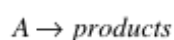


B. Analytical Integration of Rate Laws

In simple cases, it is possible to obtain analytical solutions to the rate laws, i.e. to solve the differential equation and obtain an analytical expression for the concentration as a function of time. This is relatively easy to do for first and second order rate laws, but in more complex cases it is convenient to know how to use programs such as Matlab to obtain the solution. We will first illustrate here how this is done in the simplest cases, the first and second order rate laws, but then move on to third order rate law, reversible first order rate laws and sequential first order reactions.

B1. First order reaction with out back reaction:

As a first exercise, consider again the reaction involving just one reactant



and having a first order rate law

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

This kind of equation is called a differential equation, it contains a term involving the function itself and a term involving the derivative of the function. The equation can also be written as

$$a'[t] = -k \cdot a[t]$$

where a prime means differentiation with respect to the argument of the function. This is a first order differential equation because the highest derivative of the unknown function appearing in the equation is the first derivative. To specify a unique solution to a first order differential equation it is necessary to give one boundary or initial value condition. Here, we specify that the initial concentration is a_0 at time $t=0$. The `dsolve` command in Matlab can be used to solve the problem in the following way:

```
EDU>> aoft=dsolve('Da=-k*a','a(0)=a0')
```

Unfortunately Octave doesn't yet offer this function so this lab session will have to be completed in Matlab.

In order to plot the result we need to input values for k , a_0 and the t vector. After having inputted values for k and a_0 , use the `subs` command to apply these values to `aoft`.

```
EDU>> aoft=subs(aoft)
```

Now to create the `aoft` vector we create a t vector and repeat the above command. The reason for having to do this in 2 steps is that the `subs` command cannot substitute values with different dimensions at the same time. Therefore a_0 and k are substituted at the same time while t has to be substituted separately. Note that t has to be substituted second.

Q1: Set the value of k to 0.2 and a_0 to 5.0 and plot the concentration of the chemical A as a function of time.

B2. Reversible first order reaction:

So far, back reactions have been neglected completely. The solutions have, therefore, strictly only been valid for situations where little or no product is present initially and only for short enough time intervals, before an appreciable amount of the products has built up. We will now extend the analysis to include back reactions.

Consider the reaction



with a 'forward' rate constant k_f and the reverse



with a 'backward' rate constant k_b . From mass balance we have

$$[C](t) + [A](t) = [C](0) + [A](0)$$

which can be used to eliminate $[C](t)$ from the rate law. The solution can then be found using dsolve

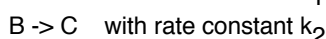
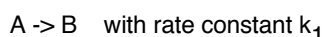
```
EDU>> clear all
```

```
EDU>> aoft=dsolve('Da=-kf*a+kb*(c0+a0-a)', 'a(0)=a0')
```

Q2: Choose numerical values for the two rate constants and the two initial concentrations and plot the concentration of A and C as a function of time. Make sure the plot extends over long enough time to be able to estimate the long time, equilibrium values of the concentrations. Calculate a value for the equilibrium constant from the values you read of the graph. How does that compare with the equilibrium constant you get directly from the ratio of the two rate constants?

B3. Sequential reactions without backreactions:

Most interesting reactions are a sequence of elementary steps. A simple example of that is



Again, ignore the back reactions. Assuming each of these elementary steps have first order rate laws, the overall rate law for the set of reactions is

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] \\ \frac{d[B]}{dt} &= k_1[A] - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B]\end{aligned}$$

This is a set of three coupled first order differential equations for the three functions $[A](t)$, $[B](t)$ and $[C](t)$. dsolve can find the analytical solution to the set of equations if the initial concentrations are given numerical values. The initial conditions are chosen to represent an experiment where no B or C is present initially.

```
EDU>> answer=dsolve('Da=-k1*a','Db=k1*a-k2*b','Dc=k2*b','a(0)=1','b(0)=0','c(0)=0')
```

Functions giving the concentration of each one of the chemicals can now be extracted from the solution returned by dsolve

```
EDU>> a=answer.a
```

```
EDU>> b=answer.b
```

```
EDU>> c=answer.c
```

In order to plot the concentrations, a numerical value of the two rate constants has to be specified. Here we assume the second step is ten times slower than the first step (note that the two rate constants are not allowed to be equal in the solution obtained above, otherwise a zero divide occurs)

```
-----  
%rxnplot.m
```

```

clear k1 k2 t

k1=1.0;
k2=0.1;
a=subs(a);
b=subs(b);
c=subs(c);
t=[0:0.1:30];
a=subs(a);
b=subs(b);
c=subs(c);
plot(t,a,t,b,t,c)
-----

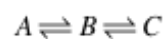
```

Q3: Which color corresponds to A, which corresponds to B and which corresponds to C?

Q4: Repeat the calculation and make another plot using $k_2=10$. If an experimental measurement shows that a large concentration of the intermediate, B, builds up at intermediate time, what does that imply about the ratio of the two rate constants?

B4. Sequential reactions with backreactions:

When back reactions are included in the sequential reaction mechanism discussed in B3,



the rate law becomes (assuming each elementary step has a first order rate law)

$$\begin{aligned} \frac{d[A]}{dt} &= -k_1[A] - k_{-1}[B] \\ \frac{d[B]}{dt} &= k_1[A] - k_{-1}[B] - k_2[B] + k_{-2}[C] \\ \frac{d[C]}{dt} &= k_2[B] - k_{-2}[C] \end{aligned}$$

The terms involving k_{-1} and k_{-2} need to be added to the set of differential equations from B3 to give

```

%rxnplot2.m

```

```

clear k1 k2 t

```

```

answer2=dsolve('Da=-k1*a+km1*b','Db=k1*a-km1*b-k2*b+km2*c','Dc=k2*b-
km2*c','a(0)=1','b(0)=0','c(0)=0')

```

%The analytical solution given by dsolve is a lot longer now that back reactions have been added, but it is as easy as before to plot the concentration of the three chemicals

```

a=answer2.a
b=answer2.b
c=answer2.c

```

%Choosing the numerical values of the four rate constants:

```

k1=1.0;
k2=0.1;
km1=0.05;

```

```

km2=0.1;

a=subs(a);
b=subs(b);
c=subs(c);
t=[0:0.1:30];
a=subs(a);
b=subs(b);
c=subs(c);
plot(t,a,t,b,t,c)

```

```
EDU>> rxnplot2
```

Q5: How does this result compare with the case when the back reactions were neglected in section B5 (but the same values used for k_1 and k_2)? How do the equilibrium concentrations compare? Roughly for how long time is the approximate solution obtained by neglecting back reactions valid?

Q6: How does the amount of B formed at intermediate time depend on the k_{-1} rate constant? Try setting the value to 2.0.

B5. The steady state approximation:

The above calculations have given exact solutions to the rate law. One can also apply the steady state approximation to this reaction. The steady state approximation is often used to simplify rate laws to make analytical calculation easier or even possible. One then assumes the intermediate, B, reaches a steady concentration, i.e.

$$\frac{d[B]}{dt} = 0$$

When applied to the rate law $d[B]/dt = k_1[A] - k_{-1}[B] - k_2[B] + k_{-2}[C]$, one can use this to isolate [B] and then eliminate [B] from the rate laws for $d[A]/dt$ and $d[C]/dt$. Carry out the derivation (on a piece of paper) of expressions for $d[A]/dt$ and $d[C]/dt$ where [B] has been eliminated. The resulting equations can, again, be solved easily by using `dsolve`

```
EDU>> dsolve('DaSS=(-k1*k2*aSS+km1*km2*cSS)/(km1+k2)', 'cSS=(k2*k1*aSS-km1*km2*cSS)/
(km1+k2)', 'aSS(0)=1.0', 'cSS(0)=0')
```

After assigning values to the rate constants and defining functions that give the concentration of A and C, the results can be plotted and compared to the exact results.

Q7: Carry out calculations using the steady state approximation and compare with the exact results. It is most convenient to create one m file that carries out both calculations. Use various sets of values of the rate constants and plot the exact and steady state results on the same graph (display the exact results with solid lines first, then display dashed lines for the steady state approximation. You get dashed lines by adding `x,y,'--'` in the plot function). Save your results in plots with different names for each set of parameters (using `>> print -depsc filename.eps`). Remember to specify clearly which set of parameters was used in each case. When can the steady state approximation be expected to work best? Can you find a set of rate constants and time interval where it is not so good?