TMV035 Analysis and Linear Algebra B, 2003

REACTION KINETICS

In this lecture we present an example from "reaction kinetics". The purpose is to describe how to set up the kinetic equations, to solve them with MATLAB, and to draw a conclusion about the reaction from the computation. Perhaps this will be useful in your own `chemistry project`.

1. Oxidation of NO

Inspired by: P. Atkins and L. Jones, *Chemical Principles. The Quest for Insight.* Freeman, New York, second edition, 2002, pp. 720–721.

We consider the oxidation of NO to NO_2. The following rate of formation of NO_2 has been observed experimentally:

$$\frac{d}{dt}[\mathrm{NO_2}] = k[\mathrm{O_2}]\,[\mathrm{NO}]^2. \qquad (\texttt{mol/(L\,s)}) \tag{1}$$

This corresponds to the formula

$$2\mathrm{NO} + \mathrm{O_2} \xrightarrow{k} 2\mathrm{NO_2} \tag{2}$$

Here $[\mathrm{NO_2}]$, measured in `mol/L`, is the concentration of NO_2. The rate constant k is measured in $\texttt{L}^2\texttt{/(mol}^2\texttt{s)}$. This is a *third order reaction*, because the rate is proportional to the product of three concentrations.

In order to explain this empirical formula one has proposed the following two-step reaction mechanism.

Step 1. NO is decomposed into an intermediate product N_2O_2 in a fast reaction:

$$2\mathrm{NO} \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} \mathrm{N_2O_2} \tag{3}$$

Step 2. The intermediate product reacts with O_2 in a slow reaction:

$$\mathrm{N_2O_2} + \mathrm{O_2} \underset{k_{22}}{\overset{k_{21}}{\rightleftharpoons}} 2\mathrm{NO_2} \tag{4}$$

We now write down the reaction rates for the four elementary reactions (`mol/(L s)`):

$$\begin{aligned} r_{11} &= k_{11}[\mathrm{NO}]^2 &&= k_{11}u_1^2,\\ r_{12} &= k_{12}[\mathrm{N_2O_2}] &&= k_{12}u_3,\\ r_{21} &= k_{21}[\mathrm{N_2O_2}]\,[\mathrm{O_2}] &&= k_{21}u_3u_2,\\ r_{22} &= k_{22}[\mathrm{NO_2}]^2 &&= k_{22}u_4^2. \end{aligned} \tag{5}$$

Here we introduced the variables

$$u_1 = [\mathrm{NO}],\ u_2 = [\mathrm{O_2}],\ u_3 = [\mathrm{N_2O_2}],\ u_4 = [\mathrm{NO_2}]. \qquad (\texttt{mol/L}) \tag{6}$$

What are the units of the rate constants $k_{11}, k_{12}, k_{21}, k_{22}$?

Finally, we write down the rates of formation for the four substances:

$$\begin{aligned} \dot u_1 &= -2r_{11} + 2r_{12},\\ \dot u_2 &= -r_{21} + r_{22},\\ \dot u_3 &= r_{11} - r_{12} - r_{21} + r_{22},\\ \dot u_4 &= 2r_{21} - 2r_{22}. \end{aligned} \tag{7}$$

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This is a system of four coupled nonlinear ordinary differential equations. The numbers $\pm 1, \pm 2$ that occur in front of the rates are called *stoichiometric numbers*. For example, the stoichiometric numbers of NO_2 in reactions 21 and 22 are 2 and -2, respectively.

The equations are implemented and solved in the MATLAB programs `no2.m`, `no2a.m`, `no2test.m`. The file `no2test.m` is a *script file*, which starts the computations and plots the solutions.

We use the data $k_{11} = 10,\ k_{12} = 10$ (fast reaction), $k_{21} = 0.01,\ k_{22} = 0$ (slow reaction), and initial values $u_{10} = 0.5$, $u_{20} = 1$, $u_{30} = 0$, $u_{40} = 0$. Download the programs and compute!

In order to test if the proposed two-step mechanism explains the empirical third order rate law (1), which is $\dot{u}_4 = k u_2 u_1^2$, we also compute the quotient

$$\frac{\dot{u}_4}{u_2 u_1^2}\,. \tag{8}$$

If (1) holds, then this quotient should be constant $= k$. A calculation in Atkins and Jones shows that $k = 2k_{21}k_{11}/k_{12}$. The quotient (8) is plotted with black dots, and we see that it quickly becomes constant $= 2k_{21}k_{11}/k_{12}$.

This shows that the two-step mechanism is consistent with the empirical rate law (1).

The calculation in Atkins and Jones is based on the so-called *steady-state approximation*, which amounts to setting the net rate of formation of the intermediate product N_2O_2 to zero, i.e., $\dot{u}_3 = 0$. The justification for this is that the reactions in step 1 are so fast that they keep the concentration of the intermediate constant. They also assume that there is no reverse reaction in step 2, i.e., $r_{22} = 0$. This gives

$$\dot{u}_3 = r_{11} - r_{12} - r_{21} + r_{22} = k_{11}u_1^2 - k_{12}u_3 - k_{21}u_3u_2 = 0,$$

so that we can eliminate u_3:

$$u_3 = \frac{k_{11}u_1^2}{k_{12} + k_{21}u_2}.$$

Then the rate of formation of NO_2 becomes

$$\dot{u}_4 = 2r_{21} - 2r_{22} = 2k_{21}u_3u_2 = \frac{2k_{21}k_{11}u_1^2u_2}{k_{12} + k_{21}u_2} \approx \frac{2k_{21}k_{11}}{k_{12}}u_1^2u_2,$$

where in the last step we assumed that k_{12} is much larger than $k_{21}u_2$. With these approximations we thus find $k = 2k_{21}k_{11}/k_{12}$.

You can download the MATLAB programs from

http://www.math.chalmers.se/cm/education/courses/0304/ala-b/matlab/facit/