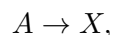


Part B: Analytical Integration of Rate Laws

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 Mathematica to obtain the solution. In class, it was illustrated how this is done in the simplest cases, the first and second order rate laws. Now we can move on to third order rate law, reversible first order rate laws and sequential first order reactions.

B1: First order reactions

Go over what we did in class, and generate an analytic solution for the concentration of A given that the reaction

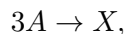


is first order

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

B2: Higher order reactions with one reactant

Considering again the simple reaction



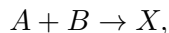
using an analytic solver, find the expression for the concentration as a function of time for a third order rate

$$-\frac{d[A]}{dt} = k[A]^3,$$

and plot the concentration as a function of time.

B3: Second order reactions with two reactants

For a bimolecular elementary reaction involving two reactants A and B



the rate law is

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

This can also be written in terms of the rate of decrease of chemical B with time

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

These two expressions are entirely equivalent. The two functions $[A](t)$ and $[B](t)$ are related by mass balance. Since the stoichiometric coefficients here are both unity, the mass balance equation is

$$[B](t) = [B](0) - [A](0) + [A](t).$$

This can be used to eliminate $[B]$ from the rate law, giving

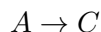
$$-\frac{d[A](t)}{dt} = k [A](t) \{ [B](0) - [A](0) + [A](t) \}.$$

- a) Use an analytic solver [DSolve in Mathematica] to find $[A]$ as a function of time.
- b) Choose numerical values for k , A_0 and B_0 . Assume the initial concentration of B is $2A_0$. Then, plot the concentration of A and B as a function of time on the same graph. Note, that A_0 cannot equal B_0 in the solution obtained by DSolve. Why is that?

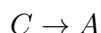
B4: Reversible first order reactions

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

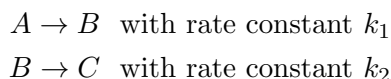
$$[C](t) + [A](t) = [C](0) + [A](0)$$

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

- a) 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?

B5: Sequential reactions without back-reactions

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 $[C](t)$. Solve for the concentration of A , B , and C , taking initial conditions of $A_0 = 1.0$, $B_0 = C_0 = 0$.

- substituting values of $k_1 = 1.0$ and $k_2 = 0.1$, plot the concentrations of each species as a function of time.
- 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?

B6: Sequential reactions with back-reactions

When back reactions are included in the sequential reaction mechanism discussed in **B5**



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

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

- Add the terms involving k_{-1} and k_{-2} to your solution of the previous question, and solve for the concentrations of each species. Use values of $k_1 = 1.0$, $k_2 = 0.1$, $k_{-1} = 0.05$, and $k_{-2} = 0.1$.
- 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?

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

B7: 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.

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

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 of expressions for $d[A]/dt$ and $d[C]/dt$ where $[B]$ has been eliminated.

Carry out calculations using the steady state approximation and compare with the exact results. Use various sets of values of the rate constants and plot the exact and steady state results on the same graph. Clearly indicate which curve is the approximate steady state solution. Save your results in plots with different names for each set of parameters. 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?