{ mathematically (important if the numbers are not simple)}: \}
   \[ y = \ln \left( \frac{k_{\text{obs}1}}{k_{\text{obs}2}} \right) / \ln \left( \frac{[\text{E}]_1}{[\text{E}]_2} \right); y = \ln \left( \frac{0.45}{0.90} \right) / \ln \left( \frac{1.00}{2.00} \right); y = \ln \left( \frac{0.5}{0.5} \right) / \ln \left( \frac{5}{5} \right); y = 1 \}
   f. \[ k = 0.45M^{-2}s^{-1} \quad \{\text{use } k_{\text{obs}1} = k([\text{E}]_1)^1; 0.45 = k(1.0)^1; k = 0.45; \text{ using } k_{\text{obs}2} = k([\text{E}]_2)^1; 0.90 = k(2.0)^1; k = 0.45\} \]
   g. \[ \text{rate} = k[D]^2[\text{E}] \]

11. a. order for E = 2 \quad \{\text{if } 1/[\text{E}] \text{ versus time yields a line } \rightarrow 2\text{nd order; rate} = k[D]^x[\text{E}]^y; \text{ rate} = k_{\text{obs}}[\text{E}]^y \text{ where } k_{\text{obs}} = k[D]^x \}
   b. order for D = 1 \quad \{\text{When } [\text{D}] \text{ was doubled going from } 1.0M \text{ to } 2.0M, k_{\text{obs}} \text{ doubled as well } (0.1/0.05 = 2). \text{ Since } k_{\text{obs}} = k[D]^x \text{ and } k \text{ is constant, then if } [\text{D}] \text{ doubles and } k_{\text{obs}} \text{ doubles } \rightarrow x = 1; \text{ note } k_{\text{obs}} \text{ is the slope of the line given in the equation of the line shown on the plot; can also be done using } x = \ln \left( \frac{k_{\text{obs}}}{k_{\text{obs}2}} \right) / \ln \left( \frac{[\text{D}]_1}{[\text{D}]_2} \right); x = \ln \left( \frac{0.10}{0.05} \right) / \ln \left( \frac{10}{10} \right); x = \ln \left( \frac{5}{5} \right) / \ln \left( \frac{2}{2} \right); x = 1 \}
   c. \[ k = 0.05M^{-2}s^{-1} \quad \{\text{use } k_{\text{obs}} = k[D]^x; \text{ can use either experiment: } 0.1 = k(2)^1; k = 0.05M^{-2}s^{-1}; \text{ for the other experiment: } 0.05 = k(1)^2; k = 0.05M^{-2}s^{-1}\} \]
12. a. rate = k[A]^2  \{Approximate the first two half-lives: From 1.0M to 0.50M, t_start = 0 and t_finish = 2200 → t_{1/2} ≈ 2200s; from 0.50M to 0.025M, t_start = 2200 and t_finish = 6600 → t_{1/2} ≈ 4400s. Regardless of the exact values note that t_{1/2} is increasing → 2nd order.\}

b. k = 4.6 x 10^{-4} M^{-1}s^{-1} \{for 2nd order: t_{1/2} = \frac{1}{k[A]_0}; for first half-life t_{1/2}(1): 2200s = \frac{1}{k(1.0)}; 2200s = \frac{1}{k}; k = 4.55 x 10^{-4} M^{-1}s^{-1}; could also use the second half-life, t_{1/2}(2): 4400s = \frac{1}{k(0.5)}; 2200s = \frac{1}{k}; k = 4.55 x 10^{-4} M^{-1}s^{-1}\}

c. 3.8 x 10^{-4}M/s \{initial rate = \frac{\Delta[A]}{\Delta t}; select points starting at t = 0 and a second point as close as possible to t = 0; for convenience, I chose t = 500s with [A] = 0.81M; initial rate = \frac{(1.0 - 0.81)}{(0 - 500)} = 3.8 x 10^{-4}M^{-1}s^{-1}\}

13. rate = k[A] \{Since a plot of rate versus [A] was linear, this implies that the order of A is 1. Consider that Rate = k[A]^1 can be thought of as y = mx + b with y = Rate, m = k, x = [A], and b = 0\}

14. a. Rate = k[B]^x[C]^y  b. The new rate law is now: rate = k_{obs}[C]^y. Since [B] is approximately constant since it is flooding the reaction, then let k_{obs} = k[B]^x.

c. order with respect to C = 1 \{Using the B = 1.0M graph (you could also have used the [B] = 2.0M graph), determine the half-life for two intervals. t_{1/2}(1) = 18s; t_{1/2}(2) = 19.5s; this is approximately constant so the order of C is 1. If the half-life decreased by a factor of 2 it would be zero order; if it increased by a factor of 2 it would be second order.\}

d. order with respect to B = 1 \{The half-life of [C] when [B] was doubled to 2.0M was determined to be 9s (the measurements used on the graph to determine this second half-life are not shown on the graph below). k_{obs} can be calculated as done in the lab: k_{obs} = 0.693/t_{1/2}; k_{obs}(1) = 0.693/18.75 = 0.03696; k_{obs}(2) = 0.693/9 = 0.0777; (t_{1/2} = 18.75s is the avg of 18s and 19.5s)\}

x = \ln\left(\frac{k_{obs1}}{k_{obs2}}\right)/\ln\left(\frac{[B]_1}{[B]_2}\right); x = \ln\left(\frac{0.037}{0.077}\right)/\ln\left(\frac{1.0}{2.0}\right);

x = \ln(0.48)/\ln(0.5); x = 1.06 = 1;

Another way to determine x is as follows: The t_{1/2} was cut in half going from ~18sec to ~9sec. This means the rate must have doubled since the time was cut in half. If the rate doubles when [B] doubles it means the order of B must be 1\}

e. k = 0.0377M^{-1}s^{-1} \{k_{obs}(1) = k([B]_1)^x; (0.03696) = k(1.0)^x; k = 0.03696; repeat for k_{obs}(2); k_{obs}(2) = k([B]_2)^x; 0.077 = k(2.0)^1; k = 0.03850; average k = (0.03696+0.03850)/2 = 0.03773\}
The goal of a kinetics experiment is to determine the order(s) of the reactant(s) and the value of k. If two chemicals are reacting this creates an experimental challenge since experiments require that only one chemical concentration change at a time while the other stays constant (i.e., one can study only one variable at a time). To achieve this, one of the two chemical concentrations is held constant.

When two chemicals are reacting, e.g., $A + B \rightarrow AB$, this is a flooding experiment question!

**Example:** A reaction, $A + B_2 \rightarrow AB + B$, was studied and the rate law was to be determined. Since two chemicals are reacting the “flooding” or “isolation” technique is used.

Write the rate law: $Rate = k[A]^x[B_2]^y$

If the concentration of $[B_2]_o >> [A]_o$, over the time of the reaction $[B_2]$ will be constant. For example, if $[A]_o = 0.005\text{M}$ and $[B_2] = 0.50\text{M}$ the following table shows how the concentrations change during the reaction assuming it goes to completion:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>0.0050</th>
<th>0.5000</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (start)</td>
<td>C</td>
<td>-0.0050</td>
<td>0.0000</td>
<td>+0.0050</td>
<td>+0.0050</td>
</tr>
<tr>
<td>C (change)</td>
<td>F</td>
<td>0.495</td>
<td>0.0050</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Note how $[B_2]$ is constant to 2 significant figures; re-write the Rate law taking into account that $[B_2]$ is constant and make a substitution: $k_{\text{observed}} = k_{\text{obs}} = k[B_2]^y$; this can be done since both $k$ and $[B_2]$ are constant.

Write the new rate law: $Rate = k_{\text{obs}}[A]^x$

this new rate law has only one chemical present, A, and can now be solved experimentally.

**Solve for order of A, x variable:**


From the graphs below, the linear plot for $\ln[A]$ versus time indicates the reaction is 1st order with respect to A.

since $\ln[A]$ vs time yields a line: $x = 1$
**Solve for y:**

To determine the order of \( B_2 \), repeat the above experiment, change \([B_2]_0\) while also maintaining \([B_2]_0 >> [A]_0\). The experiment now has: \([A]_0 = 0.005M\) and \([B_2] = 1.00M\). Collect data of \([A]\) versus time and again plot ln\([A]\) versus time.

![Graph](image)

For whole number orders of \( y (0, 1, 2) \), \( y \) can be determined by inspection:
- 0 order: the slope doesn’t change when \([B_2]\) changes;
- 1st order: the slope doubles when \([B_2]\) doubles, etc.;
- 2nd order: the slope quadruples when \([B_2]\) doubles, etc.

In this case, \([B_2]\) was doubled (0.50M → 1.00M) and the slope (\(k_{obs}\)) quadrupled (0.001 → 0.004); hence, the order of \( y \) is 2.

The value of \( y \) can also be determined algebraically. The graphs are plots of ln\([A]_1 = -kt + \ln[A]_0\) with the “\( k \)” being \( k_{obs} \) and therefore the slope = \( k_{obs} \). Use the slopes from the two graphs to determine the order of \( B_2 \). First some algebra:

1. \( k_{obs1} = k[B_2]_1^y \) and \( k_{obs2} = k[B_2]_2^y \) (this was from above when the original substitution into the rate law was made)

2. \[
\frac{k_{obs1}}{k_{obs2}} = \left( \frac{[B_2]_1}{[B_2]_2} \right)^y
\]
   (divide one equation by the other, eliminate \( k \), and raise the combined fraction to the \( y \)-power)

3. \[
\ln \left( \frac{k_{obs1}}{k_{obs2}} \right) = y \ln \left( \frac{[B_2]_1}{[B_2]_2} \right)
\]
   (take ln of both sides and move \( y \) in front)

4. \[ y = \frac{\ln \left( \frac{k_{obs1}}{k_{obs2}} \right)}{\ln \left( \frac{[B_2]_1}{[B_2]_2} \right)} \] (solve for \( y \))

Plug in numbers and solve for \( y \):

\[
y = \frac{\ln \left( \frac{0.001}{0.004} \right)}{\ln \left( \frac{0.50}{1.00} \right)} = \frac{\ln(0.25)}{\ln(0.50)} = 2
\]

**Solve for k:**

To determine \( k \) (rather than \( k_{obs} \)) again use: \( k_{obs} = k[B_2]_y \).

1. \( k_{obs1} = k[B_2]_1^y \) (plug in values for \( k_{obs1}, [B_2]_1, \) and \( y \) from the first experiment)
2. \( 0.001 = k(0.50)^2 \) (solve for \( k \))
3. \( k = 0.004 \)

4. Repeat with experiment 2: \( 0.004 = k(1.00)^2 \rightarrow k = 0.004 \)
5. Average the \( k \) values: \( k = (0.004 + 0.004)/2 = 0.004M^{-2}s^{-1} \)

\[
k = 0.004M^{-2}s^{-1} \quad \text{(include units)}
\]

**Rate =** \( k[A]_1[B_2]^2 \) with \( k = 0.004M^{-2}s^{-1} \)