Assignment 1 modelling of reaction kinetics

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1 Introduction

Any chemical process, where some reactant molecules are transformed into product molecules has an associated mechanism, which is how these molecules are transformed into each other. In the application of any molecule or material (for example in catalysts) it is important to know and understand the mechanism by which it works. Especially when designing new molecules or materials that can operate fast, more efficiently or in more favorable reaction conditions is it necessary to know how it works. The main difficulty in studying reaction mechanisms is that in a single elementary reaction step, one (or multiple) molecules go to a so-called transition state, which is short lived (on the order of the period of a molecular vibration) and therefore has a very low concentration at any given point in time, which is a challenge to measure spectroscopically[1]. Because of this difficulty we can never be fully sure about a mechanism, we can only falsify mechanism and show that a mechanism is consistent with spectroscopy data.

In the python assignment we will use python to calculate how the concentrations in a reaction mixture evolve given a certain mechanism and initial concentrations. We could use these changes in concentrations to compare with experiments in order to see if the mechanism (which you can never be fully sure of) is consistent with the data.

2 Mathematics

Mathematically speaking, a reaction mechanism is nothing more than a set of first-order coupled differential equations. In other words, a set of equations that contain first order derivatives and are coupled in the sense that depend on each other in a way that we cannot solve each equation separately, we have to solve them all together. Here is an

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[1]an exception is unimolecular photochemical reactions, since we can then have proper timing control of when molecules are undergoing a reaction by apllying an ultrashort light pulse

example of a reaction mechanism common:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \tag{1}$$

$$C \overset{k3}{\longrightarrow} D \tag{2}$$

For all the four species (A, B, C and D) in the mechanism, we can write a first order differential equation, all four are:

$$\frac{d[A]}{dt} = -k1[A][B] + k2[C] \tag{3}$$

$$\frac{d[B]}{dt} = -k1[A][B] + k2[C] \tag{4}$$

$$\frac{d[C]}{dt} = +k1[A][B] - k2[C] - k3[C] \tag{5}$$

$$\frac{d[D]}{dt} = +k3[C] \tag{6}$$

These equations are called coupled, because in order to solve the first equation for [A] as a function of time, we need to know [B](t) and [C](t) beforehand. But we can only get those by solving the second and third equations first, but for that we need to know [A](t) already! So these problems are - most of the time, impossible to solve analytically. There are only a handful of cases that can be solved analytically, without making use of approximations (i.e. that all equations can be solved to obtain concentrations as functions of time). Two important examples are the unimolecular and bimolecular elementary reactions, the unimolecular elementary reaction is:

$$A \overset{k}{\rightarrow} B \tag{7}$$

Which mathematically means:

$$\frac{d[A]}{dt} = -k[A] \tag{8}$$

$$\frac{d[B]}{dt} = +k[A] \tag{9}$$

These equation can be solved quite straighforwardly, since the top equations (8) is not coupled: it only contains $[A]$ and $d[A]/dt$. We can solve using seperation of variables:

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

$$\frac{1}{[A]}\frac{d[A]}{dt} = -k$$

Then if we integrate with respect to time t', from $t' = 0$ (start of measurement/experiment) to $t' = t$, then we get:

$$\int_{t'=0}^{t'=t} \frac{1}{[A]} \frac{d[A]}{dt} dt' = \int_{t'=0}^{t'=t} -k dt'$$

Since the time integration and derivation with respect to time are inverse operation, they cancel out and we are left with:

$$\int_{A[t'=0]}^{A[t'=t]} \frac{1}{[A]} dA' = \int_{t'=0}^{t'=t} -k dt'$$

$$[\ln [A]]_{[A](t'=0)}^{[A](t'=t)} = -kt$$

$$\ln [A](t) - \ln A(0) = -kt$$

$$\ln [A](t) = -kt + \ln [A](0)$$

$$[A](t) = \exp(-kt + \ln [A](0))$$

$$[A](t) = [A](0) \exp^{-kt}$$

Which is just exponential decay.

2.1 Bimolecular

Another important analytical example is the bimolecular elementary reaction:

$$A + A \xrightarrow{k} B \tag{10}$$

The corresponding differential equation is then:

$$\frac{d[A]}{dt} = -k[A]^2 \tag{11}$$

Note that the units of this second-order rate constant k_2 is different than for the first-order reaction. This equation can be solved in a similar way as equation 10 above using separation of variables and subsequent time integration:

$$\frac{1}{[A]^2} \frac{d[A]}{dt} = -k$$

$$\int_{t=0}^{t=t'} \frac{1}{[A]^2} \frac{d[A]}{dt} dt' = \int_{t=0}^{t=t'} -k dt'$$

$$\int_{A(t=0)}^{A(t=t')} \frac{1}{[A]^2} dA' = \int_{t=0}^{t=t'} -k dt'$$

$$\left[-\frac{1}{[A]} \right]_{A(t=0)}^{A(t=t')} = -k(t - 0)$$

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

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Rearranging this last equations the following expression is obtained:

$$[A](t) = \frac{A[0]}{1 - ktA[0]} \tag{12}$$

2.2 Numerical Methods

However full reaction mechanism are almost never so easy as the examples above. So in general we have to resort to numerical methods for calculating our concentrations in time by solving our coupled system of first-order differential equations. This is where python comes in. Since we only have 'full' derivatives (not parital derivatives such as $\partial/\partial x$), our differential equations are so-called ordinary different equations (ODE's), which are also called initial value problems (IVP's). Numerically these can be solved using numerical time integration, which can be done using multiple methods. Here we will not go into the exact details of all methods, as they are all ready implemented in python, we only have to use them and not code them ourselves (luckily). But I will give an outline of how - in general - these methods work.

First we have to define our model as in equations (3)-(6) above, together with all rate constants. We also have to know our initial concentrations (i.e. the concentrations we do the experiment at). Then we use discrete time, instead of solving our equations with a continuous variable t (as above) we use time steps i.e. t = 0 s, 1 s, 2 s, 3 s ... . For t=0, we can calculate all the derivatives numerically, as we know all the concentrations now. So we know all the derivatives on the left hand side of our model. Now to first order, for a small enough time step:

$$[A](t = 1) \approx [A](t = 0) + \frac{d[A]}{dt}(t = 0) \tag{13}$$

We can do this for all concentrations [A], [B], [C] and so forth. Then we know all concentrations at t=1, so we can calculate the derivatives at t=1 now, we can use those derivatives to calculate concentrations at t=2 now, and so forth untill we have gone through all the relevant time steps.

In reality a more complicated equation is often used then equation 13, as it turns out to be more efficient to take fewer time steps and a more complicated method. A common method is to go to fourth order in the integration, this is the so called 'Runge Kutta 4'[1] (rk4) method. This is the default method for the "solve_ivp" function we are going to use in the python exercise. Although many more method exist to solve these ODE's, they just vary in the expression used to update the values at the next time step (equation 13).

References

[1] John C Butcher. On the implementation of implicit runge-kutta methods. *BIT Numerical Mathematics*, 16(3):237–240, 1976.