

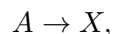
Problem Set 1: Rate Laws

In this exercise you will study how the concentration of chemicals change in a system where one or more reactions are occurring. You will explore the relationship between the rate law of chemical reactions and the variation in concentrations of the chemicals as a function of time. You will first of all analyze ‘experimental’ data and determine whether the rate law for the reaction is first order or second order. This is the content of the first notebook (part A). You will then analytically obtain the concentration of the various chemicals as a function of time from the rate law. This is the content of the second notebook (part B). Finally, you will see how simple numerical methods can be used to obtain the concentrations from the rate law (part C).

Part A: Plotting data and determining the order of a rate law

A1: First order rate laws

Start by considering a reaction



with a first order rate law

$$-\frac{d[A]}{dt} = k[A],$$

i.e. the concentration of A appears to the first power. In order to compare this with experimental measurements of the concentration of the reactant A as a function of time, it is necessary to ‘integrate’ the rate law, i.e. solve the differential equation and obtain the concentration of the reactant as a function of time, $[A](t)$. In this simple case it is easy to show that the solution is (verify this by differentiating $[A]$)

$$[A](t) = A_0 e^{-kt}.$$

Starting with numerical values $A_0 = 1$ and $k = 1$, make a plot of $[A](t)$ and determine (approximately) the half-life of the reaction (recall, the half-life is the time it takes the concentration to fall by a factor of one half). [Using Mathematica, you can get a numerical reading of points on the graph by right-clicking on the graph and selecting ‘Get Coordinates’.] The algebraic expression for the half-life is

$$t_h = \ln(2)/k$$

a) Compare the value obtained from this expression with the approximate value you read from the graph. Change the value of the rate constant, k , to 10 and re-plot the concentration as a function of time. Is the change in half-life predicted from the algebraic expression consistent with the values you obtained from the graphs?

b) If the logarithm of the concentration is plotted as a function of time instead

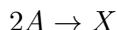
of the concentration itself, a linear plot is obtained. This can be seen by taking the logarithm on both sides of the expression for $[A](t)$

$$\ln[A](t) = -k t + \ln[A_0]$$

Plot the log of your graph in part (a). What is the slope on this graph (i.e. how does it relate to the value of k and A_0 ? What is the intercept with the y -axis? Does the slope and intercept that you read from the log plot agree with the numerical values you are using for k and A_0 ?

A2: Second order rate laws

a) Consider the simple reaction



If the mechanism of the reaction involves the collision of two A molecules, then the rate law is second order

$$-\frac{d[A]}{dt} = k[A]^2.$$

The solution to this differential equation, subject to the initial condition $[A](0) = A_0$, is

$$\frac{1}{[A](t)} - \frac{1}{[A](0)} = kt,$$

or, rearranging this equation to give $[A](t)$ explicitly

$$[A](t) = \frac{[A](0)}{kt[A](0) + 1}.$$

a) Set the value of A_0 to 1.0 and the value of k to 0.5 and plot the concentration of A as a function of time. Choose the range of time in the graph in such a way that a drop in A to approximately 0.1 is seen on the graph.

b) It is always possible to define a half-life, but for a second order rate law the half-life depends on the initial concentration in addition to the rate constant, and is therefore not as useful a concept as for first order rate laws. Determine the first and second half-life from your plot (i.e. in the first case start with the initial concentration from (a) and in the second case start with the concentration $A_0/2$).

c) Plot $1/[A](t)$ vs. t . You should get a straight line, as you can see from the expression for $[A](t)$ above. How does the slope of the straight line relate to the constants (rate constant and initial concentration)? How does the intercept with the y -axis relate to the constants? Are the values you obtain by reading from the plot consistent with the numerical values you specified?

d) Plot the logarithm of $[A](t)$ as a function of time. In the case of a first order rate law this gave a straight line. Is that true in this case, i.e. for a second order rate law? (Make sure your plot spans a long enough time interval).

A3: Determining the rate law order from measured data

Often, the task is to determine the order of a rate law from a measurement of the concentration of a reactant as a function of time. An example data set, where the concentration has been measured every second starting at $t = 0$ and up to 15 seconds can be found in the file *rate1.dat*.

a) Plot the concentration as a function of time. [In Mathematica, you can use the ListPlot command.]

The question now is whether the data corresponds to a first order or a second order rate law. (Other orders of the rate law are possible but will not be considered here). Given the results from above, the rate law must be first order if a plot of the logarithm of the concentration as a function of time is linear, but it must be second order if a plot of the inverse of the concentration as a function of time is linear.

b) Plot the logarithm of the concentration in the data set as a function of time. Then, plot the inverse of the concentration as a function of time. Is the rate law for this data first order or second order?

c) Repeat this procedure for the data in *rate2.dat* to determine whether the data corresponds to a first order or second order rate law.

d) In addition to learning whether the rate law is first or second order, one usually would also like to extract an optimal estimate of the rate constant from the data. Working with the transformed data that gives a straight line plot (either logarithm or inverse), use a best fit line to determine the intercept and slope of the data.

e) What is the rate constant for the reaction corresponding to the data in the file *rate2.dat*?

f) To test the quality of the fit, compare the best fit line with the data by plotting the two on the same graph.