Chemical Reaction Rates II
Solving Kinetics Problems Involving Integrated Rate

Chemical kinetics is the study of the speed or rate of a chemical reaction under various conditions. Collisions must occur in order for chemical reactions to take place. These collisions must be of sufficient energy to make and break bonds. The collisions must also be “effective” which means they not only have sufficient energy during the collision but that the molecules also collide in the proper orientation. The speed of a reaction is expressed in terms of its “rate” — some measurable quantity is changing with time.

\[
\text{Rate} = \frac{\text{Change in concentration of a reactant or a product}}{\text{Change in time}}
\]

Most commonly, we discuss four different types of rate when discussing chemical reactions: relative rate, instantaneous rate, differential rate, and integrated rate. Although these sound complicated, they are actually quite simple. This activity will focus primarily on the last two types, differential rate and integrated rate.

First, we need to discuss factors that affect the rate of a chemical reaction:

1. **Nature of the reactants**—Some reactant molecules react quickly, others react very slowly.

2. **Concentration of reactants**—more molecules in a given volume means more collisions which means more bonds are broken and more bonds are formed.

3. **Temperature**—“heat ‘em up & speed ‘em up”; the faster the molecules move, the more likely they are to collide and the more energetic those collisions will be.
   - An increase in temperature produces more successful collisions because more collisions will meet the required activation energy. There is a general increase in reaction rate with increasing temperature.
   - In fact, a general rule of thumb is that increasing the temperature of a reaction by 10°C doubles the reaction rate.

4. **Catalysts**—accelerate chemical reactions by allowing for more effective collisions, thus lowering the activation energy. The forward and reverse reactions are both accelerated to the same degree. Catalysts are not themselves transformed in the reaction, so they may be used over and over again.

5. **Surface area of reactants**—exposed surfaces affect speed.
   - Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases.
• The greater the surface area exposed, the greater the chance of collisions between particles, hence, the reaction should proceed at a much faster rate. Example: coal dust is very explosive as opposed to a piece of charcoal. Solutions provide the ultimate surface area exposure!

**INTEGRATED RATE**

Differential rate law expresses how the rate depends on concentration. This is the most common and what we have been discussing. Integrated rate law expresses how the concentrations depend on time. If the data you have been given contains “Rate” and “Concentration” data, you use the differential rate law methods. If the data you have been given contains “Concentration” and “Time” data, you use the integrated rate law methods. Why on Earth do we need two methods? It is a result of experimental convenience.

When we wish to know how long a reaction must proceed to reach a predetermined concentration of some reagent, we can construct curves or derive an equation that relates concentration and time. This sounds scary, but is quite simple as long as you appreciate some elegant patterns. First the graphs…

When graphing the concentration of a reactant vs. time, one of the following two shapes is observed:

- Zero order, always a straight line. No further analysis is needed—just read the graph.

- If the graph is a curve, it could be 1st or 2nd order! Further analysis is needed to determine which one. This involves creating two additional graphs in search of a linear relationship.
GRAPHICAL METHODS FOR DISTINGUISHING FIRST AND SECOND ORDER REACTIONS

Why are we in search of a linear relationship? \( y = mx + b \) is the friendly little equation format for a straight line that you already know and love. It allows you to quickly solve for anything you need. You need to know HOW to determine zero, first, and second order relationships from concentration vs. time graphs.

**Question:** How do I get a linear relationship?

**Answer:** Set up your axes so that time is always on the x-axis. Next, sketch your two new graphs so that you can determine whether the reactant is first or second order. Plot the natural log (\( \ln[A] \), NOT log) of the concentration on the y-axis of the first graph and the reciprocal concentration on the y-axis of the second graph. You are in search of linear data! Here comes the elegant part… If you do the set of graphs in this order with the y-axes being “concentration”, “natural log of concentration” and “reciprocal concentration”, the alphabetical order of the y-axis variables leads to 0, 1, 2 orders respectively for that reactant.

You can now easily solve for either time or concentration once you know the order of the reactant. Just remember \( y = mx + b \). Pick up the variables that gave you the straight line and insert them in place of x and y in the equation. “A” is reactant A and \( A_0 \) is the initial concentration of reactant A at time zero [the y-intercept].

\[
\begin{align*}
Y &= mx + b \\
\text{zero order} & \quad [A] = -kt + [A_0] \\
\text{first order} & \quad \ln[A] = -kt + \ln[A_0] \\
\text{second order} & \quad 1/[A] = kt + 1/[A_0]
\end{align*}
\]

It is also useful to remember that \( |\text{slope}| = k \), since the rate constant is NEVER negative. If you are asked to write the rate expression [or rate law] it is simply \( \text{Rate} = k[A] \) if you determined from analyzing the graphs.
PURPOSE
In this activity you will determine the order of a reactant from the method of integrated rate law. You will also use a graphing calculator and concentration-time data to determine the order of a reactant using the graphical methods of differential rate law.

MATERIALS
- calculator
- paper and pencil

PROCEDURE
Solve the problems found on your student answer page. Be sure to show all work paying attention to the proper use of significant digits and units.
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**ANALYSIS**

The following TI-83 or TI-83+ calculator steps may prove useful when applying the graphical methods of the integrated rate law.

To determine the order of a reactant:
- Press `2nd` `[0]` and scroll down to DIAGNOSTICS ON and press `[ENTER]` `[ENTER]` so that your calculator will display the linear correlation coefficient, $r$, for each linear regression you perform.
- Press `MODE` and use your arrow keys to select FLOAT, press `[ENTER]` `[2nd]` `[MODE]` to quit.
- Press `CLEAR` to clear your screen.
- To enter data, press `[STAT]` and `[ENTER]` to select EDIT. Use the summary below to prepare your analysis of the data:

<table>
<thead>
<tr>
<th>L1</th>
<th>time (x variable throughout!)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2</td>
<td>concentration</td>
</tr>
<tr>
<td>L3</td>
<td>ln concentration</td>
</tr>
<tr>
<td>L4</td>
<td>reciprocal concentration</td>
</tr>
</tbody>
</table>

- Perform 3 linear regressions. Begin by pressing `[STAT]` `[4]`, LinReg(ax + b) is now displayed.
- Press `2nd` `[1]` `,` `2nd` `[2]` to select your $x$-values from L1 (time) and your $y$-values from L2. Make note of the $r$ value. You seek the best linear fit for your data. The best fit will have an $r$ value closest to ±1.
- Press `2nd` `[ENTER]` to re-display the LinReg command, press `[4]` `[2nd]` `[3]` to replace L2 with L3, press `[ENTER]` to execute the command and make note of the $r$ value.
- Press `2nd` `[ENTER]` to re-display the LinReg command, press `[4]` `[2nd]` `[4]` to replace L3 with L4, press `[ENTER]` to execute the command and make note of the $r$ value.
- Examine your $r$ values and decide which set of data gives the best linear fit.
- Paste the regression equation into [Y=] by pressing `[2nd]` `[ENTER]` until you return to the LinReg command that yielded the best fit.
- Once the L1, L2 combination is properly displayed, press `[1]` `,` `[VARS]` `[1]` to Y-VARS then `[1]`. If you were successful, you’ll see LinReg(ax + b) L1, L2, Y1 displayed on your screen. Press `[ENTER]` to execute the command and paste the regression equation into Y1.

**More helpful hints:**
Recall that the order of the reaction is 0; 1; 2 respectively for each L1, L2; L1,L3; L1,L4 combination respectively and $|\text{slope}| = k$ and Rate = $k[\text{reactant}]^{\text{order}}$.

Next, since you have created a line, never forget: $y = mx + b$ (TI uses an “a” instead of an “m”).
If L1,L3 was your best “r” then, the reaction is first order and
\[ y = mx + b \] becomes
\[ \ln [\text{conc.}] = -kt + \ln [\text{conc.}_0] \]

*Notice that you must respect the sign of \( k \) when substituting into the \( y = mx + b \) format.

Do the same substitutions into \( y = mx + b \) for the other formats!

To determine the concentration at a given time:
- Set up your STAT PLOT by pressing \( \text{[2nd]} \{Y=\} \). Make sure only one plot is on and that you choose \( \text{[Graph]} \) and select the list combination that generated the regression line you pasted into Y1.
- Press \( \text{[ZOOM]} \{9\} \) to display the graph.
- Press \( \text{[2nd]} \{TRACE\} \{ENTER\} \) to select CALCULATE and VALUE. An X= is displayed in the lower left-hand corner of the screen. Enter the time you were given in the problem and press \( \text{[ENTER]} \). Record the y-value displayed. Recall what you placed on your y-axis. It is most likely not \( L2 \) or the concentration. It is more likely either the natural log value of the concentration or the reciprocal of the concentration. Solve for the actual concentration before recording your answer.
- If you get an ERR:INVALID message, press \( \text{[WINDOW]} \) and re-set your Xmax value. The calculator can only calculate what it displays. Choose a value for Xmax that includes your desired time value.

To determine the time at a given concentration:
- Press \( \text{[Y=]} \) then \( \text{[Graph]} \) to Y2. Recall the command that generated your regression equation in Y1. Write an equation that is either the concentration, ln concentration or reciprocal concentration based on whether your y-value was \( L2 \), \( L3 \), or \( L4 \) respectively.
- Press \( \text{[2nd]} \{TRACE\} \{5\} \) to select CALCULATE and INTERSECT. Press \( \text{[ENTER]} \{ENTER\} \{ENTER\} \). Record the x-value displayed since it is the time value.
- If you get an ERR:INVALID message, press \( \text{[WINDOW]} \) and re-set your Ymax or Ymin values.
1. Data for the decomposition of N₂O₅ in a solution at 55°C are as follows:

<table>
<thead>
<tr>
<th>[N₂O₅] (mol/L)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.08</td>
<td>3.07</td>
</tr>
<tr>
<td>1.67</td>
<td>8.77</td>
</tr>
<tr>
<td>1.36</td>
<td>14.45</td>
</tr>
<tr>
<td>0.72</td>
<td>31.28</td>
</tr>
</tbody>
</table>

Use graphical methods of the integrated rate law to determine the following:

a. What is the order for the reaction?

b. What is the rate constant for the reaction?

c. Write the rate law that is consistent with the data?

d. What is the concentration of N₂O₅ at 2.00 minutes?

e. At what time is the concentration of N₂O₅ equal to 0.55M?
2. Sucrose, \( C_{12}H_{22}O_{11} \), decomposes in dilute acid solution to form the two isomers glucose and fructose that have the chemical formula of \( C_6H_{12}O_6 \). The rate of this reaction has been studied in acid solution, and the data in the table were obtained.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>([C_{12}H_{22}O_{11}] ) (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.316</td>
</tr>
<tr>
<td>25</td>
<td>0.289</td>
</tr>
<tr>
<td>50</td>
<td>0.264</td>
</tr>
<tr>
<td>150</td>
<td>0.183</td>
</tr>
<tr>
<td>200</td>
<td>0.153</td>
</tr>
</tbody>
</table>

Use graphical methods of the integrated rate law to determine the following:

a. What is the order for the reaction?

b. What is the rate constant for the reaction?

c. Write the rate law that is consistent with the data?

d. What is the concentration of \([C_{12}H_{22}O_{11}]\) at 75.0 minutes?

e. At what time is the concentration of \([C_{12}H_{22}O_{11}]\) equal to 0.115M?

3. Ammonia decomposes when heated according to the equation

\[
NH_3(g) \rightarrow NH_2(g) + H(g)
\]

<table>
<thead>
<tr>
<th>([NH_3]) (mol/L)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.00 x 10^{-7}</td>
<td>0</td>
</tr>
<tr>
<td>7.20 x 10^{-7}</td>
<td>15</td>
</tr>
<tr>
<td>6.55 x 10^{-7}</td>
<td>30</td>
</tr>
<tr>
<td>5.54 x 10^{-7}</td>
<td>60</td>
</tr>
</tbody>
</table>

The data in the table for this reaction were collected at 2500K.
Use graphical methods of the integrated rate law to determine the following:

a. What is the order for the reaction?

b. What is the rate constant for the reaction?

c. Write the rate law that is consistent with the data?

d. What is the concentration of NH₃ at 90.0 hours?

e. At what time is the concentration of NH₃ equal to 7.00 x 10⁻⁷ M?

4. The reaction 2HOF(g) → 2HF(g) + O₂(g) occurs at 45°C.

The following data was collected:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[HOF] (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.850</td>
</tr>
<tr>
<td>5</td>
<td>0.754</td>
</tr>
<tr>
<td>10</td>
<td>0.666</td>
</tr>
<tr>
<td>15</td>
<td>0.587</td>
</tr>
<tr>
<td>20</td>
<td>0.526</td>
</tr>
</tbody>
</table>

a. What is the order for the reaction?

b. What is the rate constant for the reaction?

c. Write the rate law that is consistent with the data?
d. What is the concentration of [HOF] at 60.0 minutes?

e. At what time is the concentration of [HOF] equal to 0.250M?

5. Data for the decomposition of dinitrogen oxide into its elements at 900°C is as follows:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[N\textsubscript{2}O] (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.0835</td>
</tr>
<tr>
<td>30</td>
<td>0.0680</td>
</tr>
<tr>
<td>80</td>
<td>0.0350</td>
</tr>
<tr>
<td>120</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

a. What is the order for the reaction?

b. What is the rate constant for the reaction?

c. Write the rate law that is consistent with the data?

d. What is the concentration of [N\textsubscript{2}O] at 240.0 minutes?

e. At what time is the concentration of [N\textsubscript{2}O] equal to 0.0500M?