# STUDENT VERSION
# KINETICS – RATE OF CHEMICAL REACTION

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**Abstract:**   Adapted from 1-11-Kinetics, SIMIODE modeling scenario [5]. We help students see the connection between college level chemistry course work and their differential equations coursework. We do this through modeling kinetics, or rates of chemical reaction. We study zeroth, first, and second order reactions and offer many opportunities to model these chemical reactions with data, some of which comes from traditional introductory chemistry textbooks. We ask students to verify their model through parameter estimation.

## SCENARIO DESCRIPTION

Chemists often use differential equations to model chemical reactions. The rate of reaction is determined by the concentrations of the reactants. This is sometimes referred to as *The Law of Mass Action*. For example, it is known that, "The rate of decomposition is dependent on the temperature and concentration of the peroxide, as well as the pH and the presence of impurities and stabilizers."[4] Thus we consider reactions to be dependent upon the concentration of a single reactant, say, $A$, where $[A]$ typically represents the concentration (perhaps in units of moles per liter) of the reactant $A$ present at time $t$. The usual rates of reaction studied in the elementary texts are of the form,

$$\frac{d[A]}{dt} = -k[A]^m, \qquad \text{with} \qquad [A](0) = [A_0].  \tag{1}$$

with $k$ the *rate constant* (presumed to be positive) and $m$ the *order* of the reaction, quite often an integer. Here $[A](0) = [A_0]$ is the initial amount of concentration of reactant. Usually the study at this level is restricted to $m = 0, 1, 2$, and these are called *zeroth*, *first*, and *second* order reactions, respectively.

In most classes and textbooks, you have probably just been *given* information like rate constants and the order of the reaction. Here, we're going to be given some data, and then see how one would actually go about determining the rate constants and order of reactions.

## ORDER OF REACTION - DEFINITIONS

For this project, you will be provided more guidance than you might normally, for we are attempting to make a bridge between the notions of chemical kinetics found in the introductory chemistry course and the applications of differential equations. In practice chemists might have some idea of the order of a reaction, as defined below, from understanding of basic chemistry, but sometimes it is determining a mathematical model of a rate equation which helps them understand the nature of the reaction. We proceed with the most common and elementary chemical reaction kinetics models.

### Zeroth Order Reaction

Zeroth order reactions are most often encountered when a substance such as a metal surface or an enzyme is required for the reaction to occur. For example, the decomposition reaction of nitrous oxide,

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g),$$
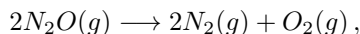
occurs on a hot platinum surface. When the platinum surface is completely covered with $N_2O$ molecules, an increase in the concentration of $N_2O$ has no effect on the rate, since only those $N_2O$ molecules on the surface can react. Under these conditions the rate is a constant because it is controlled by what happens on the platinum surface rather than by the total concentration of $N_2O$, ... [6, p. 657].

For a generic reaction we shall use $y(t) = [A] = [A(t)]$, where $[A]$ is the concentration of reactant $A$ (in moles or moles/liter) with time, $t$, in sec. Here we see the rate equation,or differential equation, is

$$\frac{dy}{dt} = -ky^0 = -k.$$

The solution to this is rather easy (the equation is separable) through direct integration, $y(t) = y(0) - kt$. Such reactions are self-evident from the data, for if we plot $y(t)$ vs. $t$ we would see a linear function starting at $y = y(0)$ with a negative slope, $-k$. We can easily enter the data in MATLAB and then have it give us the slope of "best-fit" line through this data (and, therefore, we would know the value of the rate constant $k$). Since zeroth order reactions are quite rare, we move on to first order reactions.

### First Order Reaction

Let us look at first order reactions in general:

$$\frac{dy}{dt} = -ky^1 = -k\,y \qquad \text{with} \qquad y(0) = y_0.$$

Using the separation of variables technique we obtain

$$\frac{1}{y}\frac{dy}{dt} = -k,$$

from which we can see the integrated form of our model

$$\ln(y) = -k\,t + c \quad \text{where} \quad c = \ln(y(0))\,.$$

This gives us

$$\ln(y) = -k\,t + \ln(y(0))\,. \tag{2}$$

Now we can actually solve this differential equation for $y = y(t)$–and we do–but the chemist really is interested in determining the nature (order) of the reaction as well as the parameter $k$, called the *rate of the reaction*, and often stops at this point. Chemists refer to (2) as the *integrated form* of the rate law. They quite often use *this* form of the equation to do their parameter estimation and determination of the order of the reaction. However, in mathematics we might wish to push further to a solution that reads "$y(t)$ is." Thus, after taking exponentiating both sides, we can produce a complete solution of the differential equation,

$$y = y(t) = y(0)e^{-k\,t}\,. \tag{3}$$

In the study of chemical reactions one of the simplest reactions is that of a decomposition of a substance, say hydrogen peroxide $(H_2\,O_2)$. There is the phenomena of going to the medicine chest to find the hydrogen peroxide (and iodine!) to flush and clean a cut, only to find that what is in the bottle does not produce a white froth when applied to the cut as the medicine is supposed to do while it rids the cut of germs. The medicine is old and has lost its powers! This is an example of the decomposition of $H_2\,O_2$ into water and oxygen $(2H_2O_2 \longrightarrow 2H_2O + O_2)$ and we use the basic Law of Mass Action to conjecture a rate (differential) equation for $H_2O_2$. This means for $[H_2O_2]$ moles/L of hydrogen peroxide:

$$\frac{d\,[H_2O_2]}{dt} = -k \cdot [H_2O_2]^m\,,$$

for some number $m$. We seek two things: (1) the value of the reaction constant $k$, and (2) to determine if this reaction is first order, i.e. if $m = 1$.

In Supporting Documents, you will find the file `H2O2_kinetics.m` that contains the vectors `time` and `data` containing the times and concentrations that appear in Table 1.

1)  a) Create a vector called `log_of_data` that contains the natural log of the data in the vector `data`. If you don't know the MATLAB command for natural log, google it!

   b) From (2) we can see that a first order reaction will produce a linear relationship between $\ln(y)$ and $t$. Confirm that this is a first order reaction by plotting $\ln[H_2O_2]$ vs $t$.

   c) Now we'll use the command `polyfit` in MATLAB to find the best-fit line. Use this information to determine the reaction constant $k$.

   d) Use MATLAB's `fminsearch` command to find the model parameters $y_0$ and $k$ that minimize the sum of squared errors. Plot the best-fit model on the same axes as the data.

| Time $t$ (sec) | $[H_2O_2]$ (mol/L) |
|:---:|:---:|
| 0 | 1.00 |
| 120 | 0.91 |
| 300 | 0.78 |
| 600 | 0.59 |
| 1200 | 0.37 |
| 1800 | 0.22 |
| 2400 | 0.13 |
| 3000 | 0.08 |
| 3600 | 0.05 |

**Table 1.**   Collected data [6, p. 682] on the reaction $2H_2O_2(g) \longrightarrow 2H_2O + O_2(g)$.

**Second Order Reaction**

Now let us look at second order reactions in general:

$$\frac{dy}{dt} = -ky^2 \qquad \text{with} \qquad y(0) = y_0\,.$$

Using the separation of variables technique we obtain

$$\frac{1}{y^2}\frac{dy}{dt} = -k\,,$$

from which we can integrate to see

$$\frac{1}{y} = k\,t + c \quad \text{where} \quad c = \frac{1}{y(0)}\,.$$

This gives us

$$\frac{1}{y} = k\,t + \frac{1}{y(0)}\,. \tag{4}$$

Now we can actually solve this differential equation for $y = y(t)$ and we do, but again the chemist really is interested in determining the nature (order) of the reaction and the parameter $k$ and will often stop at this point. A function for a solution to the rate or differential equation can be found by inverting both sides in (4),

$$y = y(t) = \frac{1}{k\,t + \frac{1}{y(0)}} = \frac{y(0)}{y(0)k\,t + 1}\,. \tag{5}$$

2) Revisit the decomposition of hydrogen peroxide in Table 1 and show it is *not* a second order reaction. Offer as complete a defense as you can - data fitting, plots, verbal argument, etc.

We summarize things so far in Table 2.

| Order of reaction | Differential Equation | Integrated Form | solution Form |
|:---:|:---:|:---:|:---:|
| 0 | $y'(t) = -ky(t)^0 = -ky(t)$ | $y(t) = y(0) - kt$ | $y(t) = y(0) - kt$ |
| 1 | $y'(t) = -ky(t)^1 = -ky(t)$ | $\ln(y(t)) = -kt + c$ | $y(t) = y(0)e^{-kt}$ |
| 2 | $y'(t) = -ky(t)^2 = -ky(t)^2$ | $\dfrac{1}{y(t)} = kt + \dfrac{1}{y(0)}$ | $y(t) = \dfrac{y(0)}{y(0)kt + 1}$ |

**Table 2.**  Summary of $m = 0, 1, 2$ order kinetics differential equations with differential equation model, the integrated form of the solution through which chemists can obtain possibly a linear plot to confirm the order of the reaction, and a complete solution for a fully developed model.

## EXAMPLES OF DIFFERENT REACTION ORDERS

### Decomposition of $C_4H_6$

Consider the following data (Table 3) for the reaction of $C_4H_6$, butadiene, to form its dimer, a chemical structure formed from two similar sub-units.

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g) \tag{6}$$

| Time $t$ in s | $[C_4H_6]$ mol/L |
|:---:|:---:|
| 0 | 0.01000 |
| 1000 | 0.00625 |
| 1800 | 0.00476 |
| 2800 | 0.00370 |
| 3600 | 0.00313 |
| 4400 | 0.00270 |
| 5200 | 0.00241 |
| 6200 | 0.00208 |

**Table 3.**  Data [6, p. 654] for the reaction of $C_4H_6$, butadiene, to form its dimer.

3) In Supporting Documents you will find the file C4H6_kinetics.m, which contains the data in Table 3.

   a) Plot the data.

   b) From the plot make a conjecture as to the order ($m = 0, 1, 2$) of the reaction.

   c) Conduct a complete analysis, determining the order and the parameters. Plot the data and the model, being sure to defend your model (and explain what the order is and what the order is not vis-á-vis $m = 0, 1, 2$ orders).

**Decomposition of $N_2O_5$**

Consider the following data (Table 4) for the reaction describing the decomposition of $N_2O_5$, dinitrogen pentoxide.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2 \tag{7}$$

| Time $t$ in s | $[N_2O_5](t)/M$ |
|---:|---|
| 0 | 0.310 |
| 600 | 0.254 |
| 1200 | 0.208 |
| 1800 | 0.172 |
| 2400 | 0.141 |
| 3000 | 0.116 |
| 3600 | 0.0964 |
| 4200 | 0.0812 |
| 4800 | 0.0669 |
| 6000 | 0.0464 |

**Table 4.** Data [1] for the decomposition of $N_2O_5$ is given.

4) In Supporting Documents you will find the file N2O5_kinetics.m, which contains the data in the Table 4.

   a) Plot the data.

   b) From the plot make a conjecture as to the order ($m = 0, 1, 2$) of the reaction.

   c) Conduct a complete analysis, determining the order and the parameters. Plot the data and the model, being sure to defend your model (and explain what the order is and what the order is not vis-á-vis $m = 0, 1, 2$ orders).

**SECOND ORDER REACTIONS OF THE TYPE $A + B \longrightarrow AB$**

From [2, p 121] we are advised, "In general, whenever one shows that a given chemical reaction is of the second order, one may assume the reaction to be bimolecular."

Thus far we have considered $m^{\text{th}}$ order reactions of the form (1). However, a more general definition of order describes situations like

$$A + B \longrightarrow AB. \tag{8}$$

We say a reaction is a general *second order* reaction if the rate of the reaction is proportional to the product of the concentrations of the two reacting substances; here this is $A$ and $B$.

Now, if we denote $C_A(t)$ and $C_B(t)$ as the concentrations of $A$ and $B$, say in moles per liter then by the Law of Mass Action (which simply says the rate of the reaction is proportional to the product of the reactants available for the reaction) (8) yields the differential equation model in (9) and (10),

$$C_A'(t) = -kC_A \cdot C_B, \quad C_A(0) = A_0, \tag{9}$$

$$C_B'(t) = -kC_A \cdot C_B, \quad C_B(0) = B_0. \tag{10}$$

$C_A(0) = A_0$ and $C_B(0) = B_0$ are the number of moles per liter of $A$ and $B$ at the start of the reaction.

It turns out that it's often easier to start thinking about this as keeping track of the quantity of reactant that has reacted, rather than the quantity of reactant remaining. This line of thinking can help us get this system down to a single differential equation. Note that if one mole of reactant $A$ has reacted, then exactly one mole of $B$ has reacted (because of the coefficients in the chemical reaction equation (8)). So it's safe to define $y(t)$ to be the the number of moles per liter of $A$ or $B$ that have reacted in time $t$.

Let's rewrite the differential equation (9) so that it's entirely in terms of $y$. First write an equation for $C_A(t)$ in terms of $y(t)$ :

$$C_A(t) = \underline{\hspace{3cm}}$$

Now take the derivative of this equation:

$$C_A'(t) = \underline{\hspace{3cm}}$$

We also need an equation for $C_B(t)$ in terms of $y(t)$ :

$$C_B(t) = \underline{\hspace{3cm}}$$

Then $A_0 - y$ and $B_0 - y$ identify the concentrations of $A$ and $B$ remaining at time $t$. Now the differential equation (rate of reaction equation), (9), actually can be rewritten in terms of $y$ as (11),

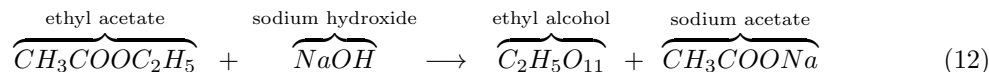$$y'(t) = \underline{\hspace{3cm}}, y(0) = 0. \tag{11}$$

Here $k > 0$, as the traditional way to offer rate constants as positive numbers.

We have two cases to study: Case I when the initial concentrations of $A$ and $B$ are the same, i.e. $A_0 = B_0$ and Case II when the initial concentrations of $A$ and $B$ are not the same, i.e. $A_0 \neq B_0$.

5)  a) Find the analytic solution to (11) for Case I, using $A_0 = B_0 = 0.5$ with $y(0) = 0$ and $k = .0073$. Plot the solution over the time interval $t \in [0, 600]$ s. What is the long term limit of $y(t)$? Explain why you are not surprised at this number.

  b) Part (a) gives the amount of reactant that has reacted. How can we use this to find out how much product $AB$ there is over time?

**Ethyl acetate and sodium hydroxide**

Consider the reaction of ethyl acetate with sodium hydroxide,

$$\overbrace{CH_3COOC_2H_5}^{\text{ethyl acetate}} \; + \; \overbrace{NaOH}^{\text{sodium hydroxide}} \; \longrightarrow \; \overbrace{C_2H_5O_{11}}^{\text{ethyl alcohol}} \; + \; \overbrace{CH_3COONa}^{\text{sodium acetate}} \tag{12}$$

For ease in notation let $A = A(t)$ be the concentration of $CH_3COOC_2H_5$ in moles/liter at time $t$ in seconds and let $B = B(t)$ be the concentration of $NaOH$ in moles/liter at time $t$ in seconds. Notationally let us write $AB$ as the concentration of the product $C_2H_5O_{11}$ in moles/liter and denote $CH_3COONa$ as a by product of the reaction.

Reicher [3] offers experimental data in Table 5 where $t$ is time in seconds and the entries in the second row are the concentration of the product $AB$ in moles/liter at time $t$.

| $t$ | 0 | 393 | 699 | 1010 | 1265 |
|-----|-----|--------|--------|--------|--------|
| $y(t)$ | 0.0 | 0.0772 | 0.1171 | 0.1525 | 0.1759 |

**Table 5.**   Data collected by Reicher [3] shows the time ($t$) in seconds and amount of ethyl alcohol produced in moles per liter ($y(t)$) at time $t$.

In [3], we find that $A_0 = 0.5638$ moles/liter and $B_0 = 0.3114$ moles/liter. So we need the solution to Equation (11) such that $A_0 \neq B_0$. The differential equation is separable, but requires a partial fraction decomposition followed by pages of tedious algebraic manipulation to get to an explicit solution. I trust that you are capable of doing this, so I'll spare you the painful exercise. The explicit analytic solution to the IVP is given by

$$y(t) = \frac{A_0 B_0 \left( e^{kA_0 t} - e^{kB_0 t} \right)}{A_0 e^{kA_0 t} - B_0 e^{kB_0 t}}. \tag{13}$$

6) In Supporting Documents you will find the file `ethyl_alcohol_kinetics.m`, which contains the data in Table 5.

   a) Find the sum of square errors (14) for the difference between the model predictions (13) at time $t_i$ where $i = 1, 2, \ldots 5$ goes through the five observation data point we have in Table 5 and the data on the concentration of product $AB$ offered in the second row of Table 5, i.e, $AB_i$, for $i = 1, 2, \ldots 5$:

   $$SSE(k) = \sum_{i=1}^{5} \left[ y(t_i) - AB_i \right]^2 . \tag{14}$$

   Use $k = 0.005$ as an initial guess for the reaction constant $k$.

   b) Use MATLAB's `fminsearch` function to find the $k$ that minimizes the sum of squared errors. Plot the best-fit model and the data on the same set of axes.

## REFERENCES

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