Ozone in the Stratosphere: Rates of Reaction
Using Graphs and Kinetics Equations

When we think about chemical reactions, scientists often want to know how fast that reaction will proceed. Some reactions proceed quite quickly, such as the ignition of fuel in your car engine, while some are quite slow, such as a rusting pipe. In this project, you are going to explore some of the equations and graphs that chemists use to analyze data in order to understand the kinetics (speed) of a reaction. For this analysis, we will focus on an important environmental compound known as ozone and how it decomposes.

Ozone is a key chemical in the atmosphere made of three oxygen atoms bonded together. At the Earth's surface, ozone can cause respiratory problems, such as aggravating asthma and emphysema (https://www3.epa.gov/region1/airquality/oz_prob.html). However, when found in the stratosphere, the layer of the atmosphere where aircraft fly, ozone is a "good" chemical because it absorbs radiation from the sun, which prevents that sunlight from reaching the surface and causing sunburns and skin damage. There are a class of compounds known as greenhouse gases that include carbon dioxide, methane, and many fluorinated and chlorinated compounds that interact with ozone in the stratosphere. Ozone will break down and the concentration of ozone in the stratosphere decreases, which leads to an ozone hole in the atmosphere over the Antarctic at certain times of the year. In fact, it isn't really a hole, but an area where the concentration is lower than average, and even small changes will allow more UV radiation to reach the surface. Therefore, understanding how ozone decomposes is very important. Scientists study reactions like this both in the lab and in real-world settings in order to find out how quickly they proceed and what conditions affect the speed of the reaction. In this project, you will look at how a scientist uses reaction data to learn about reaction rates.

Part 1: Concentration vs Time Graph

To understand the rate of a reaction, chemists measure the change in concentration (amount) as a function of time. Start with a new spreadsheet and put your name in cell A1 and a title for the project in cell A2. The data you will work with is concentration versus time. Enter the data in Table 1 into your spreadsheet including the column titles, starting in cell A4 (**Time (hours)**) and B4 (**Ozone conc. (M)**). (In spreadsheet notation, E represents 10^ so 1.00E-5 is 1.00×10^{-5}). Note: In this project, bold terms are formulas or text to be typed into the spreadsheet.

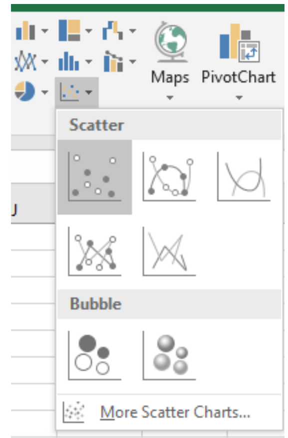
Table 1: Data for ozone decomposition

Time (hours)	Ozone concentration (M)
0	1.00E-05
2.00E+03	4.98E-06
7.60E+03	2.07E-06
1.23E+04	1.39E-06
1.70E+04	1.12E-06
2.50E+04	7.78E-07

data from:
https://batch.libretexts.org/print/url=https://chem.libretexts.org/Courses/CSU_San_Bernardino/CHEM_2100%3A_General_Chemistry_I_(Mink)/12%3A_Kinetics/12.E%3A_Kinetics_(Exercises).pdf

Creating a Scatter Plot Using Excel

- One of the first things you might want to know as a scientist is how the concentration of ozone changes with time. You want to plot x,y pairs of data, so you will use an x-y scatter plot of points. Under the insert tab, select an x-y scatter plot (icon looks like a graph with random spots).
- Under “chart tools”, click on “select data”, and then “add” data. In the “Series X values” box, delete anything in the box and then highlight the time data (just numbers), and in the y-box, delete anything in that box and then highlight the concentration data (just numbers). Click ok twice, and a plot should appear.



1. Describe the shape of this data set. Is it linear or curved? Does the concentration increase or decrease over time? Does this plot represent a reactant that is used up during the reaction or a product that is made during the reaction?

<u>Part 2: Rate of Reaction from a Graph</u>

The rate of a reaction is defined as the change in concentration over a specific period of time. Some reactions go very quickly, while others take much longer. We can determine different rates of reaction based on the slope of this graph. Remember, the slope is the change in y over the change in x. For this graph, that would be the change in concentration over the change in time, which is how scientists define the rate of reaction. Scientists use the greek symbol delta to represent “change” in some variable, so you may see rates written as Δconc./Δt (t for time).

2. Does the rate (slope) stay constant over time, based on your graph, or does the rate increase or decrease as the reaction proceeds? Explain.

3. Calculate the initial rate, which is defined as the rate at the beginning of the reaction. In this case, let’s define the initial rate as the change in concentration from 0-2000 hours, which corresponds to seasonal changes over a few months. Show your work.

4. We can also determine an average rate over a small period of time. Calculate the average rate by creating a column of data that contains $\Delta y/\Delta x$. Your formula in cell C6 would be **=(B6-B5)/(A6-A5)**. Compare the rate of change from your calculated values at the beginning of the reaction to the end of the reaction. (Note: Be careful with negative exponents. Remember, a larger value as a negative exponent means it is a smaller number. For example, 10^{-2}=0.01, and 10^{-3} = 0.001.)

   Rate at the beginning of the reaction: ____________________

   Rate at the end of the reaction: ____________________

   Does the rate increase, decrease or stay the same? Do these values match what you observed from the graph in question 2?

Part 3: Rate Law Analysis

Although this graphical analysis that you just investigated is useful to study a particular reaction, it is difficult to compare different reactions using this method. Determining rates of reaction are time-consuming and depends on the temperature and initial amounts of all reactants. Instead, scientists use a rate law that relates all of those factors to the rate of the reaction through a rate constant, known as k. There are several forms of rate laws, shown in Table 2, depending on how a reactant (labelled as A) is related to the rate of reaction. The order of reaction is the power of A. If a reaction does not depend on the amount of the reactant, it is said to be zeroth-order. Whether you have a lot or just a little of A, the reaction proceeds at a constant rate. If the rate of reaction is proportional to the concentration of A, it is said to be first-order, and it would have a different k value. Some reactions are proportional to the square of the concentration of A with another k value. Although the rate law is useful, it is really a manipulated form, known as the integrated rate law, that is most useful. Chemists use a mathematical process known as integration to generate these integrated rate law equations, and they are also rearranged so that they are in y=mx+b form, which is the equation of a straight line. It is easier to analyze a straight line rather than a curve to determine which equation fits the experimental data best. Chemists use both visual inspection of a graph and linear trendlines to fit the data to determine which rate law best fits a data set. A characteristic of a good linear fit is an R^2 value that is close to one. Using these relationships, chemists can determine the rate law for an experimental data set. You will use the ozone data to determine the order of reaction for the decomposition of ozone in the atmosphere in the next part of this exercise.

Table 2: Rate law and integrated rate law equations used to determine the order with respect to reactant A (ozone). k is the rate constant.

	Rate law	Integrated rate law (y=mx+b form)
Zeroth-order	Rate = k $(A)^0$ = k	A = - kt + $A_{initial}$
First-order	Rate = k $(A)^1$	ln (A) = -kt + ln $(A)_{initial}$
Second-order	Rate = k $(reactant)^2$	1/A = kt +1/$A_{initial}$

If a reaction is zeroth-order, a graph of ozone concentration vs time would be linear. The slope (m) would be equal to -k and the y-intercept (b) would be the initial amount of ozone. You have already made this graph in Part 1. You will be making other graphs to test the other orders, so add a title to this graph by clicking in the chart title block and labeling it **ZEROTH-ORDER GRAPH** (if there isn't a block for a title, click on the graph and a plus sign will appear, where you can add a chart title or axes labels).

If a reaction is first-order, a graph of ln (ozone) vs. time would be linear. To create this graph, add a title of **'ln(ozone)** (the apostrophe indicates text instead of an equation) in the next column in your data table. Enter the formula **=ln(B5)** in the cell below the title and copy that formula to the bottom of the data set by either using copy/paste or by clicking on the small box in the lower right corner and dragging it down the column to the last data point. Using the directions from Part 1, create a scatter plot, where x is time (just the numbers) and y is ln (ozone) (just the numbers). Add a title by clicking in the chart title block and labeling it **FIRST-ORDER GRAPH**.

If a reaction is second-order, a graph of 1/ozone vs. time would be linear. To create this graph, in the next column of your data table, add a title called **'1/ozone**. Then, enter a formula in the cell below the title that is **=1/B5** and copy that formula down to the bottom of the data set as you did before. See the directions in Part 1 to create a scatter plot and select the data for this new graph, where x is time (just the numbers) and y is 1/ozone (just the numbers To check to see if it is linear, under the design tab, add a chart element and add a linear trendline, which will take all the data and add a best-fit line. Choose the linear option and add the equation and R^2 value, by checking the boxes at the bottom of the trendline menu. Add a title by clicking in the chart title block and type **SECOND-ORDER GRAPH**.

5. Which of the three graphs appears to be most linear? Explain your answer in 1-3 sentences.

To check to see if a graph is linear, click on the graph, and under the design tab click on add a chart element and then click on more options, which will take all the data and add a best-fit line. In the trendline menu, choose the linear option, and add the equation and R^2 value, by checking the boxes at the bottom of the menu. Repeat this for all three graphs.

6. Which integrated rate law best fits the data? How do you know (hint: reread the introduction to this part of the project)? Explain your answer in 1-3 sentences.

7. Does the rate law you determined from your visual inspection (question 5) and your trendline analysis (question 6) match? If not, discuss your answers with your instructor.

8. What is the rate constant (k) for your rate law? (Note: rate constants are always positive).

9. If you start with the initial amount (A_o) of 1.00×10^{-5} M (same amount of ozone as this data set), at what time will you have 75% left (A)? Hint: you will need to use the k from question 8.

10. There are 720 hours in a month. Based on your answer to question 9, approximately how many months would it take to decrease the concentration by 25%? Round to the closest whole number of months.

11. Would you think a decrease of 25% of ozone in the stratosphere could be a problem? Explain your answer in 1-3 sentences.

12. This rate law is defined for a specific temperature and composition of other gases in the stratosphere. If more greenhouse gases are emitted and reach the stratosphere, the rate of decomposition would increase. Would the amount of ozone left at the end of the first month be more or less than under the conditions for the current data set? Explain in 1-3 sentences.