Order	0th	1st	2nd
rate law	$r = k$	$r = k[A]$	$r = k[A]^2$
units for k **ex.:**	$\dfrac{conc}{time}$ $\dfrac{M}{sec}$ $M \cdot s^{-1}$	$\dfrac{1}{time}$ $\dfrac{1}{min}$ min^{-1}	$\dfrac{1}{conc \cdot time}$ $\dfrac{1}{M \cdot sec}$ $M^{-1} \cdot s^{-1}$
integrated rate expression	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$ or $\ln\dfrac{[A]_t}{[A]_0} = -kt$ or $[A]_t = [A]_0 e^{-kt}$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$
plot as y	$[A]$	$\ln [A]$	$\dfrac{1}{[A]}$
plot as x	t	t	t
slope	$-k$ (neg. slope)	$-k$ (neg. slope)	k (pos. slope)
y-intercept	$[A]_0$	$\ln[A]_0$	$\dfrac{1}{[A]_0}$
$t_{1/2}$	$\dfrac{[A]_0}{2k}$	$\dfrac{0.693}{k}$	$\dfrac{1}{k[A]_0}$

BAR Experiment Lab Report Tips

1. When graphing you must use a computer to do the graphs. Excel can be used to make the tables, do the calculations and make the graphs.   It will do regression analysis or "trend lines" (least squares fitting) you can use this to plot your lines. Excel can also do smooth nonlinear curves. There are other programs which will work but Excel is preferred since you have free access. You should include the trend line produced by Excel, both on the graph and in your report. You should also report the correlation coefficient (usually signified as R or R^2) which gives you some idea how good the fit is. The closer R is to ± 1 ($R^2 = 1$) the better your fit is to a trend line, i.e. the closer your points are to falling on trend line (R=$\pm$l means all your points should fall exactly on the chosen trend line). Some programs report an X^2 or variance of the fit, s_t^2 which tell you how good the fit is. Excel report R^2.

    A graph should occupy essentially the whole page (margins of 0 inches), one graph per page. Generally, they should be in Landscape mode (unless told otherwise). Spread out your axes so your data occupies as much of the graph area and page as possible. It does not have to start at the origin, (0,0). You want to minimize the empty space.

2. For the Beer's Law Graph, you will have 4 experimentally determined data points and the (0,0) point (5 data points in all). Fit the points to a best-fit straight line (linear) while forcing the line through the origin, the (0,0) point.. Excel allows this in the same window in which you set the type of fit and tell Excel to include the equation for the line and R^2 on the graph. You can tell if it's been forced through the origin since the intercept in the equation for the line from Excel should be zero (y = m*x).

3. Use Excel for the calculations for the zero, first and second-order tables and graphs. You have free access to it. It doesn't work well on an iPad or the on-line version. The computers in 170 CE have Excel on them as do most of those around campus. If you use Excel (any spreadsheet program) you can program the columns to do the calculations for you (there's a minimum of 170 calculations) and then use the spreadsheet (with the appropriate titles, column headings and units) in your report. In your spreadsheet make time (elapsed time) and absorbance columns and then program the spreadsheet do the appropriate calculations for you. You should have a separate spreadsheet (worksheet) for each solution, just like the report form. Don't have the tables span more than one page (i.e. don't break it across pages unless you have to because it's too big to fit on a single page). I've listed below what should go in the columns of your spreadsheet. You also need to show an example of each of these calculations for one of the solutions in your report (see the rubric).

    Column 1:   elapsed time (do not use "wall-clock time)

    Column 2:   Absorbance (A)

    Column 3: $[Dye]_t = A/m$

          where,   A = absorbance
               m = slope of the Beer's Law Graph.

    Column 5: $\ln [Dye]_t$
          Just take the natural log of each cell in Column 3.

    Column 6: $l/[Dye]_t$
          Just take the reciprocal of Column 3.

4. Excel can do regression fits (linear, exponential, polynomial, etc.).   In Excel highlight the columns you want to plot and then click "Insert" (this may be different depending on your version of Excel or spreadsheet, in older versions you click on the chart wizard icon). A chart dialogue box pops up. Choose a "scatter" plot with no lines (points only).   Once you have the graph, right click on a data point and choose "trendline". Follow the directions in the dialogue box. You can do linear or curved trend lines. In the options box choose to have it print the equation for the line and the R^2 value.   What ever you do, don't tell it to connect the points so you get a jagged line. It's not hard to figure it out and there are tutorials on-line or get help from a TA or myself. It's a good thing to learn so you can use it in the future.

    The reaction is NOT zero order with respect to the Dye. You do NOT have to make this graph for the report. There is a question in the report which asks what this graph should look like so you might consider doing this graph just to see what it looks like.

    For the first-order and second-order graphs use linear fits for both even though technically only one of the graphs should have straight (linear) lines and the other should be curved. Print the equations and R^2 values and put them near the name for each solution in the legend (pull everything inside the graph so it has room to spread out). One of these graphs should have parallel straight lines. The other will have lines which diverge and the points don't fit the linear trend line well (they'll look parabolic in relation to the straight lines). The correct order is determined from the graph with the most parallel straight lines. You need to discuss why they should be parallel.

Chapter 14 - Kinetics
Additional Practice Problems

1) A hypothetical reaction A ----> products is second order in A. The half-life of a reaction that was initially 1.66 M in A is 310 min. What is the value of the rate constant, k?

2) A reaction shows the same half-life regardless of the starting concentration of the reactant. Is it a zero-order, first-order or second-order reaction?

3) In three different experiments the following results were obtained for the reaction A ----> products: $[A]_0 = 1.00$ M, $t_{1/2} = 50$ min; $[A]_0 = 2.00$ M, $t_{1/2} = 25$ min; $[A]_0 = 0.50$ M, $t_{1/2} = 100$ min. Write the rate equation for this reaction and indicate the value of k.

4) Ammonia decomposes on the surface of a hot tungsten wire. Following are the half-lives that were obtained at 1100 °C for different initial concentrations of NH_3: $[NH_3]_0 = 0.0031$ M, $t_{1/2} = 7.6$ min; 0.0015 M, 3.7 min; 0.00068 M, 1.7 min. For this decomposition reaction, what is (a) the order of the reaction; (b) the rate constant k?

5) The gas-phase reaction of chlorine with carbon monoxide to form phosgene, Cl_2 (g) + CO (g) ----> $COCl_2$ (g), obeys the following rate law:

$$\text{Rate} = \frac{\Delta[COCl_2]}{\Delta t} = k\,[Cl_2]^{3/2}\,[CO] \qquad \text{(exp. rate law)}$$

A mechanism involving the following series of steps is consistent with the rate law:

$$Cl_2 \rightleftharpoons 2Cl$$
$$Cl + CO \rightleftharpoons COCl$$
$$COCl + Cl_2 \rightleftharpoons COCl_2 + Cl$$
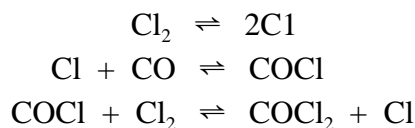
Assuming that this mechanism is correct, which of the steps above is the slow, or rate-determining, step? Explain.

Hint: try making each step the slowest step (rate-det. step) and see what rate law you get and if it agrees with the experimental rate law given.

The following is a problem I want you to think about. I mentioned this in class and told you to think about it. I will NOT be giving the answer and neither will the TAs. You need to work on it yourself and come see me or a TA to see if you did it correctly. We will tell you yes or no. If you don't have it correct, we will give you hints but will not tell you how to do it. That is up to you to figure out. If you get it correct, don't simply give someone else the answer. You can help them but only tell them if they are or aren't on the right track.

What you have is the following:

1) $r = k [A]^n$ (a general rate law)

2) Experimental data of rate and [A]. For instance:

rate	[A]
1.0	1.0
3.0	2.0
4.5	3.0

Something like that (not actual data).

3) You can mathematically manipulate the equation in (1) so you get a linear equation. Then you can plot something that will graphically give you k and n in a fairly easy way (somehow related to the slope and intercept, not necessarily in that order).

You do NOT have to do any integration. You won't be using an integrated rate law. You don't have [A] and time data. You have rate and [A] data.

This is NOT an initial rate method problem. That is NOT how I want you to think about this.

Think about what you might be able to do mathematically to the equation in (1) to get a linear equation. Then think about what you need to plot so that you can get k and n.