Exploring Rate Laws

The file "Exploring Rate Laws" in your group's Dropbox folder contains data for the hypothetical reaction R → P under zero-order, first-order, and second-order kinetic conditions. The rate constant, k, is the same for all curves; thus, any differences between the curves is due to the effect of concentration on rate. Working together, complete the following tasks:

1. Decide which curve corresponds to which reaction order. Be sure you clearly state the reasons for your decisions. After you reach a conclusion, you can add a legend to the graph by (*i*) clicking on the graph to select it; (*ii*) selecting Options:Graph Options from the main menu; and (*iii*) checking Legend on the Graph Options tab. Are your assignments correct? If not, then discuss the flaws in your reasoning.

   The rates of these reactions at any point in time is equal to the slope of a tangent line to the data. For a zero-order process, the rate is constant, which corresponds to a straight line. With equal values of k, the reaction showing the greatest initial change in [R] will be the one with the higher order; thus, the symbol ♦ corresponds to the second-order data and the symbol ▲ corresponds to the first-order data.

2. Explore how the rates of these three reaction orders vary with time (use the tangent tool to do this). Discuss any trends you see in each case and between the cases.

   The rate for the zero-order reaction remains constant for all times. The rates for the first-order and second-order reactions decrease over time. Note that the initial rate of the second-order reaction is greater than that for the first-order reaction, but that after a brief time the rate of the first-order reaction becomes greater than that for the second-order reaction. This is because rate is a function of both the rate constant, k, and the [R], which for the second-order reaction approaches zero very quickly.

3. Look at the data on Page 2. Can you unambiguously deduce the reaction's order and, therefore, its rate law? Clearly explain your reasoning. Look at the data on Page 3 and repeat this analysis. Briefly summarize your conclusions about the usefulness of a plot of [R] vs. *t* as a means for determining a reaction's order.

   The data on Page 2 clearly is zero-order because a plot of [R] vs. time is a straight line. It is tempting to predict that the data on Page 3 is second-order because the [R] decreases so quickly. However, one can change the appearance of this plot by rescaling the x-axis. Both first-order and second-order kinetic decay show a curved decrease in [R] as a function of time and it is impossible to determine the reaction's order using just a qualitative observation of this plot. As shown below, however, we can analyze the data in other ways.

4. Another way to analyze kinetic data is to look at the reaction's half-life, which is the time it takes for the concentration of R to decrease by 50%. Estimate the first four half-lives for each curve on Page 1 (these are the Δt values when the concentration changes from 100 to 50, from 50 to 25, from 25 to 12.5, and from 12.5 to 6.25. Use the Examine tool to make your measurements, estimating concentrations and time as necessary. You may need to rescale the x-axis, which contains data up to a time of 1001, in order to make some measurements. Use the following table to organize your results:

		Δt for…		
half-life number	change in [R]	zero-order	first-order	second-order
1	100→50	500	6.9	0.11
2	50→25	250	6.9	0.20
3	25→12.5	125	7.0	0.41
4	12.5→6.25	63	6.8	0.79

What patterns do you observe in these half-lives? Clearly explain how you might use this information to determine if a reaction is zero-order, first-order, or second-order.

Although your values for Δt may be slightly different, your trends should be the same. Each successive half-life for a zero-order reaction is ½ of the previous half-life. In the case of a first-order reaction, the half-lives are constant. For a second-order reaction, each successive half-live is twice the preceding half-life. Examining half-lives provides another approach to determining a reaction's order.

5. Return to page 3 and determine the reaction order using half lives. Does your result agree with your earlier prediction? If not, then explain why you were fooled when you originally examined the data.
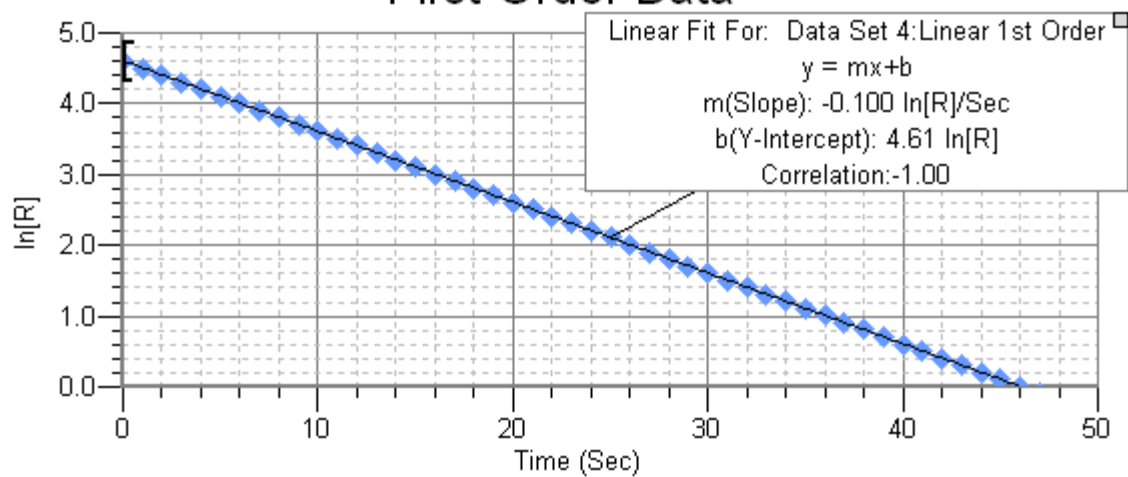
The first four half-lives for this data are 1.0, 1.1, 1.0 and 1.1 seconds. A constant half-life indicates that the reaction is first-order. Remember that the qualitative appearance of data can be deceiving!

6. Another way to analyze kinetic data in which the concentration of a reactant is monitored over time, is to use what is called an integrated form of the rate law. Pick up a copy of the handout outlining the integration of the differential rate law and then go to Page 4 for the last assignment.

For the first-order data, plot ln[R] vs. time to see the linearized form of the rate law (see graph on the next page). Fitting a straight line to the data gives the rate constant as 0.100 and ln[R] as 4.61, which gives [R] as 100.5.

For the second-order data, plot 1/[R] vs. time to see the linearized form of the rate law (see graph on the next page). Fitting a straight line to the data gives the rate constant as 0.100 and 1/[R] as 0.01, which gives [R] as 100.

First-Order Data

Linear Fit For: Data Set 4:Linear 1st Order
y = mx+b
m(Slope): -0.100 ln[R]/Sec
b(Y-Intercept): 4.61 ln[R]
Correlation:-1.00

Second-Order Data

Linear Fit For: Data Set 4:Linear 2nd Order
y = mx+b
m(Slope): 0.100
b(Y-Intercept): 0.0100
Correlation:1.00