# Rates of Chemical Reactions

In this lab session you will use Matlab to study how the concentration of chemicals changes in a system where one or more reactions are occuring. 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 use Matlab to analyse '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 see how Matlab can in certain cases be used to 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.

A. Plotting data and determining the order of a rate law

A1. First order rate laws:

We begin with the simplest chemical reaction where there is only one reactant and the back reaction is ignored

$$A \rightarrow products$$
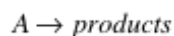
and we assume the rate law is first order

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

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 $[A]$).

$$[A](t) = [A]_0 \, e^{-kt}$$

It is easy to plot the concentration as a function of time for given values of the rate constant, k, and initial concentration, $[A]_0$. A good way to approach this is to first define a function that gives the concentration at any time

```
------------------------------
function y=Aconc(t,a0,k)
y=a0*exp(-k*t);
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```

The time evolution of the concentration can then be plotted using the plot command. For example, pick the initial concentration to be 1.0 and the rate constant to be 0.5.

```
EDU>> t=[0:0.01:10];
EDU>> plot(t,Aconc(t,1,0.5))
```

EDU>> title('First order rxn')

The interval for the independent variable, t, is chosen here to be from t=0 to t=10.

Q1: Reading from the graph, determine approximately what the half-life of the reaction is (recall, the half-life is the time it takes the concentration to fall by a factor of one half). The algebraic expression for the half-life is

$$t_{1/2} = \ln(2)\,/\,k$$

Compare the value obtained from this expression with the approximate value you read from the graph. How do they compare? Change the value of the rate constant, k, to 10 and replot the concentration as a function of time. You will need to change the time interval shown on the graph in order to see better how the concentration is falling with time. After doing that, determine the half-life from the graph. Is the change in half-life predicted from the algebraic expression consistent with the values you obtained from the graphs? (Note: you can evaluate the natural logarithm in using the log() function in Matlab).

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)

$$\ln [A](t) = -\,k\,t + \ln [A]_0$$

A logarithmic plot can be made easily using the log function inside the plot function

EDU>> plot(t,log(Aconc(t,1,0.5)))

Q2:   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 logarithmic plot agree with the numerical values you are using for k and $[A]_0$?

A2. Second order rate laws:

Consider again the simple reaction

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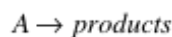
If the mechanism of the reaction involves the collision of two A molecules, then the rate law is second order

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

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

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

Q3:   Define a function a2[t] that gives the concentration of A in a second order reaction. Set the value of a0 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.

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.

Q4: Determine the first and second half-life from your plot (i.e. in the first case start with the initial

concentration $[A]_0$ and in the second case start with the concentration $[A]_0/2$.

A3. Determining the order from measured data

Often, the task is to determine the order of a rate law from a laboratory measurement of the concentration of a reactant as a function of time. Below is an example data set, where the concentration has been measured every second starting at t=0 and up to 15 seconds.

----

t=[0,1,2,3,4,5,6,7,8,9,10,11,12,13,14,15];

conc=[0.4,0.30303,0.243902,0.204082,0.175439,0.153846,0.136986,0.123457,0.11236,0.103093,0.0952381,0.0884956,0.0826446,0.0775194,0.0729927,0.0689655]

To plot the data:

EDU>> plot(t,conc)

It is also possible to leave the points unconnected and circular.

EDU>> plot(t,conc,'ok')

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. I

Another example of data is contained in the file 'ratedata.dat' which is available from the web page. To make a copy of the file onto your working directory, press the 'select' button and and then click on the link for 'ratedata.txt'. The data is organized in such a way that each line contains the time and concentration obtained in a measurement. Matlab can read in the data from the file directly using the load command. Load returns a 8x2 matrix, so it is necessary to extract the time and concentration vectors.

----
load ratedata.txt;
t=ratedata(:,1);
conc=ratedata(:,2);

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 logaritm or inverse), the optimal straight line can be fitted in a least squares sense using this linear fit function.

```
function linfit(x,y)
% Take care that x and y are line vectors

x=x';
y=y';
A=[ones(size(x)) x];
c=inv(A'*A)*A'*y;
a=c(1)
b=c(2)
% a and b are the constants from y=a*x+b
% that give the best fit

% remove the following command if using Octave
display(['y=' num2str(a) '+' num2str(b) 'x'])
```

Note that you should be fitting either the logarithmic data or the inverse data depending on which transformation gave you a straight line when plotted as a function of time. The output from the linfit function is a function that gives the straight line fit, as well as the slope of the line. The rate constant can be obtained from the slope.

Q9:   What is the rate constant for the reaction corresponding to the data in the file ratedata.txt?

Q10: To test the quality of the fit, compare the best fit line with the data by plotting the two on the same graph.