This is an English translation of the publication "Mathematische Modellierung im Chemieunterricht der gymnasialen Oberstufe: Chemische Kinetik" *CHEMKON 28(3) 112-121 (2021)*
https://doi.org/10.1002/ckon.201900053 (all content refers to the German school system)

Mathematical modelling in high school chemistry: Chemical kinetics

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Abstract

The observation that high school students often do not recognize the contributions of other subjects such as applied mathematics or informatics to chemistry may be countered by introducing appropriate mathematical modelling in chemistry class. It should be focussed on topics which are typically part of the regular curricula. Here chemical kinetics is employed within the introduction of the nucleophilic substitution as an example allowing conjunctions to mathematics and informatics. In this context, kinetics is deepened by quantitative considerations as well as simulations. The rate laws for the kinetics of first and second order are derived using mathematical methods that are typically included in present mathematics curricula. In addition, two quantitatively analysable model experiments can be used to allow a playfully understanding of the differential equations and their solutions. Furthermore, these model experiments can be transformed into concise computer algorithms. In this way, students learn the different methods experiment, analytical derivation, and simulation for gaining chemical knowledge.

Keywords: reaction order, simulation, differential equation

1. Introduction

Students should be made aware early on that individual disciplines cannot be viewed in isolation. In chemistry, mathematical methods are required alongside physical methods for analyzing measurement data and deriving models. Also, applied computer science is required, for example, when performing simulations. In a previous paper, mathematical skills were proposed that can be taught in chemistry classes in upper secondary school in order to explain the interrelationships between subjects [1]. In the context of chemical kinetics discussed here, equations are derived and their linearization for the evaluation of experimental data with a regression line is discussed. Solving the chemical problem requires mapping the chemical relationships to structures taught in mathematics classes. Specifically, this refers to the differential calculus of exponential functions and reciprocal functions. Reading and interpreting equations here means being able to relate the characteristic curves of the graphs and the

functions to chemical behavior. Thus, the modeling of kinetics can be used as an example of the application of mathematical modeling in chemistry education, either in addition to or as an alternative to the previously described modeling of titration curves [1].

The chemical kinetics of simple, elementary reactions has long been a subject of chemistry education. A large number of experiments suitable for schools have been proposed, as well as methods of evaluation. In addition, technical terminology and approaches to teaching have been discussed. Among other things, the concept of reaction rate (RR) has been discussed, which is often introduced using the mechanical analogy of velocity of movement [2,3]. In this context, Myers [4] provided a remarkable analogy to chemical kinetics with a model experiment on the velocity of movement of ants. Also, historical development show that mechanical velocity is probably the natural approach. Even in the first approaches to chemical kinetics in 1777, the mechanics known at the time were used, albeit initially only for the dissolution process [5]. Later, the physicist Wilhelmy [6] wrote fundamental works on chemical kinetics, but these were not widely used in chemistry for around 30 years because chemists at the time were not familiar with the physical and, in particular, mathematical methods of differential equations [7]. Thus, the foundations of chemical kinetics in chemistry were not laid until the 1880s by van't Hoff and Arrhenius [8,9]. This also demonstrates the importance of knowledge of other disciplines for the development of chemistry.

Reaction kinetics can be used to explain and teach reaction mechanisms. In this context, the question arose as to whether the analysis of kinetics is important for school chemistry. Naumer [10] questioned the usefulness of teaching reaction mechanisms in the classroom and concluded that mechanisms should indeed be taught. However, he criticizes the seemingly widespread practice at that time of teaching mechanisms without imparting a deeper understanding. As an alternative, he suggests a systematic repetition of the technical content of a few mechanisms in a spiral fashion with increasing levels of understanding. Ralle and Wilke [11] provide an overview of suitable reactions for investigating kinetics and mechanisms. They also establish criteria for selecting reactions, such as financial and safety feasibility in schools, as well as evidential value and exemplarity for a group of reactions.

Approaches to mathematical modeling that are suitable for schools were also discussed. For example, Pena [12] solves the differential equation of chemical kinetics by replacing the differential quotient with the difference quotient (slope triangle) and then considering the limit for an infinitely small time interval. If the Euler constant is derived as a limit in mathematics lessons, this approach could be used in chemistry lessons. However, the analogous consideration of the limit for second-order kinetics [12] no longer seems suitable for school use.

Ralle proposed an evaluation method based on determining the normals in the concentration-time diagram [2]. The mathematical relationships were treated as proportionalities in order to respond to the reduction in mathematical skills in the reformed upper secondary school system in the 1980s and to keep the mathematical apparatus as small as possible. Another paper [13] deals with teaching the relationship between kinetics and mechanism in school chemistry for electrophilic aromatic substitution. In addition, the historical development of the elucidation of the mechanism is discussed. In further papers, the kinetics of the S_N2 reaction were investigated [14] and experiments on third-order kinetics were developed for schools [15].

Many works do not explicitly address how to arrive at the rate laws of elementary reactions for kinetics, i.e., how to derive them mathematically on the basis of chemical relationships. It can

be assumed that this is due to the fact that differential equations are not usually taught in school (with the possible exception of advanced physics courses). The development of mathematics education has progressed steadily and sometimes requires updating for application in chemistry. Here, it is helpful to have methods at hand that make use of the students' existing mathematical knowledge. Such an approach is pursued here. The derivation is based solely on knowledge of the derivatives of the exponential function and the reciprocal function. These should be compulsory in upper secondary school mathematics lessons. Furthermore, students can use a spreadsheet program such as LibreOffice Calc to determine the rate constant from the experimental data of their experiment.

The mathematics of first-order kinetics can also be made plausible by means of model experiments. These model experiments also allow cross-references to applied computer science. This allows implementation algorithms to be created for the model experiments and then transferred to computer algorithms. This approach makes it possible to illustrate the importance of basic computer science knowledge in chemistry and in the natural and engineering sciences in general. The approach differs fundamentally from the use of ready-made programs or animations, as students are confronted with the fundamentals of the technical problem and programming. The evaluation of the simulation data from the model experiments is carried out in the same way as the evaluation of data from chemical experiments and allows the evaluation method to be introduced in several steps:

- Principle of evaluation based on deterministic simulation without fluctuations: The data is strictly systematic and easy to evaluate.
- Evaluation based on a stochastic simulation with fluctuation: This allows to discuss restrictions in the evaluation of experimental data using a simple system in an easily comprehensible manner.
- Evaluation of a real chemical experiment: Based on the findings from the model experiments, students can ideally carry out and discuss the evaluation independently.

2. Model experiments for first-order kinetics

First-order kinetics describe spontaneous decomposition reactions of molecules. This can be an exclusive decomposition reaction or a reaction in which a slow rate-determining step as in the $S_N1$reaction. The number of molecules reacting is proportional to the number of molecules present. The reaction rate $RR = \Delta c/\Delta t$ represents the change in substance concentration per unit of time. If we take into account that the concentration of molecules decreases during decay (negative sign) and additionally introduce a proportionality constant, the equation for first-order kinetics follows:

$$\frac{\Delta c}{\Delta t} = -k \cdot c$$

The constant k is the rate constant of the reaction. If, in the limiting case of small Δt, the slope triangle is replaced by the derivative, the differential equation for first-order kinetics is obtained: $c'(t) = -k \cdot c(t)$. A differential equation contains the function sought (here $c(t)$) and one or more of its derivatives.

The following section describes two model experiments that also introduce two basic simulation methods. These are a dynamic simulation, which simulates the sequence of states chronologically, and a stochastic simulation, which generates the states at random. These two approaches also exist in molecular simulation, for example. One is molecular dynamics simulation and the other is molecular Monte Carlo simulation.

2.1 Dynamic simulation

The lifting tube experiment, which can already be found in school textbooks [16], is used here as the basis for a deterministic, chronological simulation. In this experiment, water is removed from a cylinder using a tube (Figure 1). The volume of water V in the cylinder is noted and the experiment is repeated. The rate of change of the water volume obviously depends on how much water is in the cylinder $\Delta V/\Delta i \sim -V$. Here, $\Delta i = 1$ is one lifting step. The negative sign is related to the removal. The proportionality constant is the rate constant of emptying. The differential equation for the model experiment is ultimately $\Delta V/\Delta i = -k \cdot V$ or $V'(i) = -k \cdot V$. This equation reflects the fact that the instantaneous rate of change of volume is proportional to the volume of water present in the cylinder. If the cylinder is filled higher, the lifting tube imersed deeper and more water is removed.

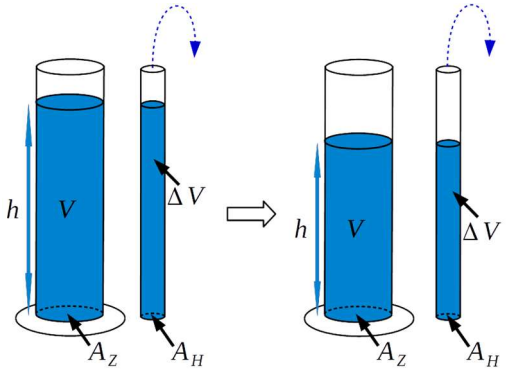


Figure 1: Schematic representation of the model experiment for emptying a cylinder with a lifting tube.

A simple computer algorithm can be created to simulate this experiment. Among other things, such a simulation allows to examine the system using a large number of calculation steps. Furthermore, the creation of the algorithm is related to basic computer science education [17]. This model experiment is particularly well suited for this purpose because it is mathematically very simple and only requires the formula for calculating the volume of a cylinder. Table 1 lists the individual steps of the water removal in the experimental algorithm and translates them into a computer algorithm as pseudocode.

The online supporting information describes how the experimental algorithm was converted into a computer algorithm for the freely available TigerJython interpreter [18]. Programming in a spreadsheet is also possible. To do this, we insert the three equations of the algorithm (Table 1) for the model experiment into each other and factor out V_i. Starting from the initial volume V_0 and with the number of lifting steps i, the resulting equation is:

$$V_i = V_0 \left(1 - \frac{A_\mathrm{H}}{A_\mathrm{Z}}\right)^i \qquad (1)$$

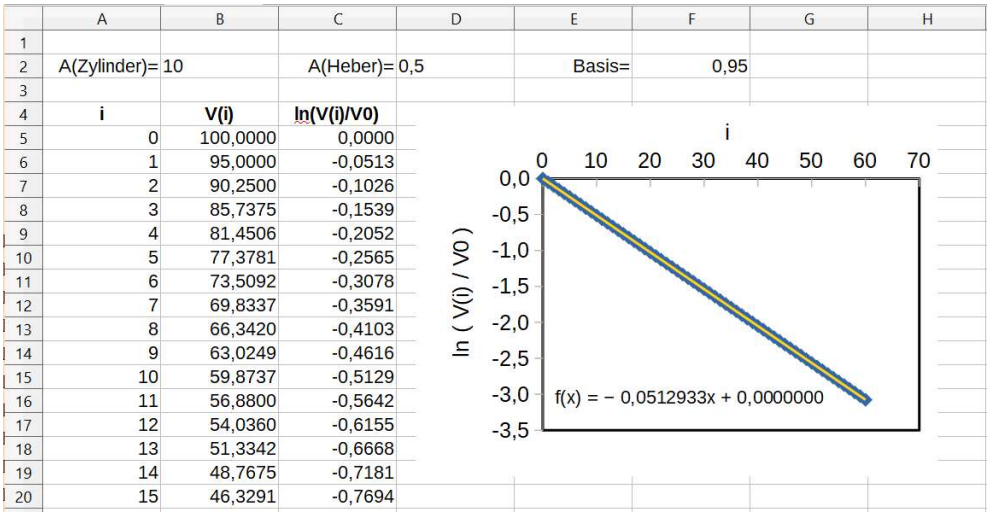
This is an exponential function of the type

$$f(x) = a \cdot b^x \, .$$

It corresponds to compound interest calculations and can be programmed in a spreadsheet (Figure 2).

The cylinder is initially filled with volume V_0. In the following, we use V_i for the volume after i emptying cycles.	
The fill height h of the cylinder is calculated from the volume of the previous step and the base area of the cylinder A_Z.	$h = \frac{V_{i-1}}{A_Z}$
The volume to be removed is the filling height of the cylinder multiplied by the base area of the lifting tube A_H.	$\Delta V = h \cdot A_H$
The volume of the cylinder is reduced by the amount removed.	$V_i = V_{i-1} - \Delta V$
Output of data. Repeat calculation.	output: i, V_i

Table 1: Experimental algorithm and pseudocode for the lifting tube experiment.



	A	B	C	D	E	F	G	H
1								
2	A(Zylinder)=	10		A(Heber)=	0,5	Basis=	0,95	
3								
4	i	V(i)	ln(V(i)/V0)					
5	0	100,0000	0,0000					
6	1	95,0000	-0,0513					
7	2	90,2500	-0,1026					
8	3	85,7375	-0,1539					
9	4	81,4506	-0,2052					
10	5	77,3781	-0,2565					
11	6	73,5092	-0,3078					
12	7	69,8337	-0,3591					
13	8	66,3420	-0,4103					
14	9	63,0249	-0,4616					
15	10	59,8737	-0,5129					
16	11	56,8800	-0,5642					
17	12	54,0360	-0,6155					
18	13	51,3342	-0,6668					
19	14	48,7675	-0,7181					
20	15	46,3291	-0,7694					

Figure 2: Data sheet for the lifting tube experiment to explain the logarithmic plot and regression. The modeling provides data that shows no fluctuations whatsoever, thus yielding a clearly linear plot. The rate constant is the negative slope $k = 0.051293$ of the regression line (trend line) in the plot of lln(V/V_0)in column B against i in column A. Entry in field F2: =1-D2/B2 , in field B6:=B5*F$2 , in field C5:=LN(B5/B$5) .

The rate constant is still unknown. Intuitively, the students suspect that the rate constant is related to the base area of the lifting tube. Accordingly, the equation $k = A_H/A_Z$ can be made plausible. However, since deviations occur during meticulous examination with the simulation,

one should be aware of the approximation contained in this equation for k: If the solution to the above differential equation $V(i) = V_0 \cdot e^{-k \cdot i}$ is logarithmized, a linear equation is obtained. The rate constant k can be determined as the negative slope from measured values of the logarithmic plot:

$$\ln \frac{V(i)}{V_0} = -k \cdot i$$

Now we also take the logarithm of equation 1 and take the reciprocal in the logarithm to change the sign:

$$\ln \frac{V(i)}{V_0} = \ln \left(\frac{1}{1 - A_\mathrm{H}/A_\mathrm{Z}} \right) \cdot i$$

Comparing the last two equations yields:

$$k = \ln \left(\frac{1}{1 - A_\mathrm{H}/A_\mathrm{Z}} \right) \tag{2}$$

This equation can be simplified to the previously assumed equation for k by expanding it into a Taylor series and considering the limiting case $A_\mathrm{H}/A_\mathrm{Z} \ll 1$.

For further analysis, the simulated data from the program in Figure 2 can be plotted in a spreadsheet according to the above-mentioned linear equation and the slope can be determined. Figure 2 shows for a simulation directly in a spreadsheet with $A_\mathrm{H} = 0.5$ and $A_\mathrm{Z} = 10$ that the negative slope of the trend line (regression line) corresponds to the exact value according to equation 2, while the approximate value with $k \approx A_\mathrm{H}/A_\mathrm{Z} = 0.05$ deviates slightly.

2.2 Stochastic simulation

An understanding of first-order kinetics can be further developed using a stochastic model experiment. This is based on Ehrenfest's urn game [19], which was originally developed to defend Boltzmann's entropy formula. Based on this, Harsch [20,21] developed simulations of chemical kinetics and Cullen [22] developed a board game, which serve as the basis here. In the board game, an $n \times n$ playing field is drawn and all fields are occupied with stones. For two conventional dice, $n = 6$ is chosen, i.e., $m = n^2 = 36$ fields. Then, two dice are used to select an x- and a y-coordinate. If there is a stone on the field (x, y), it is removed. If there is no stone on the field, nothing is done. The number of stones remaining on the board is plotted against the number of dice rolls in a spreadsheet. The game continues until there are no stones left on the board. Through this game, students learn firsthand how velocity depends on the number of stones remaining on the board: At the beginning, the stones disappear quickly, while towards the end it becomes tedious, especially if larger systems for polyhedron dice are chosen. If the negative sign for the decrease in the number of stones on the board is taken into account, this intuitively leads to the differential equation for first-order kinetics $m'(i) \sim m(i)$. Here, i is the number of dice rolls.

On the other hand, the graph can be used to reconstruct the function that describes the disappearance of the stones. The reconstruction of functions is a topic covered in school calculus. The students recognize the exponential function by the fact that it is monotonically decreasing and has no zero point, as it asymptotically approaches zero. It must be taken into account that a system of discrete particles such as game pieces or molecules can only be approximated by a continuous function if the number of particles is very high. In the relatively small board game, zero is reached at some point. The students easily deduce the prefactor $m_0 = 36$ as the y-intercept of the function based on their knowledge of the exponential function $m(0) = m_0 \cdot e^0 = m_0$. Since there is no information available on how fast the curve declines, a parameter k is introduced to determine the rate of removal of stones. In mathematics, such a function is referred to as a family of functions $m_k(i)$ with the family parameter k. The resulting function, which is also the solution to the differential equation, is then:

$$m(i) = m_0 \cdot e^{-i \cdot k}$$

By substituting the solution into the differential equation, one can check the consistency of the two equations:

$$m'(i) = -k \cdot m_0 \cdot e^{-i \cdot k} = -k \cdot m(i)$$

This means that $m'(i) \sim -m(i)$ is satisfied.

Select a playing field size $m = n \cdot n$	`n` `m = n * n`
Place a stone (value one) on each field.	`Pos[ix][iy]=1`
Roll dice for an x-coordinate and a y-coordinate	`ix=random number(1,n)` `iy=random number (1,n)`

If there is a stone on the field (ix, iy), remove it (set the field variable Pos(ix, iy) to 0) and subtract one from the number of stones m.	`If Pos[ix][iy]=1 then`
	`  Pos[ix][iy]=0`
	`  m = m - 1`

Increase the number of dice rolls by one. Record the number of dice rolls and stones. Repeat until all stones are removed.	`i = i + 1` `Print i, m`

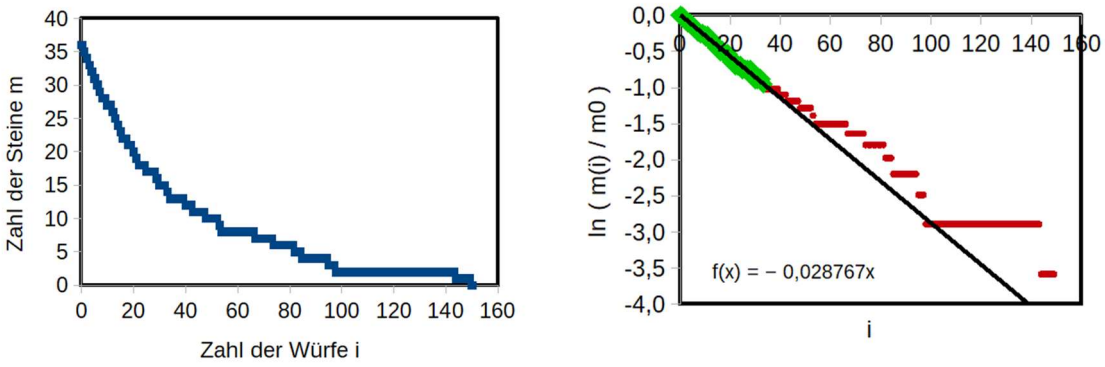
Table 2: Experimental algorithm and pseudocode for stochastic simulation of first-order kinetics.

The course of this game can again be represented as an algorithm that can be converted into a computer algorithm (Table 2). This makes it possible to simulate significantly larger $n \times n$ systems and thus represent the transition to many-particle systems in chemistry. The corresponding code in the TigerJython language is provided in the online supporting

information. As in the lifting tube experiment, the rate constant can be determined from the simulation data using a spreadsheet. To do this, divide by the initial value m_0 and take the logarithm:

$$\ln \frac{m(i)}{m_0} = -k \cdot i$$

The data is converted according to $\ln(m(i)/m_0)$, plotted against i, and a regression line is calculated. For the evaluation, only the first 34 data points were used in an example from the basic course (Figure 3) because after that, the number of stones is too small for the evaluation and there is no longer a linear relationship. In the spreadsheet, the trendline function for the first 34 data points gives a slope of -0.028767 and thus $k = 0.028767$. Here, the y-intercept was set to zero via the trendline options menu. The exact rate constant for the simplest form of simulation used here is the probability of hitting a field. It is therefore the reciprocal of the number of fields $k = 1/m_0$. For a 6×6 game board, $k = 1/36 = 0.02778$, which is close to the value of the regression line.



a) b)

Figure 3: Analysis of the board game in a spreadsheet. a) Number of pieces on the board as a function of the number of the number of dice rolls. b) Logarithmic plot and regression line (trend line). Only the data in the linear range (large green symbols) were taken into account for the linear regression. The small red symbols are the data points that were not taken into account. The slope of the function gives $k = 0.028767$.

3. Selection of the chemical experiment for first-order kinetics

Reactions with a gaseous reaction product are suitable for kinetic evaluations, as the gas volume can be easily measured with a piston sampler. When researching in textbooks or on the Internet, one repeatedly finds the reaction of magnesium with hydrochloric acid as an example that suggests or explicitly names first-order kinetics. This reaction provides data that is very easy to evaluate. However, this is a heterogeneous reaction in which diffusion control is present [23,24]. This is the case when the reaction rate is higher than the transport of the reactants to the interface. It is therefore advisable to use a homogeneous reaction that is similar to a decomposition reaction, such as the decomposition reaction of hydrogen peroxide [25-28] . It is described as a pseudo-first-order reaction whose rate constant depends on the concentration of the homogeneous catalyst potassium iodide [29]. The problem here is the time-delayed start of the reaction. This interferes with the kinetics, making linearization in the initial range difficult.

A suitable reaction should involve a rate-determining step of the first order, i.e., a slow decomposition that is even slower than the mass transfer. As an introduction to nucleophilic substitution, the textbook experiment [30] on the reaction of bromoalkanes with water is suitable for this purpose, as the conversion can be monitored via conductivity [31,32]. For measuring devices with a conductivity measuring range up to $10\,000\ \mu\mathrm{S/cm}$, the reactant quantity $V_\mathrm{E} = 0.1\ \mathrm{mL}$ mL 2-bromo-2-methylpropane can be used. This is added to $V_\mathrm{W} = 100\ \mathrm{mL}$ of distilled water and stirred at approx. 400 rpm. The maximum conductivity for an infinite period of time, which is caused by the products $\mathrm{Br^-}$and $\mathrm{H_3O^+}$, is converted into molar concentration. Using the reactant density ρ_E, its molar mass M_E, and the total volume of the reaction mixture $V_\mathrm{RK} = V_\mathrm{E} + V_\mathrm{W}$, the maximum molar concentration of the product can be calculated assuming complete conversion $c_\mathrm{P,max} = \rho_\mathrm{E} \cdot V_\mathrm{E}/(M_\mathrm{E} \cdot V_\mathrm{RK})$. The concentration of the product as a function of time can then be calculated using $c_\mathrm{P}(t) = L_\mathrm{P}(t) \cdot c_\mathrm{P,max}/L_\mathrm{max}$ from the measured conductivity L of the product. Finally, $c_\mathrm{E}(t) = c_\mathrm{P,max} - c_\mathrm{P}(t)$ can also be converted into the reactant concentration as a function of time. Figure 4a shows an example of a measurement taken by a group of students after conversion to molar concentrations.

Once students have internalized that an elementary decay reaction follows first-order kinetics, i.e., it proceeds exponentially, this can be used to explain the mechanism of the nucleophilic substitution reaction. Since the concentrations in the reaction of 2-bromo-2-methylpropane with water also follow an exponential function of time, students conclude that this must be a decay reaction. By considering the electronegativities, students further realize that the decay occurs via the release of bromide ions. Based on this, the entire mechanism can be represented and the insight developed that a slow reaction step determines the rate. In this way, the measurement of macroscopic kinetics in combination with simulation provides direct insights for elucidating the mechanism at the molecular level.

4. Mathematical derivations

4.1 Rate law for first order reaction

Based on the historical development mentioned at the beginning, the chemical reaction rate can be viewed as analogous to the mechanical velocity of the movement of bodies. Just as mechanical velocity indicates the change in location per unit of time, the reaction rate (RR) indicates the change in the amount of substance or concentration per unit of time. This equation for calculating the RR is also known from mathematics lessons as the slope triangle for calculating the slope of a gradient.

mathematics	physics	chemistry
$\text{slope} = \dfrac{y_2 - y_1}{x_2 - x_1} = \dfrac{\Delta y}{\Delta x}$	$v = \dfrac{s_2 - s_1}{t_2 - t_1} = \dfrac{\Delta s}{\Delta t}$	$\text{RR} = \dfrac{c_2 - c_1}{t_2 - t_1} = \dfrac{\Delta c}{\Delta t}$

These are all slope triangles that indicate the average rate of change or the secant slope in the interval between two points or two measured values. If the interval is reduced, the instantaneous rate of change (tangent slope) is obtained in the limiting case, i.e., the derivative of the concentration with respect to time. In mathematics, this transition is usually introduced at the beginning of upper secondary education using the h-method, which is also used repeatedly in

subsequent mathematics lessons. One can refer to this in chemistry lessons and write the RR as derivative:

$$\mathrm{RR} = c'(t)$$

The $c(t)$ diagram in Figure 4a shows that the RR is very large and negative at the start of the reaction, as the slope is very large and negative at the start. The negative sign corresponds to a decrease in the concentration of the reactant. At the end of the reaction, $\mathrm{RR} = 0$, since the slope of the discrete $c(t)$ data is also zero. This leads to the conclusion that when the reactant concentration is high (at the beginning), the RR is also very high. If the reactant concentration is low, then the RR is also low. Here, the connection to the lifting tube experiment mentioned at the beginning and to the stochastic simulation also comes into play. The more there is, the more can decay. It can therefore be assumed that the RR is proportional to the negative molar concentration:

$$\mathrm{RR} \sim -c(t)$$

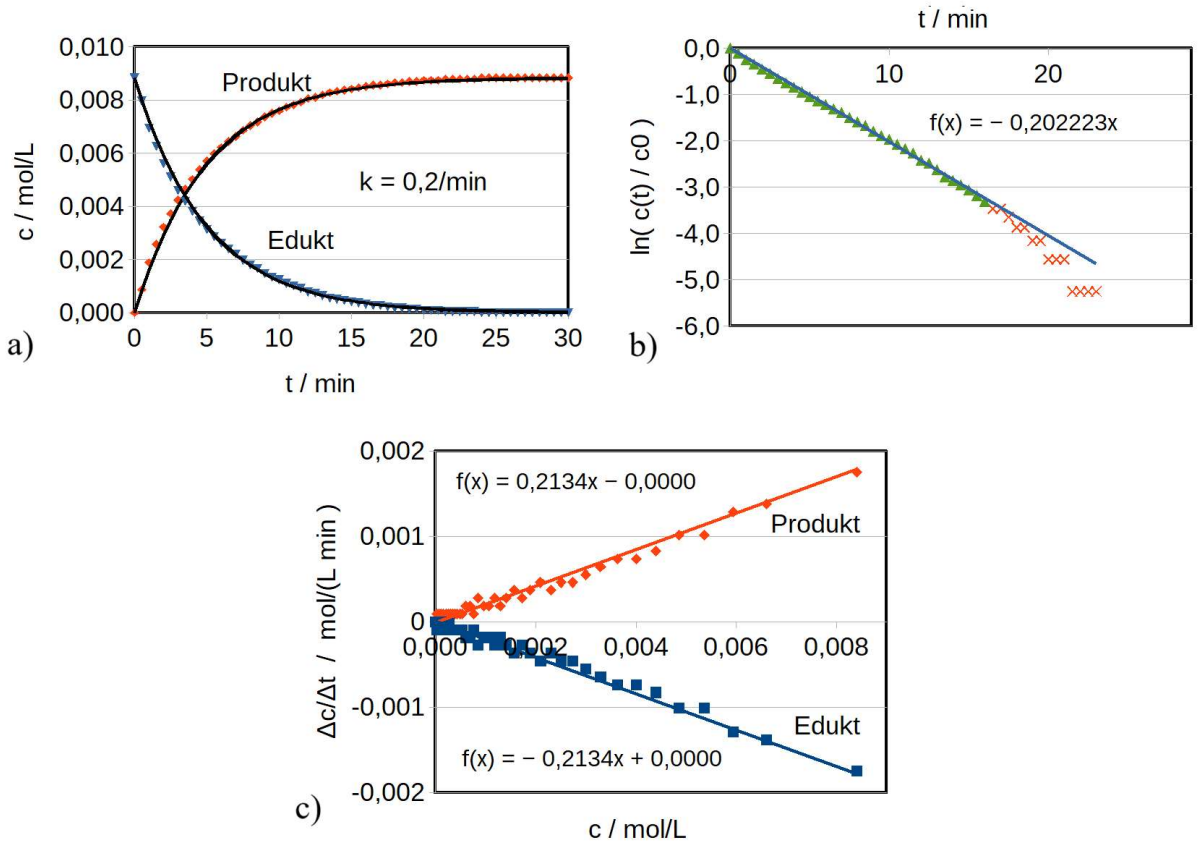


Figure 4: Analysis of the kinetics of the reaction of 2-bromo-2-methylpropane (0.1 mL) with water (100 mL, distilled). a) Symbols: Concentration calculated from the measured conductivity of the product HBr and the reactant. Curves: Concentrations calculated using the rounded value $k = 0.2\ \mathrm{min}^{-1}$. b) Logarithmic plot of the reactant concentration. The regression line with a forced intercept of zero yields $k = 0.2022\ \mathrm{min}^{-1}$. Data that deviates from the initial linear behavior (crosses) is not taken into account in the regression. c) Plot according to the equation $c'(t) = -k \cdot c(t)$. The negative slope of the regression line for the reactant yields the rate constant $k = 0.2134\ \mathrm{min}^{-1}$.

Since the RR is also the derivative in the concentration-time diagram RR $= c'(t)$, we obtain:

$$c'(t) \sim -c(t)$$

If we now introduce a proportionality constant k, the following applies:

$$c'(t) = -k \cdot c(t)$$

This equation states that the derivative of the function is proportional to the function itself, which was already discovered during the model experiments. Ideally, if the exponential function is discussed in parallel in mathematics lessons, then students will know that the exponential function to the base e already partially fulfills this criterion:

$$f(x) = a \cdot e^x \quad \Rightarrow \quad f'(x) = a \cdot e^x$$

The change in sign resulting from the chain rule of differentiation is still missing. Due to the chain rule, the factor $-k$ must appear before x or here before t in the exponent if the function is to satisfy $c'(t) = -k \cdot c(t)$. The approach is therefore:

$$c(t) = a \cdot e^{-k \cdot t}$$

The parameter k is the rate constant that describes the decrease in the reactant over time. We can verify this approach by deriving:

$$c'(t) = -k \cdot a \cdot e^{-k \cdot t}$$

On the right-hand side, we can identify $c(t)$, which shows that the required differential equation is satisfied. To obtain the meaning of the factor a, we consider the limiting case $t \to 0$, for which the exponential term assumes the value one. Thus, the factor must be equal to the concentration at the start $t = 0$ of the reaction $a = c_0$. The resulting rate law is finally:

$$c(t) = c_0 \cdot e^{-k \cdot t}$$

At the particle level, first-order kinetics describe the spontaneous decay of a particle. However, it is possible to analyze second-order reactions as pseudo-first-order reactions if one of the reactants is present in excess. In this case, its concentration changes so little during the reaction that it can be considered constant. If a catalyst is required for the decomposition of a molecule,

its concentration is basically constant. However, the reaction rate may depend on the concentration of the catalyst. This also raises the need to address the difference between reaction order and molecularity. The reaction order as the sum of the powers in the differential equation may only provide a hint to the chemical mechanism. A direct connection can only be established for elementary reactions.

4.2 Determination of the first-order rate constants

To determine the rate constant k from experimental data, we use the linear regression method (trend line) as explained at the beginning for the model experiments. To do this, we divide the equation $c(t)$ by c_0 and take the logarithm

$$\ln\left(\frac{c(t)}{c_0}\right) = -k \cdot t\,.$$

This equation corresponds to a straight line with slope $-k$. However, this procedure without an intercept is only possible if the initial concentration is known exactly or can be calculated backwards. Alternatively, linear regression can of course also be performed according to

$$\ln c(t) = \ln c_0 - k \cdot t\,.$$

Figure 4b shows an evaluation using the first equation with a forced intercept of zero. Once k has been obtained, the concentration can be calculated as a function of time using the rate law

$$c(t) = c_0 \cdot e^{-k \cdot t}$$

and compared with the experimental data (Figure 4a).

The described method is suitable for evaluation based on the reactant concentration. If, as in the case of measuring S_N kinetics with conductivity, only a measured variable is available for the product, it is necessary to either convert to the reactant concentration or use the function

$$c(t) = c_\infty \cdot (1 - e^{-k \cdot t})\,.$$

This function may be familiar to students from mathematics lessons as limited growth. Here, it is necessary to determine the limit value of the concentration for long reaction times in order to plot according to

$$\ln\left(1 - \frac{c(t)}{c_\infty}\right) = -k \cdot t\,.$$

Alternatively, one can also convert the product concentration into the reactant concentration (see paragraph 3) and evaluate this (Figure 4).

For both, the measured reactant and product concentrations, the rate constant can be obtained without knowledge of c_0 and c_∞ by plotting according to the differential equation

$$c'(t) = -k \cdot c(t)$$

(Figure 4c). To do this, the derivative is calculated numerically using the slope triangle

$$c'(t) \approx \frac{c_2 - c_1}{t_2 - t_1}$$

of two adjacent measurement points and plotted against the interval midpoint

$$c(t) \approx \frac{c_1 + c_2}{2} \ .$$

The slope of the straight line for the reactant is the negative rate constant. The linearity of this plot as well as the logarithmic plot also confirms the first-order kinetics. The difference in the rate constants of the two plots in Figures 6b and 6c is due to numerical inaccuracies.

4.3 Rate law for second order reaction

In many reactions, two reactant molecules A and B must collide in order to react. The reaction rate is therefore proportional to two molar concentrations. Concentration is considered to be the probability of encountering a molecule. The collision probability is therefore given as the product of the two molar concentrations, which corresponds to the multiplication of probabilities along a path in the tree diagram, as known from stochastics. The path rule is already introduced in mathematics lessons in lower secondary education.

$$\mathrm{RR} \sim -c_\mathrm{A}(t) \cdot c_\mathrm{B}(t) \qquad \text{for} \qquad \mathrm{A} + \mathrm{B} \rightarrow \text{products}$$

With the same initial concentrations, one can set $c(t) = c_\mathrm{A}(t) = c_\mathrm{B}(t)$. This leads to a quadratic dependence of the reaction rate on the concentration:

$$\mathrm{RR} \sim -c^2(t)$$

With RR $= c'(t)$, the following then applies:

$$c(t) \sim -c^2(t)$$

This equation states that the derivative of the function we are looking for is proportional to the negative square of itself. So again, this is a differential equation. The exponential function does not satisfy this condition. To find a solution, we can try out known functions and their derivatives. We are looking for a function in which the power is increased by one and the sign is changed when differentiated. Checking the derivative for the power function shows that it is not suitable, as the power is decreased by one when differentiated:

$$f(x) = x^n \quad \Rightarrow \quad f'(x) = n \cdot x^{n-1}$$

However, if we set $n = -1$, which corresponds to a hyperbolic or reciprocal function, then when we differentiate, the exponent changes from $n = -1$ to $n - 1 = -1 - 1 = -2$. This corresponds to squaring the function:

$$f(x) = \frac{1}{x} = x^{-1} \quad \Rightarrow \quad f'(x) = -1 \cdot x^{-2} = -\frac{1}{x^2} \quad \Rightarrow \quad f'(x) = -\left(\frac{1}{x}\right)^2$$

On the right-hand side, one can recognize the function $1/x$, which can be replaced by $f(x)$:

$$f'(x) = -f^2(x)$$

The reciprocal function therefore satisfies the condition of the differential equation for second-order kinetics. The corresponding rate law therefore has the form:

$$c(t) \sim \frac{1}{t} \quad \Rightarrow \quad c(t) = \frac{1}{k \cdot t}$$

One may also write the proportionality constant before the fraction. In the approach chosen here, the constant k is a factor before time and therefore has the unit 1/s, as in first-order kinetics.

In the following, we must also take into account the initial concentration. We first take the reciprocal of the function and then subtract the reciprocal of the initial concentration, because at time $t = 0$ it must be $c(t) = c_0$:

$$\frac{1}{c(t)} - \frac{1}{c_0} = k \cdot t \tag{3}$$

This ensures that the left side is zero when t is zero. By rearranging, we obtain the rate law for second-order kinetics:

$$c(t) = \frac{1}{\frac{1}{c_0} + k \cdot t}$$

4.4 Determination of the rate constants for second-order kinetics

The rate law for second-order kinetics (equation 3) can also be represented as a linear function $y = a \cdot x + b$ without a y-intercept ($b = 0$) if $y = 1/c(t) - 1/c_0$ is plotted against t. If c_0 is unknown, $y = 1/c(t)$ can be plotted to obtain $c_0 = 1/b$. To determine whether a reaction is first-order or second-order, the logarithm and the reciprocal of the concentration are plotted against time and it is checked which of the plots yields a linear relationship.

Unfortunately, the reactions of 1-bromobutane and 2-bromobutane with water are so slow that they cannot be easily carried out in class. In this case, measurements from the literature can be used. In some university laboratory, the saponification of esters is used as an experiment for second-order kinetics. If students are already familiar with esterification and saponification from their introduction to chemical equilibrium, the experiment can be carried out without taking up too much class time. Since conductivity is also measured in this experiment, students are also familiar with the measurement technique. The following approach is suitable for a measuring device with a measuring range up to 10 000 µS/cm: Add 10 mL of a 0.125 molar sodium hydroxide solution to 80 mL of distilled water. Start the reaction by adding 10 mL of a 0.125 molar ethyl acetate solution. The resulting initial concentration is therefore $c_0 = 0.0125\ \text{mol L}^{-1}$. To determine the initial conductivity L_0, 10 mL of the 0.125 molar sodium hydroxide solution is added separately to 90 mL of distilled water. The conductivity at the end of the reaction L_∞ is obtained by measuring it one day later. Assuming complete conversion, the conductivity can be converted to molar concentration:

$$c(t) = c_0 \frac{L(t) - L_\infty}{L_0 - L_\infty}$$

Figure 5a shows the molar concentration of the reactant over time, as measured by a group of students. The reciprocal plot in Figure 5b and the plot according to the differential equation in Figure 5c confirm that saponification proceeds according to second-order kinetics.

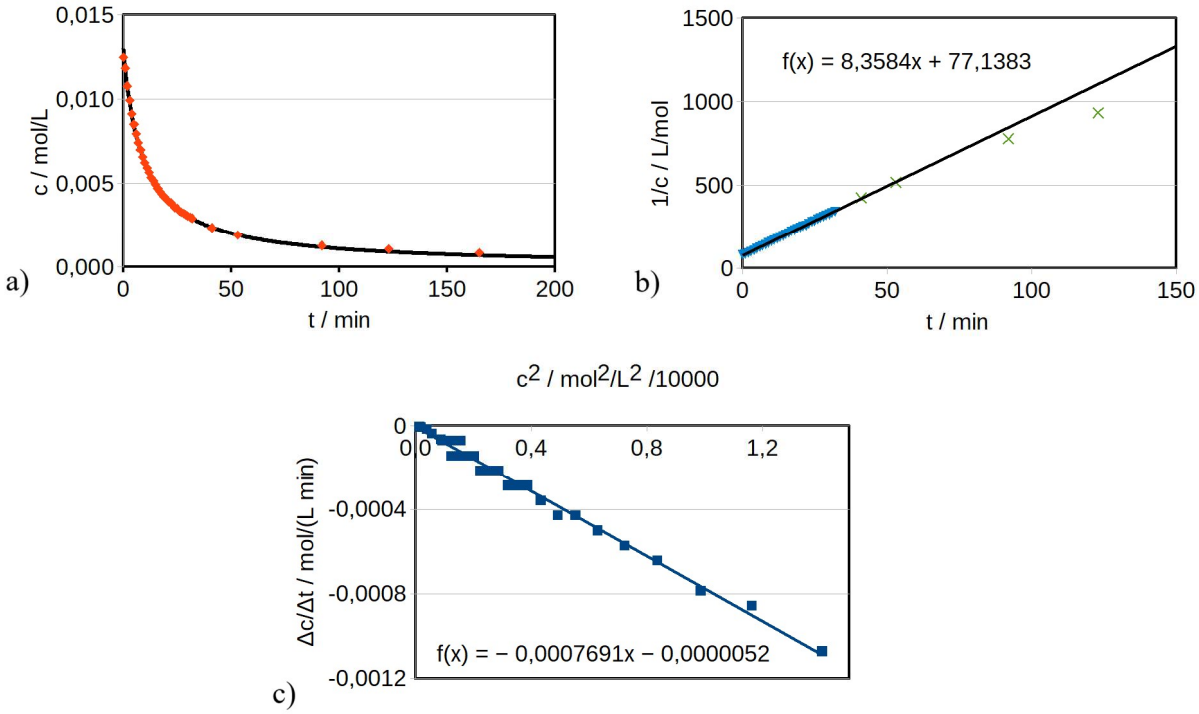


Figure 5: Analysis of the kinetics of the saponification of ethyl acetate with sodium hydroxide solution for $c_0 = 0.0125\ \text{mol L}^{-1}$. a) Symbols: Reactant concentration calculated from the measured conductivity. Curve: Concentrations calculated with $k = 8.3584\ \text{min}^{-1}$. b) Reciprocal plot of the concentration. The slope of the regression line is k. Data that deviate from the initial linear behavior (crosses) are not taken into account in the regression. The intercept gives $c_0 = 1/77.1383\ \text{mol L}^{-1} = 0.0123\ \text{mol L}^{-1}$, which deviates slightly from the weighed-in amount. c) Plotting according to the equation $c'(t) = -k \cdot c^2(t)$ yields $k = 7.691\ \text{min}^{-1}$ after conversion with the unit of the time axis.

Second-order kinetics can also be illustrated using a board game [22]. To do this, half of the playing field is covered with stones of type A and half with stones of type B. Two fields are then selected with four dice based on their respective x and y-coordinates. If one of the stones is of type A and the other is of type B, both stones are removed. In all other cases, nothing is done. A corresponding computer program can be found in the Online Supporting Information. The game allows students to experience that the reaction is obviously slower than in first-order kinetics. In addition, they obtain a straight line for the second-order plot (reciprocal of the number of stones versus the number of dice roll). This further illustrates the aforementioned distinguishing feature of first- and second-order kinetics. The same applies when the simulation is applied to third-order reactions and the reciprocal of the square of the number of stones is plotted in the evaluation.

5. Summary

The analysis of chemical kinetics in upper secondary school offers an opportunity for mathematical modeling in chemistry lessons that ties in with the topics of analysis ideally covered at the same time in mathematics lessons. This teaches a range of mathematical modeling skills that are generally required for scientific work. The two model experiments allow students to systematically approach the mathematical relationships and learn about the differences between a mathematical model and reality in the form of experimental data. As shown in Table 3, the sequence chosen here allows for the gradual introduction of mathematical

methods and a gradual transition from the idealized model concept to experimental observation. The model experiments make the relationships tangible, which would be more abstract if based on a chemical experiment alone. The difficulties described in the literature regarding students' understanding of the concept of reaction rate and possible individual deficits in differential calculus can be countered by the practical perception of velocity in the model experiments.

The repetition of the same mathematical and chemical relationships in different contexts can be understood as a local spiral curriculum. It serves to introduce and deepen students' understanding of chemical kinetics. Finally, the application of mathematics and numerical simulation illustrates the interaction between the subjects to students and, in the best case, counteracts one-dimensional thinking.

Implementation in computer programs will be possible across the board as part of the expected digitization of schools. In North Rhine-Westphalia, for example, the reintroduction of G9 (13 year school education including upper secondary education) will make two years of computer science compulsory for all students in lower secondary education. Students can learn TigerJython or comparable programming languages, which will make it easier for them to use these languages in upper secondary education.

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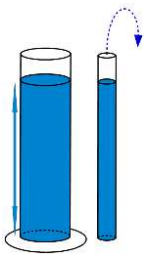
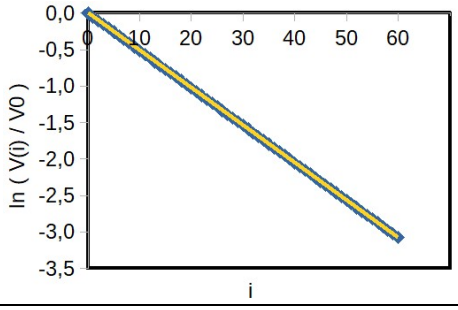
<td>  </td>
<td>
Lifting tube experiment
• Simple exponential function
• No fluctuations
• Quasi-continuous system
• Limiting behavior asymptotically zero
• Linear logarithmic plot
$$\ln\frac{V(i)}{V_0} = -k \cdot i$$


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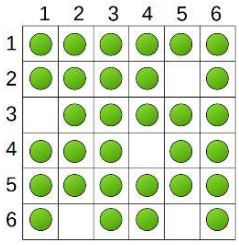
<td> 
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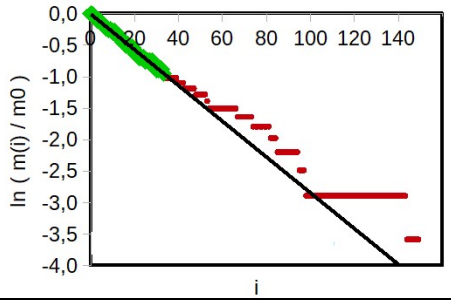
<td>
Stochastic board game
• Exponential correlation of data
• Fluctuations
• Discrete system
• Limiting behavior exactly zero
• Logarithmic plot initially linear
• Large quasi-continuous systems with computer simulations
$$\ln\frac{m(i)}{m_0} = -k \cdot i$$


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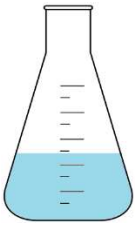
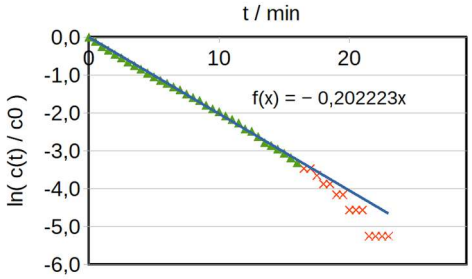
<td>  </td>
<td>
Chemical experiment
• Exponential relationship between data
• Little experimental fluctuations
• Discrete system, quasi-continuous due to high particle count
• Limiting behavior is practically zero
• Logarithmic plot is initially linear
$$\ln\frac{c(i)}{c_0} = -k \cdot t$$


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Table 3: Systematic introduction to a mathematical treatment of first-order reaction kinetics.

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