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STUDENT VERSION
KINETICS - RATE OF CHEMICAL REACTION

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STATEMENT

Rate or differential equations can model chemical reactions [7]. 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." [6] Thus we consider reactions to be dependent upon the concentration of a single reactant, say, A, where $[A]$ is the number of moles of 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.

ORDER OF REACTION - DEFINITIONS

In this modeling scenario we are going to guide more than we usually would in SIMIODE, 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, ... [8, p. 657].

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

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

The solution to this is rather easy 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 Excel and use Trendline to pick off 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 antilogarithms (or exponentiating both sides in (2) 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 to determine if this reaction is first order, i.e. if $m = 1$.

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 [8, p. 682] on the reaction $2H_2O_2(g) \longrightarrow 2H_2O + O_2(g)$.

We return to the task of determining order of the reaction and the parameter k. From (2) we can see that a first order reaction will produce a linear relationship between $\ln(y)$ and t.

1) a) Confirm that this is a first order reaction by logging the $[H_2O_2]$ (mol/L) column data in Table 5 and plotting $\log[H_2O_2]$ vs t to see a linear relationship.
   b) Use Excel's Trendline to determine the slope of the line of best fit for the logged data from Table 5, i.e. the natural logarithm of $[H_2O_2]$ (mol/L) vs. t.
   c) Use your parameter k obtained in (b) and the initial amount of $[H_2O_2]$ (mol/L) in (3) to determine what amount of $[H_2O_2]$ (mol/L) the model predicts at times t as offered in Table 5.

d) Compare these predictions with the observed data. Do you believe that the first order model does a good job of predicting?

e) Let us determine if this reaction is first order. To do this we shall assume $m = 1$ and see how the resulting model compares to the data. We can use Mathematica's `FindMinimum` command on the sum of square errors between the observed values of H_2O_2 and the predicted model values (3) for the 9 time observations. Or we could use Excel's Solver command (with parameters as true variables in Solver) to do the same minimization of the sum of square errors. Both strategies can determine the best fitting rate constant, k. Plot the model prediction over the data and comment on what you see. Note: We can, of course, obtain good results using Excel's Trendline, but Excel's Solver is a broader tool which permits optimization, in this case minimization of the sum of square errors.

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

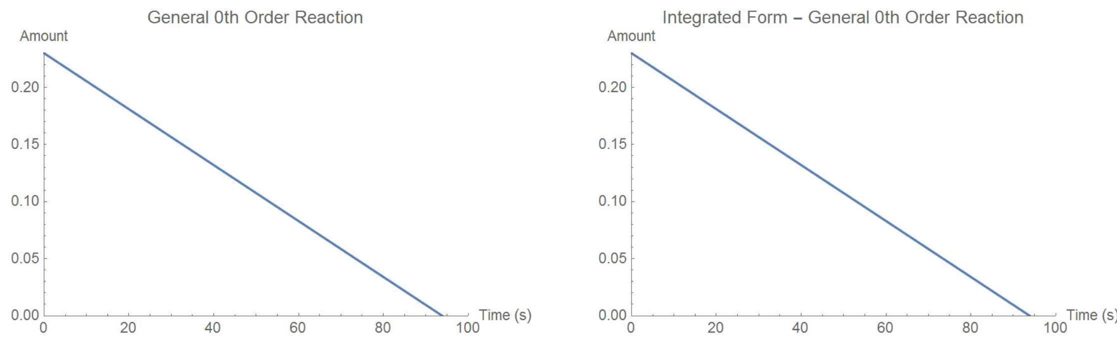
$$\frac{1}{y} = k\,t + \frac{1}{y(0)} \,. \tag{4}$$

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),

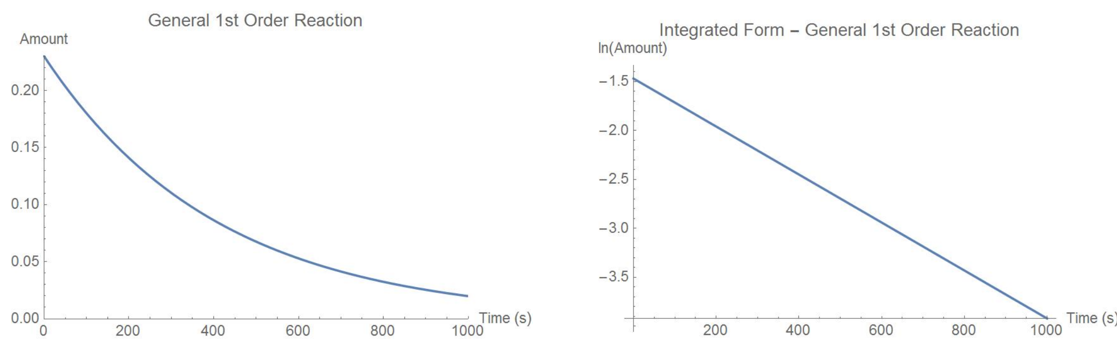
$$y = y(t) = \frac{1}{k\,t + \frac{1}{y(0)}} = \frac{y(0)}{y(0)k\,t + 1} \,. \tag{5}$$

2) Revisit the decomposition of hydrogen peroxide in Table 5 and show it is *not* a second order reaction. Offer as complete a defense as you can - data fitting, plots, verbal argument, etc.

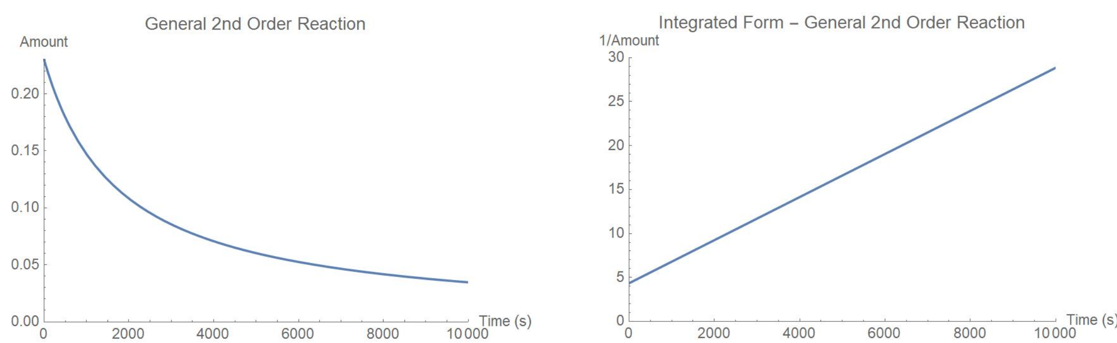
We summarize this information in Table 2 while in Figure 1 we offer general plots to illustrate the $m = 0, 1, 2,$ order reactions. In each case we give plots of the actual solution and the integrated form of the solution.



Plots of both solution and integrated form of solution for order $m = 0$.



Plots of both solution and integrated form of solution for order $m = 1$.



Plots of both solution and integrated form of solution for order $m = 2$.

Figure 1. Plots of both solution and integrated form of solution for orders (a) $m = 0$, (b) $m = 1$, and (c) $m = 2$.

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	$y'(t) = -ky(t)^2 = -ky(t)^2$	$\frac{1}{y(t)} = kt + \frac{1}{y(0)}$	$y(t) = \frac{y(0)}{y(0)kt+1}$

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 NO_2

Consider the following data (Table 3) for the reaction describing the decomposition of NO_2, nitrogen oxide.

Time t (sec)	$[NO_2]$
0.5	0.02
1.0	0.015
1.5	0.012
2.0	0.0087

Table 3. Collected data [3, p. 486] on the reaction $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$.

3) a) First, show this reaction is *not* zeroth or first order. Offer as complete a defense as you can - data fitting, plots, verbal argument, etc.

   b) Using the data in Table 3, transform the data according to (4) and determine the parameter k in terms of best fit. This is the way a chemist would do this problem.

   c) Consider the final solved form in (5) and perform a nonlinear minimization using Mathematica's `FindMinimum` command on the sum of square errors between the observed values of N_2O and the model (5) predicted values for the 4 time observations. Or we could use Excel's Solver command (with parameters as true variables in Solver) to do the same minimization of the sum of square errors. Both strategies can determine the best fitting rate constant, k. Plot the model prediction over the data and comment on what you see.

   d) Use the parameter k obtained in (b) or (c) and the initial amount of $[NO_2]$ (mol/L) in Table 3 to determine what amount of $[NO_2]$ (mol/L) the model predicts at any given time t, say $t = 3$, 5, and 10.

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.

e) Comparing the predictions with the observed data, if you believe that the second order model does a good job of predicting the amount of $[NO_2]$ (mol/L) at time t explain why. Otherwise explain why not.

Decomposition of N_2O_5

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

$$2N_2O_5 \longrightarrow 4NO_2 + O_2 \tag{6}$$

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 what the order is and what the order is not vis-á-vis $m = 0, 1, 2$ orders.

Decomposition of H_2O_2

5) Consider the following data (Table 5) for the reaction describing the decomposition of H_2O_2, hydrogen peroxide.

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \tag{7}$$

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

Time t in s	$[H_2O_2]$ mol/L
0	1
120	0.91
300	0.78
600	0.59
1200	0.37
1800	0.22
2400	0.13
3000	0.082
3600	0.05

Table 5. Data [8, p. 682] for the decomposition of H_2O_2 is given.

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

Decomposition of C_4H_6

6) Consider the following data (Table 6) for the reaction of C_4H_6, butadiene, to form its dimer, a chemical structure formed from two similar sub-units.

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g) \tag{8}$$

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 6. Data [8, p. 654] for the reaction of C_4H_6, butadiene, to form its dimer.

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 what the order is and what the order is not vis-á-vis $m = 0, 1, 2$ orders.

Your Call

7) Get an introductory chemistry text or check one out from the library and look up the section on chemical kinetics. Find a data set problem with directions to ascertain the order of the reaction and offer a write up in this regard.

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

From [4, 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^{th} order reactions of the form (1). However, a more general definition of order describes situations like

$$A + B \longrightarrow AB\,. \tag{9}$$

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) (9) yields the differential equation model (10,

$$C_A'(t) = C_B'(t) = kC_A \cdot C_B\,, \text{ with } C_A(0) = A_0 \text{ and } C_B(0) = B_0\,. \tag{10}$$

$C_A(0) = A_0$ and $C_B(0) = B_0$ are the number of moles per liter of A and B at the start of the reaction. So if $y(t)$ represents the number of moles per liter of A or B that have reacted in time t , 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), (10), actually can be rewritten as (11),

$$y'(t) = k(A_0 - y)(B_0 - y)\,, y(0) = 0. \tag{11}$$

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. $A_0 \neq B_0$.

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

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

Table 7. Data collected by Reicher [5] shows the time (t) in seconds and amount of AB produced in moles per liter ($y(t)$) at time t.

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 [5] offers experimental data in Table 7 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.

9) In Table 7, we see there is initially $A_0 = 0.5638$ moles/liter concentration of A and $B_0 = 0.3114$ moles/liter concentration of B.

   a) Since it takes one mole/liter of each of A and B to produce one mole/liter of AB build a mathematical model for $y'(t)$ the rate of change in $y(t)$ at time t. Defend every term in the model.

   If we solve (using Mathematica's `DSolve`) for $y(t)$ and place $A_0 = 0.5638$ and $B_0 = 0.3114$ into the solution we obtain the following function:

$$y(t) = \frac{0.149709e^{0.3114k\cdot t} - 0.149709e^{0.5638k\cdot t}}{0.265536e^{0.3114k\cdot t} - 0.480762e^{0.5638k\cdot t}}\,. \tag{13}$$

   b) Construct the sum of square errors function (14) for the difference between the model (13) predictions at time t_i where $i = 1, 2, \ldots 5$ goes through the five observation data point we have in Table 7 and the data on the concentration of product AB offered in the second row of Table 7, i.e, AB_i, for $i = 1, 2, \ldots 5$:

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

   c) Minimize $SSE(k)$ with respect to k and obtain $k = 0.00139862$ (using Mathematica's `FindMinimum`) with an actual $SSE(0.00139862) = 0.0000134864$. Here, create a very good fit. Indeed, we offer a plot of the data over the model in Figure 2.

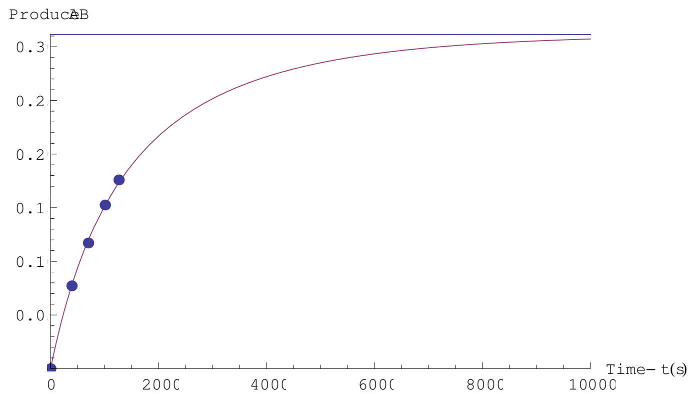


Figure 2. Plot of the model over the data. We also include the horizontal line at value of $B_0 = 0.3114$ for this is the limiting value of the concentration of product AB as it takes one mole/liter of each of A and B to produce one mole/liter of AB and the concentration of B is the smaller, and hence limiting, of the two concentrations.

SUBLIMATION OF CAMPHOR - . . . SOMETHING COMPLETELY DIFFERENT

Camphor is a compound used to moth-proof clothing and possesses a strong odor, primarily because it sublimates from solid to gas. In [2] experiments were conducted to model the rate of sublimation and compare it to the collected data. An assortment of camphor balls was set aside and observations on the diameter of these spherical balls was taken over a period of 41 days. We display the average diameter information for this set of camphor balls at various times in Table 8.

10) Form a mathematical model for the sublimation of camphor balls and validate the model with the data in Table 8.

Time (days)	Average Diameter (mm)
0.00	18.52
20.50	14.56
41.00	11.47

Table 8. Data from [2] on the average diameter of camphor balls in ambient temperature over a 41 day period.

In Table 9 we see the data displayed, but with the addition of the average volume of the camphor balls sampled at each time.

REFERENCES

[1] Henold, K. L. and F. Walmsley. 1984. *Chemicals: Principles, Properties, and Reactions*. Reading MA: Addison-Wesley.

Time (days)	Average Diameter (mm)	Average Volume (mm^3)
0.00	18.52	3325.99
20.50	14.56	1616.15
41.00	11.47	790.112

Table 9. Data from [2] on the average diameter of camphor balls in ambient temperature over a 41 day period.

[2] Kareem, S. A. 2000. Kinetics of camphor decomposition in ambient condition. *Research Communication in Chemistry*. 1(1): 8-11.

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