

Mathematical modelling in high school chemistry: Titration curve

Thomas Kraska

Institute of Physical Chemistry, Faculty of Science, University of Cologne

Greinstrasse 4-6, 50939 Cologne, Germany

E-Mail: T.Kraska@uni-koeln.de

Abstract

In high school and beyond students regard the subjects often isolated from each other. In contrast, every subject always requires contributions from other subjects. The subject chemistry requires, besides others, mathematical skills. In order to illustrate the relation between chemistry and applied mathematics the principles of mathematical modelling can already be introduced in high school. Here a practical example is employed to show how it is possible to simulate a standard experiment in high school chemistry, namely the titration of monoprotic strong and weak acids with a strong base. The mathematical derivation is merely based on mathematical skills, which are typically taught in 9th grade. The topic fits well in the chemistry curricula as a deepening. This approach of implementing mathematics in chemistry also aims to counteract the possible estrangement of the high school subject chemistry from the university subject chemistry. The mathematical derivations are very detailed with focus on the traceability and should be adjusted for application in high school. The way of deriving the equations also allows teaching general methods of mathematical modelling in natural science.

Keywords: mathematics, titration, acids and bases

1. Introduction

In everyday school experience, it appears that students generally have the impression that chemistry has little to do with mathematics. Since most students develop their assessment of subjects in school, chemistry lessons do not seem to do much to counteract this impression. Here, an example of mathematical modeling in chemistry lessons that can serve to counteract this is discussed. It is adapted to the mathematical knowledge of upper secondary education students, fits into the core curriculum, and has been tested in chemistry classes in upper secondary education.

In the past, a number of mathematical skills required for chemistry have been identified. The 10 skills listed by Denny in 1971 [1] are found largely unchanged in several more recent works [2,3]. These include, for example, working with logarithms, algebraic manipulation, and calculating percentages. In addition to deepening of such basic mathematical skills, the application of mathematics also enables the teaching of higher-level modeling skills. These higher-level skills arise from the perspective of the natural sciences and engineering and are suitable for school. They include:

- Balancing with conservation laws as basic approaches
- Deriving equations, from approaches to ready-to-use equations
- Approximations for simplifying equations
- Linearization of equations and adjustment of linear functions
- Mapping mathematical equations from chemistry to familiar structures from mathematics lessons
- Reading and interpreting mathematical equations in a chemical context

School physics reports that mathematization is not particularly problematic [4], which specifically refers to deriving formulas and developing formulas from experiments. At a comparable level with a focus on chemistry, these skills can also be utilized and taught in chemistry lessons. Woest and Vischer [5] have developed a university chemistry seminar in which they have integrated mathematical methods. To this end, they first compiled the mathematical topics required for chemistry. They took into account the extent to which these topics are important for science, are necessary for understanding chemical content, and are required in specific situations. The content was selected with a focus on chemical applications. The starting point of a teaching unit is the chemical question, followed by data analysis of measurable and modelable variables, the development of a mathematical model, its application, the establishment of new testable relationships, and finally the formulation of a law. Using this approach, the authors [5] were able to achieve a significant improvement in the students' mathematical skills.

The cause of the problem can be surmised earlier. It can be assumed that awareness of the fact that mathematical methods are a natural part of chemistry is more likely to develop if they are practiced at an early stage. Thus, the aspect of mathematics can be taken into account right from the start of chemistry lessons by emphasizing the cross-references to school mathematics. Of course, this must be tailored to the students' level of knowledge of mathematics in the respective grade.

In the literature one finds detailed examples of how mathematical methods can be incorporated into different areas of chemistry teaching [6]. Reiners and Struve [7] emphasize that learning difficulties in chemistry cannot be overcome in either chemistry or mathematics alone, but only in combination. They consider equations that are first introduced in mathematics and then, when introduced in chemistry, can lead to comprehension difficulties. Beyond the application of mathematics in chemistry, modeling in chemistry education allows teaching of electronic data processing skills [8], which are also discussed here.

The inclusion of mathematics in school chemistry does not mean fewer experiments. Rather, it is a necessary complement to experiments and serves to evaluate them by setting up models and performing simulations. Without adequate evaluation, an experiment is of no use, not in research nor in teaching. Even though the literature describes [9] that students enjoy conducting experiments but tend to reject thinking about experimental design, observation, and especially evaluation, they must ultimately learn that these things belong together. However, a bridge can be built here by orienting the modeling closely to the experiments previously conducted by the students in terms of language and content.

By integrating these topics into existing curriculum content, it is possible to avoid potential overload and avoid contradicting the call for curriculum streamlining that emerged in the 1990s. The streamlining of curricula mainly referred to extensive detail in topics relating to inorganic chemistry [10]. Streamlining created space for the in-depth study of overarching fundamental principles that can be applied to broad areas of chemistry. With regard to the topic of acids and bases a reduction in the

number of subtopics was also recommended [11]. Whether and which aspects of this extensive field are omitted can be decided on a case-by-case basis. However, this does not preclude the in-depth study of a particular aspect with the aim of achieving a more fundamental understanding.

With regard to the potentially higher degree of difficulty involved in modeling, it is questionable whether low-threshold access to chemistry in school, which is based, among other things, on avoiding mathematical methods as much as possible, is helpful in the long term in attracting students to chemistry. Low-threshold access to science subjects can also lead to frustration if, for example, the choice of subjects in upper secondary education is irreversible and a false impression of the subject has been conveyed in the preceding school years. This is quite independent of the question of the application of mathematics. Rather, it is a question of whether, with the aim of attracting as many students as possible, a subject should be made seemingly attractive by simply avoiding factors that make it difficult. The problem becomes even more apparent during the transition to university, when the difference between the school subject and the university subject of chemistry becomes apparent. Kimpel and Sumfleth report on differences in passing chemistry exams in high school and at university [12]. They attribute the difference to the fact that the proportion of mathematical problems to be solved in the Abitur exams in German state North Rhine-Westphalia from 2009 to 2014 was significantly lower (8% to 12%) than in the exams in chemistry studies (55%). Goldhausen finds an average of 27.7% of mathematical tasks in the central Abitur exams across five German federal states [13]. These observations show how the school subject of chemistry has become partially decoupled from the requirements of chemistry. Schools appear to be suggesting false prerequisites for studying chemistry in some cases.

Conversely, the application of mathematics in natural science subjects can also have an impact on mathematics teaching. Natural sciences can provide real-world contexts that do not appear contrived. Mathematical application tasks are often merely “clothing for mathematical content” [13,14]. For example, a carpenter would certainly not use integral calculus to calculate his material consumption. Nor would one model the number of young people in a discotheque using a third-degree polynomial in order to then calculate when the crowd is at its largest. Scientific applications are real, in contrast to such artificially constructed contexts in school mathematics.

This example here shows how to simulate an experiment with manageable effort and mathematical requirements appropriate for the grade level. It involves calculating titration curves for acid-base titration. This titration is a standard school experiment that allows a direct comparison between the data measured by the students and the simulation equations derived and programmed by the students. The overarching topic of acids and bases is a central concept in chemistry, which is also of great importance for other areas of chemistry. For example, it has been found in universities that an improved understanding of acids and bases had a positive effect on performance in organic chemistry, which was taught subsequently [15]. Various options for preparing lessons are presented here. The main text discusses the conversion of equations in detail and supplements it with a derivation scheme. In addition, a figure is included that illustrates the calculation of the concentration of counterions Na^+ and Cl^- through dilution during titration in the particle model. Finally, the online supporting information includes a possible example for a derivation puzzle.

Gräber and Lindner [9] found an increase in students' interest in the topic of acids and bases in studies published between 1990 and 2008. They attribute this to the success of teaching methods that are more closely oriented toward everyday life, which can be implemented in this topic using everyday chemicals. In the same paper, the authors explain that discussing benefits and dangers of a lesson's content contributes significantly to students' interest. In this context, the simulation discussed here can

be related to specific applications of acid-base system modeling. These can be biochemical systems [16-19] or modeling in chemical process engineering [20] to the modeling of ecological systems [21].

Goldhausen analyzed the core curricula for chemistry in upper secondary education in the German federal states as well as school textbooks [13]. The overarching topic of acids and bases is the most prominent in the curricula, accounting for approximately 21%. The Henderson-Hasselbalch equation for buffers, which was selected as representative of the mathematization of acids and bases, is included in the advanced course in most federal states. This shows that mathematization is already relatively advanced in the field of acids and bases and that the transition to calculating a titration curve is not very difficult.

The mathematical derivations and transformations may seem extensive at first glance, but they are only formulated in small steps in order to provide teachers and multipliers with all the necessary information. Not surprisingly, it has been found that an increasing number of formulas has a deterrent effect on students [22], which teachers should take into account when preparing their lessons. In this context, the detailed derivation in the text is supplemented here by the previously mentioned derivation scheme for the titration of a strong acid with a strong base. This scheme can also be used to indicate the points that need to be modified when transitioning from strong to weak acids. It can serve as a basis for preparing lessons. The depth with which the topic is covered in class always depends on the learning group. One can also consult the didactic literature on mathematics [14,23], dealing with mathematical modeling of real-world contexts.

Of the basic mathematical skills, only algebraic manipulation and mapping to the pq formula for solving quadratic equations are required here. The example shows that particle and charge balances alone can be used to construct a mathematical model that describes the experimental data and can be used for further analysis of the chemical content. Here, balances represent the interaction between chemistry and mathematics, which should be used equally [24], and are ultimately based on the particle model. Work from the 1990s showed [25,26] that the restriction to teaching chemical calculations without any connection to the microscopic concept, which seemed to be common practice at US universities at the time, led to students being able to work through the calculation algorithms but having no or incorrect ideas about the chemistry of acids, bases, and aqueous solutions. Balances, on the other hand, allow a connection between the microscopic model and the mathematical formulation. At the same time, the concept of mathematical approximation can be introduced to simplify equations. This allows us to convincingly demonstrate how an approximation makes a derivation possible but at the same time limits the validity of a model.

2. Modeling titration curves

2.1 Titration of a strong acid with a strong base

In acid-base titration, a distinction is made between determining the endpoint with an indicator and measuring a titration curve. Limiting oneself to determining the endpoint can certainly be avoided in a basic course, as well as in the upper secondary education, due to the ease with which titration curves can be measured. Modeling the titration curve provides an explanation for its characteristic course. It also serves to solve problems required in modeling tasks [24], for example, with regard to the question of the exact location of the first endpoint for weak acids and the assignment of this point to the pK_a value. During the initial measurement of a titration curve, students expressed doubts about the course of their measurement curve, as the pH value initially changed only minimally and then suddenly rose very sharply. Modeling provides an explanation for this course and the interpretation of special points plotted on a titration curve.

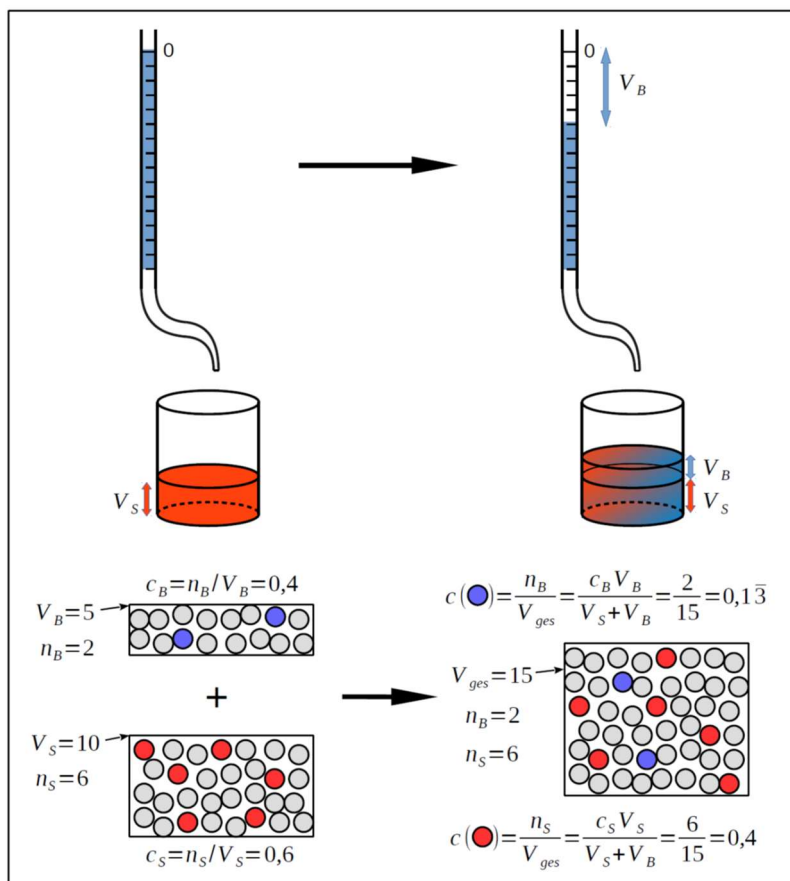


Figure 1: Schematic representation of the change in concentration of the counterions Na^+ and Cl^- during titration of HCl with NaOH by mutual dilution. At the beginning, only the hydrochloric acid with the chloride ions is in the sample and the base with the sodium ions is in the burette. The right-hand side shows the situation after an amount of base has been added to the sample. Below this, the material balances of the acid anions chloride (red) and the base cations sodium (blue) are schematically indicated in a particle model. This representation is reduced to the material balance and does not contain any charges or explicitly show the H^+ and OH^- ions. Units have also been omitted.

2.1.1 Balances and conservation laws

The literature contains a number of derivations of equations for calculating titration curves based on balances or conservation laws [27] or Le Chatelier's principle [28]. Another approach is based on calculating the inverse titration curve [29], which simplifies the calculation but seems less suitable for comprehensible teaching due to the necessary rethinking. Another approach is based on the clever use of trigonometric functions [30], which, however, are not represented in this form in school mathematics. Didactically motivated derivations for multiprotic acids have also been proposed [31], but these also do not seem suitable for schools due to the mathematical effort involved. In contrast, the derivation here allows equations to be obtained with the help of simple approximations that are linear for strong acids and quadratic for weak acids in terms of oxonium ion concentration $c(\text{H}_3\text{O}^+)$, and are therefore suitable for use in upper secondary education.

Students may be familiar with balance sheets from economics. In the simplest case, profit is the difference between revenue generated and costs incurred. Ultimately, money is not lost; it just ends up in someone else's pocket. Balance sheets are also familiar from physics, where they are based on conservation laws such as the conservation of energy, momentum, charge, and mass. In chemistry, balances occur when setting up reaction equations or when balancing charges in redox reactions. The charge balance and substance quantity balances are required for modeling a titration curve. Charge balance means that there must be an equal number of positive and negative charges in the titration beaker at every point during titration so that the solution as a whole is uncharged. Students can be convinced of this because no one has ever experienced an electric shock from a solution. The word "uncharged" should perhaps be preferred to the word 'neutral' because of the use of "neutral" for the pH value. The charge balance for the titration of hydrochloric acid with sodium hydroxide solution for

the molar concentrations $c = n/V$ (n =molar amount of substance, V =volume of the solution) [27] is as follows:

$$c(\text{H}_3\text{O}^+) + c(\text{Na}^+) = c(\text{Cl}^-) + c(\text{OH}^-)$$

With the commonly used equation $\text{pH} = -\lg(c(\text{H}_3\text{O}^+))$ [32], we obtain the pH value that we want to calculate when modeling the titration curve. The three other molar concentrations are unknown and must be replaced by known quantities.

We can calculate the unknown molar concentrations $c(\text{Na}^+)$ and $c(\text{Cl}^-)$ using mass balances. When calculating mass balances, it must be taken into account that the total volume of the solution increases as a result of titration. This is therefore a mutual dilution of the counterions Na^+ and Cl^- in the mixture. The dilution during titration is therefore naturally taken into account by the stoichiometric balances. The mathematical model is therefore complete and does not contain any approximations in this context. As shown in [Figure 1](#), V_a is the volume of acid placed in the beaker. The volume added from the burette is V_b .

The total volume in the beaker is then $V_{\text{tot}} = V_a + V_b$. To calculate $c(\text{Cl}^-)$, we need the amount of Cl^- ions present at the start of the titration. After rearranging the definition of the molar concentration $c = n/V$, we obtain the molar amount of acid n_a present and thus also the amount of acid anions Cl^- during the entire titration by $n_a = c_a V_a$. In the beaker, this amount of substance is distributed over the total volume. Thus, we obtain the concentration of chloride ions solely through dilution during titration:

$$c(\text{Cl}^-) = \frac{n_a}{V_{\text{tot}}} = \frac{c_a V_a}{V_a + V_b}$$

A comparable balance can be drawn up for the sodium ions, whereby the amount of substance Na^+ in the beaker is calculated from the titrated amount of sodium hydroxide n_b :

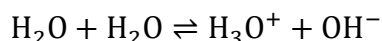
$$c(\text{Na}^+) = \frac{n_b}{V_{\text{tot}}} = \frac{c_b V_b}{V_a + V_b}$$

[Figure 1](#) illustrates these two equations using the particle model. Such an illustration can be used to allow students to work out the material balances and the effect of dilution themselves.

Now we insert the terms for the concentrations $c(\text{Cl}^-)$ and $c(\text{Na}^+)$ into the charge balance equation:

$$c(\text{H}_3\text{O}^+) + \frac{c_b V_b}{V_a + V_b} = \frac{c_a V_a}{V_a + V_b} + c(\text{OH}^-)$$

The hydroxide ion concentration is still unknown. The basis for converting it into the oxonium ion concentration is the autoprotolysis of water, which is considered to have already been dealt with at this point. In pure water, water molecules dissociate to a small extent of 10^{-7} mol/L into OH^- and H^+ ions. The H^+ ions attach to H_2O molecules and, as a first approximation, form oxonium ions H_3O^+ .



The corresponding law of mass action is:

$$K = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{OH}^-)}{c^2(\text{H}_2\text{O})}$$

Since the H_2O concentration can be considered constant due to the low dissociation, it can be combined with the equilibrium constant. The result is the ion product for water $K_w = c(\text{H}_3\text{O}^+) \cdot c(\text{OH}^-)$. It follows that:

$$c(\text{H}_3\text{O}^+) + \frac{c_b V_b}{V_a + V_b} = \frac{c_a V_a}{V_a + V_b} + \frac{K_w}{c(\text{H}_3\text{O}^+)} \quad (1)$$

In addition to the quantity $c(\text{H}_3\text{O}^+)$ to be calculated and the variable in a titration V_b , this main balance equation contains only known quantities that are constant for a given titration. Since the oxonium ion concentration is required to calculate the pH value, equation 1 must be transformed accordingly. The resulting equation contains a quadratic and a linear term in $c(\text{H}_3\text{O}^+)$. It is therefore a quadratic equation. At this point, it is necessary to recognize the general quadratic equation in pq form in the equation that was derived in the chemical context (see appendix). Finally, we obtain the equation for the oxonium ion concentration

$$c(\text{H}_3\text{O}^+) = -\frac{c_b V_b - c_a V_a}{2(V_a + V_b)} + \sqrt{\frac{(c_b V_b - c_a V_a)^2}{4(V_a + V_b)^2} + K_w} \quad (2)$$

which can also be written as follows if one wants to show the direct relationship to the material balances:

$$c(\text{H}_3\text{O}^+) = -\frac{c(\text{Na}^+) - c(\text{Cl}^-)}{2} + \sqrt{\left(\frac{c(\text{Na}^+) - c(\text{Cl}^-)}{2}\right)^2 + K_w}$$

ca = 0.2	$cH(V_b) = -\frac{c_b V_b - c_a V_a}{2(V_a + V_b)} + \sqrt{\left(\frac{c_b V_b - c_a V_a}{2(V_a + V_b)}\right)^2 + K_w}$	⋮
= 0.2		
Va = 50	$= -\frac{0.1 V_b - 0.2 \cdot 50}{2(50 + V_b)} + \sqrt{\left(\frac{0.1 V_b - 0.2 \cdot 50}{2(50 + V_b)}\right)^2 + 0}$	
cb = 0.1		
= 0.1	pH(Vb) = -log ₁₀ (cH(Vb))	⋮
Kw = 10 ⁻¹⁴	$= -\log_{10}\left(-\frac{0.1 V_b - 0.2 \cdot 50}{2(50 + V_b)} + \sqrt{\left(\frac{0.1 V_b - 0.2 \cdot 50}{2(50 + V_b)}\right)^2 + 0}\right)$	
= 0		

Figure 2: GeoGebra input based on equation 2 with the values specified in the text for calculating a titration curve.

The latter equation shows that the pH value is dominated by the difference in molar concentrations of the counterions Na^+ and Cl^- and their dilution, as illustrated in Figure 1. Diagram 1 (at the very end) summarizes the derivation process. If we substitute the values $c_a = 0.2$ mol/L, $c_b = 0.1$ mol/L, $V_a = 50$ mL, and $K_w = 10^{-14}$ mol²/L², we obtain (without units)

$$c(\text{H}_3\text{O}^+) = -\frac{0.1 \cdot V_b - 0.2 \cdot 50}{2(50 + V_b)} + \sqrt{\left(\frac{0.1 \cdot V_b - 0.2 \cdot 50}{2(50 + V_b)}\right)^2 + 10^{-14}}$$

and thus the pH value. The equivalence point (EP) is at $V_b = c_a \cdot V_a / c_b = 100$ mL, i.e., it makes sense to plot the graph in the range $0 \text{ mL} \leq V_b \leq 200 \text{ mL}$. The graph of the titration curve can be programmed and displayed using free school mathematics programs such as GeoGebra or a spreadsheet program such as LibreOffice Calc. Figure 2 shows the input in GeoGebra. It is important to note that in GeoGebra, the K_w value is entered as a constant, which is then used in the pq formula. Figure 3a shows the resulting graph of the titration curve.

By entering experimental data as points in GeoGebra such as $(20, 1.2)$, one can check the agreement with the model [32]. In addition to the titration curve, one can display the oxonium ion concentration in GeoGebra. A comparison with the titration curve shows that its characteristic course of the curve is essentially caused by the logarithm.

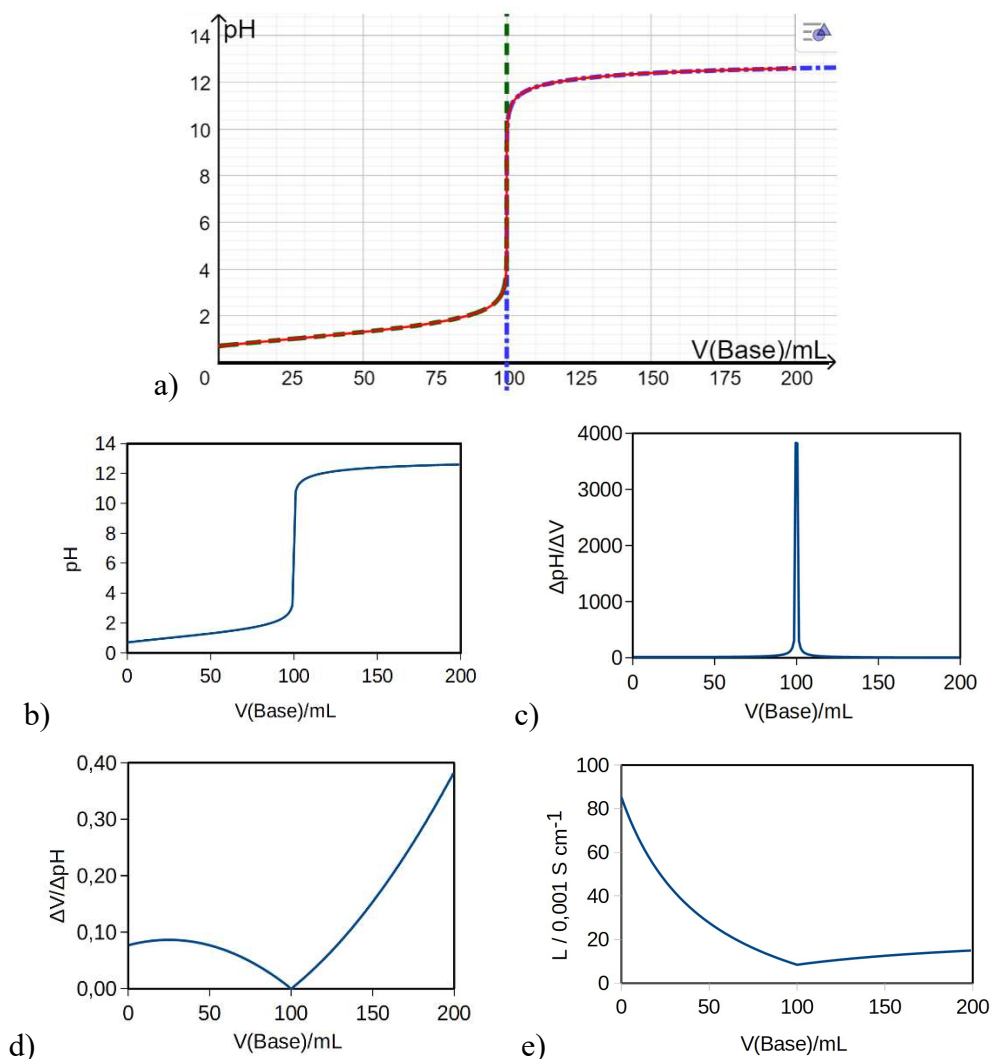


Figure 3: a) Graph of the titration curve in GeoGebra, generated using the code shown in Figures 2 and 4. Red solid curve: Equation 2; green dashed curve: Equation 3; blue dotted curve: Equation 4. b) Titration curve generated with LibreOffice Calc. c) Numerical derivative of the titration curve using the slope triangle. d) Gran plot of the titration curve. e) Conductivity curve of the same titration.

With the help of the titration curves simulated in this way, methods for detecting the EP can also be discussed. LibreOffice Calc is better suited for this purpose (Figure 3b). A common method for determining the EP uses a numerical derivative, for which we plot the slope triangle of two adjacent pairs of measured values $\Delta\text{pH}/\Delta V_b$ against the interval midpoint of V_b . As can be seen in Figure 3c, the peak of the numerical derivative lies at the EP, which is therefore easy to determine. In the less well-known plot according to Gran [33], the reciprocal of the derivative is plotted in the simplest case. Here, the EP appears as a kink, which is also easy to recognize (Figure 3d). This plot is well suited for determining the EP from experimental data if the linear ranges are extrapolated until the extrapolation lines intersect (see Online Supporting Information).

2.1.2 Approximation method: Calculation of the acidic side pH < 7

Approaches such as the charge balance, in which the material balances were used, often cannot be solved by mathematical manipulations. Such a solution using mathematical manipulations is called an analytical solution. If analytical solutions are no longer possible, one can try to simplify the mathematical equation by using a so-called approximation. A mathematical approximation is related to a chemical or physical assumption.

To introduce the approximation, we intervene in the derivation carried out above at the point in the charge balance where the material balances have already been used and subtract the hydroxide ion concentration on both sides:

$$c(\text{H}_3\text{O}^+) + \frac{c_b V_b}{V_a + V_b} = \frac{c_a V_a}{V_a + V_b} + c(\text{OH}^-) \quad | - c(\text{OH}^-)$$

$$c(\text{H}_3\text{O}^+) - c(\text{OH}^-) + \frac{c_b V_b}{V_a + V_b} = \frac{c_a V_a}{V_a + V_b}$$

If we now limit ourselves to the part of the titration curve that lies at a low pH value, i.e., the acidic range before the EP, then the concentration of hydroxide ions is much lower compared to that of oxonium ions. Let's take an example:

For pH = 3 it is $c(\text{H}_3\text{O}^+) = 10^{-3} \text{ mol/L}$

with $c(\text{H}_3\text{O}^+) \cdot c(\text{OH}^-) = K_w$ it follows $c(\text{OH}^-) = 10^{-11} \text{ mol/L}$

and finally:

$$c(\text{H}_3\text{O}^+) - c(\text{OH}^-) = 10^{-3} \text{ mol/L} - 10^{-11} \text{ mol/L} = 0.000\,999\,999\,990 \text{ mol/L} \approx 10^{-3} \text{ mol/L}$$

This calculation shows that for a much smaller hydroxide concentration than oxonium ion concentration $c(\text{OH}^-) \ll c(\text{H}_3\text{O}^+)$, the hydroxide ion concentration can be neglected compared to the oxonium ion concentration. Taking this into account, the term $c(\text{OH}^-)$ can be neglected in the charge balance, resulting in:

$$c(\text{H}_3\text{O}^+) + \frac{c_b V_b}{V_a + V_b} \approx \frac{c_a V_a}{V_a + V_b}$$

Since this equation is linear in $c(\text{H}_3\text{O}^+)$, unlike the quadratic equation, it can easily be rearranged to $c(\text{H}_3\text{O}^+)$. The approximately equal sign indicates that this is an approximation. However, in the following, it is replaced by the equal sign again. Algebraic manipulation yields a simple equation for $c(\text{H}_3\text{O}^+)$:

$$c(\text{H}_3\text{O}^+) = \frac{c_a V_a - c_b V_b}{V_a + V_b} \quad \text{or} \quad c(\text{H}_3\text{O}^+) = c(\text{Cl}^-) - c(\text{Na}^+)$$

Neglecting the OH^- ion concentration, the H_3O^+ ion concentration and thus the pH value are determined solely by the difference in counterions in terms of charge balance and thus by the dilution of the counterions, as indicated in [Figure 1](#). Thus, the pH value for the acidic side is given up to the EP by:

$$\text{pH} = -\lg\left(\frac{c_a V_a - c_b V_b}{V_a + V_b}\right) \quad (3)$$

Mathematically, this function is only defined in the acidic range $c_a V_a > c_b V_b$, because otherwise the term in the logarithm would become negative. This is, of course, consistent with the previously assumed

approximation. We can now add this function to the GeoGebra file that we started above (Figure 4). Entering `Function[pHS (Vb) , 0, 200]` in the input line finally produces the graph. The dashed curve in Figure 3a is the approximation for the acidic side. It can be seen that it is only valid up to the EP, where it diverges.

$$\begin{aligned} \text{pHa}(V_b) &= -\log_{10}\left(\frac{c_a V_a - c_b V_b}{V_a + V_b}\right) \\ &= -\log_{10}\left(\frac{0.2 \cdot 50 - 0.1 V_b}{50 + V_b}\right) \end{aligned}$$

Figure 4: Supplementary GeoGebra input of equation 3 for the acidic side with the values given in the text.

2.1.3 Approximation method: Calculation of the alkaline side $\text{pH} > 7$

Similarly, the alkaline side $c(\text{OH}^-) \gg c(\text{H}_3\text{O}^+)$ can be approximated by assuming that $c(\text{H}_3\text{O}^+)$ is negligible compared to $c(\text{OH}^-)$.

$$\frac{c_b V_b}{V_a + V_b} \approx \frac{c_a V_a}{V_a + V_b} + c(\text{OH}^-)$$

One can then set up the equation for the pOH value $\text{pOH} = -\lg(c(\text{OH}^-))$. Using the ion product of water $\text{pH} = 14 - \text{pOH}$, the pH value can then be calculated from pOH. The resulting equation for the alkaline side is only defined for $c_b V_b > c_a V_a$, i.e., beyond the EP:

$$\text{pH} = 14 + \lg\left(\frac{c_b V_b - c_a V_a}{V_a + V_b}\right) \quad \text{or} \quad \text{pH} = 14 + \lg(c(\text{Na}^+) - c(\text{Cl}^-)) \quad (4)$$

This curve is also plotted in Figure 3a. It follows that the entire titration curve can ultimately be modeled using two very simple functions.

This calculation method makes the idea of approximation comprehensible to students. Illustrating the equations with GeoGebra clarifies the limited validity of the approximations. Some students were impressed that these approximations can be used to model the titration curve using two simple equations. Some students were also amazed by the universal validity of the equations for the combination of all monoprotic strong acids and strong bases. However, it should be mentioned that the approximation used here, neglects the activity coefficient [32].

In the case discussed here involving a strong acid and a strong base, approximations are actually not necessary; they were only used to explain the principle and give students an easy way to calculate a titration curve. In the following case of titrating a weak acid with a strong base, an analytical solution is not possible using school mathematics methods. Therefore, we have to rely on the approximations described above.

2.1.4 Conductivity titration

Based on the equations obtained so far, the curve for a conductivity titration can also be modelled without much effort. For this purpose, the concentrations obtained in 2.1.1 can be used without approximations, or the approximation equations derived in 2.1.2 and 2.1.3 can be used. The contribution of the conductivity L of an ion species to the total conductivity is, as a good approximation, the product of the limiting ion conductivity for infinite dilution multiplied by the molar concentration. Adding the contributions of the individual ion species gives the conductivity of the solution:

$$L = c(\text{H}_3\text{O}^+) \cdot L(\text{H}_3\text{O}^+) + c(\text{Na}^+) \cdot L(\text{Na}^+) + c(\text{Cl}^-) \cdot L(\text{Cl}^-) + c(\text{OH}^-) \cdot L(\text{OH}^-)$$

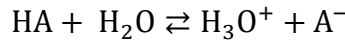
For the molar concentrations of the ions, the material balances or dilution equations for Na^+ and Cl^- during titration are used here, as well as the approximate concentrations for H_3O^+ and OH^- :

$$c(\text{H}_3\text{O}^+) = \frac{c_a V_a - c_b V_b}{V_a + V_b} \quad c(\text{Na}^+) = \frac{c_b V_b}{V_a + V_b} \quad c(\text{Cl}^-) = \frac{c_a V_a}{V_a + V_b} \quad c(\text{OH}^-) = \frac{c_b V_b - c_a V_a}{V_a + V_b}$$

Since $c(\text{H}_3\text{O}^+)$ and $c(\text{OH}^-)$ become negative in the range for which the respective approximation is not valid, the calculation can be divided into two parts. Alternatively, the $\text{MAX}(L, 0)$ function can be used in a spreadsheet calculation, which sets a value for $c(\text{H}_3\text{O}^+) \cdot L(\text{H}_3\text{O}^+)$ or $c(\text{OH}^-) \cdot L(\text{OH}^-)$ to zero if it is negative. The result of the calculation is shown in [Figure 3e](#).

2.2 Titration of a weak acid with a strong base

The difference between a weak acid and a strong acid is that the molecules of a weak acid do not dissociate completely, as assumed for strong acids within good approximation. There is therefore an equilibrium reaction for which the law of mass action applies with the acid dissociation constant K_a :



$$K = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{A}^-)}{c(\text{H}_2\text{O}) \cdot c(\text{HA})} \quad \text{with} \quad c(\text{H}_2\text{O}) \approx \text{const} \quad \text{it follows} \quad K_a = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{A}^-)}{c(\text{HA})}$$

To derive the equation for modeling the titration curve of a weak acid HA (A^- = acid anion) with a strong base MOH (M^+ = metal cation), we start again with the charge balance:

$$c(\text{H}_3\text{O}^+) + c(\text{M}^+) = c(\text{A}^-) + c(\text{OH}^-)$$

Again, we first apply the mass balance for the titrated strong base MOH:

$$c(\text{H}_3\text{O}^+) + \frac{c_b V_b}{V_a + V_b} = c(\text{A}^-) + c(\text{OH}^-)$$

This is where the difference to a strong acid becomes apparent, namely when deriving a term for $c(\text{A}^-)$. In weak acids, acid anions are either dissociated as A^- or undissociated as HA. Thus, the given amount of substance corresponds to the sum of the molar concentrations of these two species:

$$c(\text{HA}) + c(\text{A}^-) = \frac{n_a}{V_{\text{tot}}} \quad \Rightarrow \quad c(\text{HA}) + c(\text{A}^-) = \frac{n_a V_a}{V_a + V_b}$$

In this term, we replace $c(\text{HA})$ with the rearranged mass action law

$$c(\text{HA}) = \frac{c(\text{H}_3\text{O}^+) \cdot c(\text{A}^-)}{K_a}$$

and obtain:

$$\frac{c(\text{H}_3\text{O}^+) \cdot c(\text{A}^-)}{K_a} + c(\text{A}^-) = \frac{c_a V_a}{V_a + V_b}$$

This equation is now rearranged to $c(\text{A}^-)$ in several steps. To do this, $c(\text{A}^-)$ is factored out and the factor in front of $c(\text{A}^-)$ is moved to the other side by division:

$$c(\text{A}^-) = \frac{c_a V_a}{V_a + V_b} \cdot \frac{K_a}{c(\text{H}_3\text{O}^+) + K_a} \quad (5)$$

Inserting this term into the charge balance gives the main balance equation

$$c(\text{H}_3\text{O}^+) + \frac{c_b V_b}{V_a + V_b} = \frac{c_a V_a}{V_a + V_b} \cdot \frac{K_a}{c(\text{H}_3\text{O}^+) + K_a} + \frac{K_w}{c(\text{H}_3\text{O}^+)}, \quad (6)$$

in which $c(\text{OH}^-) = K_w/c(\text{H}_3\text{O}^+)$ is already inserted. Before we continue with this equation, let us consider the limiting case of a strong acid. Here, $K_a \rightarrow \infty$ applies, which means that the term $K_a/(c(\text{H}_3\text{O}^+) + K_a)$ takes the value one and this equation consistently transitions into the equation for the titration of a strong acid with a strong base.

This equation also shows that after algebraic transformation (multiplication by $c(\text{H}_3\text{O}^+) + K_a$, multiplication by $c(\text{H}_3\text{O}^+)$, and finally bringing all terms to one side), a third-degree polynomial, i.e., a cubic function in $c(\text{H}_3\text{O}^+)$, is obtained:

$$0 = c^3(\text{H}_3\text{O}^+) + \left(K_a + \frac{c_b V_b}{V_a + V_b}\right) \cdot c^2(\text{H}_3\text{O}^+) + \left(\frac{c_b V_b - c_a V_a}{V_a + V_b} - K_w\right) \cdot c(\text{H}_3\text{O}^+) - K_w \cdot K_a$$

Mathematically, increasing the degree of the function leads to an additional inflection point in the titration curve $\text{pH} = f(V_b)$. This additional inflection point is located at half the volume of the titrated base of the EP (half-equivalence point: HEP). As the acid constant K_a increases (decreasing $\text{p}K_a$ value), i.e., towards stronger acids, this inflection point disappears. To calculate the titration curve, the cubic equation can be solved with a calculator for a step-by-step specified base volume and plotted $\text{pH} = -\lg(c(\text{H}_3\text{O}^+))$ against V_b . In principle, Cardano's formula [34] or numerical methods [35] can be used to solve cubic equations, whereby in both cases particular attention must be paid to numerical stability.

2.2.1 Calculation of the acidic side $\text{pH} < 7$

Since cubic equations cannot be solved using school mathematics, the approximations mentioned above can be used. As already mentioned, in the acidic range, the hydroxide ion concentration $c(\text{OH}^-)$ can be neglected compared to $c(\text{H}_3\text{O}^+)$ in equation 6 $c(\text{OH}^-) \ll c(\text{H}_3\text{O}^+)$:

$$c(\text{H}_3\text{O}^+) + \frac{c_b V_b}{V_a + V_b} \approx \frac{c_a V_a}{V_a + V_b} \cdot \frac{K_a}{c(\text{H}_3\text{O}^+) + K_a}$$

After a few algebraic manipulations, a quadratic equation in $c(\text{H}_3\text{O}^+)$ results. Both sides are multiplied by $c(\text{H}_3\text{O}^+) + K_a$, all terms are moved to one side, and then $c(\text{H}_3\text{O}^+)$ is factored out:

$$c^2(\text{H}_3\text{O}^+) + c(\text{H}_3\text{O}^+) \cdot \left(K_a + \frac{c_b V_b}{V_a + V_b}\right) + \frac{c_b V_b - c_a V_a}{V_a + V_b} \cdot K_a = 0$$

Substituting into the $\text{p}q$ formula gives:

$$c(\text{H}_3\text{O}^+) = -\frac{1}{2} \left(K_a + \frac{c_b V_b}{V_a + V_b}\right) + \sqrt{\frac{1}{4} \left(K_a + \frac{c_b V_b}{V_a + V_b}\right)^2 - \frac{c_b V_b - c_a V_a}{V_a + V_b} \cdot K_a} \quad (7)$$

Now let's perform a calculation for a weak acid with the acid constant $K_a = 10^{-6}$, i.e. $\text{p}K_a = 6$. The solid red curve in [Figure 5a](#) shows that the calculation is only possible up to the EP, because that is where the function diverges. [Figure 5a](#) shows an inflection point at half the volume $V_b(\text{HEP}) = 50$ mL of the EP. The pH value at the HEP is 6, which is exactly the $\text{p}K_a$ value of the acid. It follows $\text{pH}(\text{HEP}) = \text{p}K_a$ which can be used to determine the $\text{p}K_a$ value. By varying c_a , it can be shown, for example, that this leads to a stretching or compression in the direction of the abscissa, but the $\text{pH}(\text{HEP})$ always remains at the $\text{p}K_a$ value.

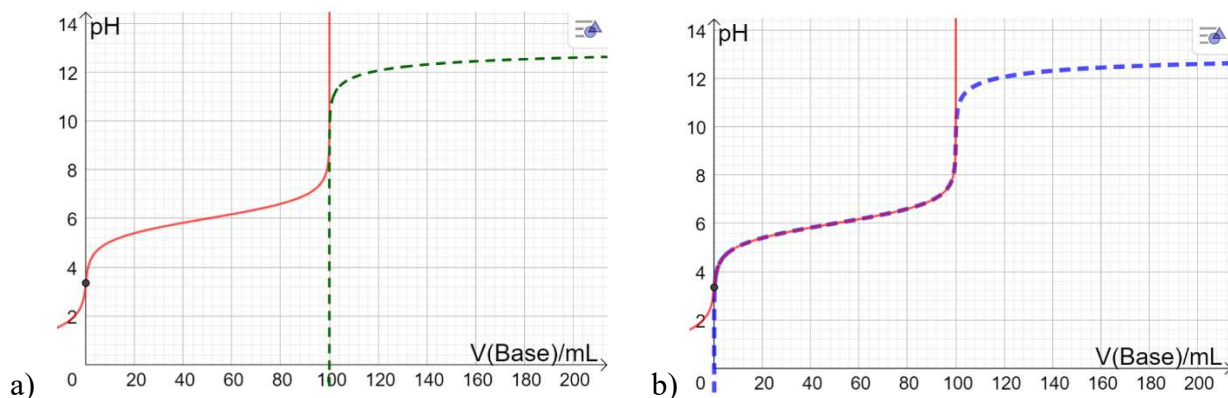


Figure 5: Titration curve of a weak acid ($pK_a = 6$) with a strong base using the values given in the text. a) The solid red curve is the approximation for the acidic side (equation 7) and the green dashed curve is the approximation for the alkaline side (equation 4). The point indicates the pH value of the pure weak acid. b) The same titration curve, but with equation 9 for the alkaline side (blue dashed curve).

2.2.2 Calculation of the alkaline side $pH > 7$

Similarly, the approximation $c(OH^-) \gg c(H_3O^+)$ in equation 6 can also be used to calculate the titration curve in the alkaline range:

$$\begin{aligned} \frac{c_b V_b}{V_a + V_b} &\approx \frac{n_a V_a}{V_a + V_b} \cdot \frac{K_a}{c(H_3O^+) + K_a} + c(OH^-) \\ \frac{c_b V_b}{V_a + V_b} &\approx \frac{n_a V_a}{V_a + V_b} \cdot \frac{K_a}{c(H_3O^+) + K_a} + \frac{K_w}{c(H_3O^+)} \end{aligned} \quad (8)$$

In doing so, $c(H_3O^+)$ was only neglected against $c(OH^-)$. One could also additionally neglect $c(H_3O^+)$ compared to K_a in the denominator. Then equation 8 reduces to equation 4. This is the same result as for the titration of a strong acid with a strong base. Quantitatively, the curve in the alkaline range (but only there) is practically identical to the curve we will obtain with equation 8. Consequently, the titration curve of a weak acid with a strong base can be composed of a quadratic function in $c(H_3O^+)$ for the acidic side (equation 7) and a linear function in $c(H_3O^+)$ for the alkaline side (equation 4). **Figure 5a** shows a curve calculated in this way.

However, we will only neglect $c(H_3O^+)$ against $c(OH^-)$ here and continue working with equation 8. After a series of algebraic manipulations (see Online Supporting Information), we obtain the equation for the alkaline side:

$$c^2(H_3O^+) + c(H_3O^+) \cdot \left(K_a + \left(\frac{c_a V_a}{V_a + V_b} \cdot K_a + K_w \right) \cdot \frac{V_a + V_b}{c_b V_b} \right) - \frac{V_a + V_b}{c_b V_b} \cdot K_w \cdot K_a = 0 \quad (9)$$

This function can be solved again using the pq formula for $c(H_3O^+)$, and then the pH value can be calculated [36]. The curve is plotted in **Figure 5b**. It is also noticeable that the approximation for the alkaline side also accurately reflects the pK_a value at the HEP. This applies at least to $pK_a > 4$, which can be investigated by varying the K_a value in GeoGebra. Only the pH value of the pure weak acid at $V_b = 0$ cannot be accurately reproduced with this approximation. Instead, the function diverges to $-\infty$. Thus, this approximation can be used for almost the entire range, except for $V_b = 0$. The point at $V_b = 0$ can be calculated using the transformed mass action law for the pure weak acid with $c(HA) \approx c_a$ by $pH = (pK_a - \lg(c_a))$.

2.2.3 Conductivity titration

As with the titration of strong acids with strong bases, conductivity can be calculated from the sum of the individual ion conductivities. For the titration of acetic acid (HAc) with sodium hydroxide solution, the following applies:

$$L = c(\text{H}_3\text{O}^+) \cdot L(\text{H}_3\text{O}^+) + c(\text{Na}^+) \cdot L(\text{Na}^+) + c(\text{Ac}^-) \cdot L(\text{Ac}^-) + c(\text{OH}^-) \cdot L(\text{OH}^-)$$

The stoichiometric balance $c(\text{Na}^+) = c_b V_b / (V_a + V_b)$ is used for the molar concentrations of sodium ions. For $c(\text{H}_3\text{O}^+)$, the approximation of the base side (equation 9) can be used. For $c(\text{OH}^-) = K_w / c(\text{H}_3\text{O}^+)$, the ion product of water with $c(\text{H}_3\text{O}^+)$ from equation 9 is used. Similarly, $c(\text{H}_3\text{O}^+)$ from equation 9 is used in equation 5 for $c(\text{Ac}^-)$. Figure 6 shows the result of the calculation.

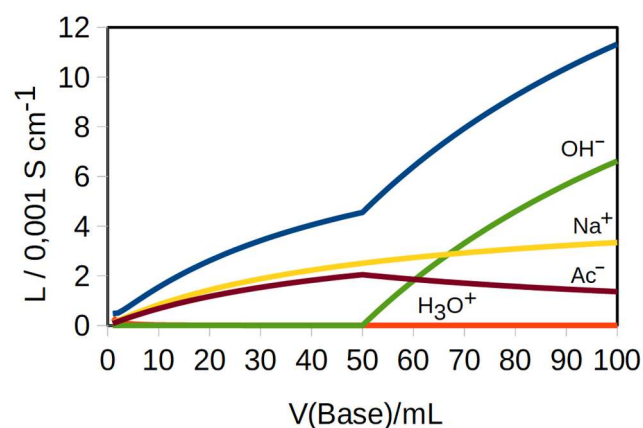


Figure 6: Calculated curve of the conductivity titration of acetic acid ($\text{p}K_a = 4.75$, $V_a = 50$ mL, $c_a = 0.1$ mol/L) with sodium hydroxide solution ($c_b = 0.1$ mol/L). The quadratic approximation was used for the alkaline side (equation 9). In addition, the conductivity of the individual ions is plotted.

3. Conclusion

When modeling the titration curve of a strong acid with a strong base, a quadratic equation in the oxonium ion concentration is obtained. Using approximations, two linear functions in $c(\text{H}_3\text{O}^+)$ (not in V_b) can be derived, which can be easily rearranged to $c(\text{H}_3\text{O}^+)$. The dilution during titration is taken into account via the material balances. Together, the two functions describe the entire titration curve. For weak acids, the mass action law for the dissociation of the acid must be included. It follows that the titration curve must be calculated from a cubic function. Here, too, it is possible to reduce the degree of the function by one using approximations. The quadratic approximation in $c(\text{H}_3\text{O}^+)$ for the base side (equation 9) proves to be particularly powerful, as it can reproduce almost the entire titration curve for $\text{p}K_a > 4$, except for the limiting case of the pH value of the pure weak acid. Furthermore, with a further approximation, a linear function in $c(\text{H}_3\text{O}^+)$ can be obtained, which is, however, limited to the base side.

This example shows how mathematical modeling or simulation of a chemical experiment can also be carried out in a school setting. During the derivation process, students can be supported with learning aids that are helpful in terms of independent work and the heterogeneity of the learning group [24]. Help cards or a derivation puzzle can be used for this purpose. Programs such as GeoGebra or LibreOffice Calc can be used to graphically represent the resulting equations and empirically investigate the influence of the various parameters. Depending on the learning group, modeling can be used in different ways. For example, it is possible to derive the approaches with the students, skip the algebraic manipulations, and then examine the final equations in GeoGebra or LibreOffice Calc. In more advanced groups, parts of the transformations and/or programming can be added. In a basic course, the calculations for strong acids may be sufficient to illustrate the principle. The transition to weak acids is conceivable with a reference to the addition of the mass action law without further

derivations. The results can then be discussed using a GeoGebra program. In advanced courses, it is also conceivable to calculate the titration curve for a weak acid or to assign it as a presentation topic. School experience shows that regular use of mathematical methods in chemistry lessons leads to a familiarization effect. The rejection of mathematics in chemistry lessons, which is reported in the literature, seems to fade when the application of mathematics becomes a regular matter.

In combination with the corresponding student experiments, students learn about the principles and benefits of modeling and simulating experiments. The relevance of mathematics becomes clear and it is possible to practice mathematical transformations in context. In this context, it may also be useful for chemistry teachers to examine the technical and didactic aspects of mathematics that are relevant to chemistry in schools.

A possible application of computers in chemistry teaching described in the literature [8]. That article discusses an interactive simulation using a school mathematics program and a spreadsheet. It avoids the linearity of earlier electronic media criticized by the authors [8] as well as the use of ready-made simulation software. Instead, students can “program” the derived equations and examine them, which of course requires structuring and assistance from the teacher. The sense of achievement that comes from having independently “programmed” the simulation of an experiment can be used to motivate students. In addition, the general importance of modeling and simulation in research and development as well as in today's professional world can also be emphasized. Finally, the application of mathematics in chemistry lessons discussed here, with its implementation in computer programs, also covers parts of current government guidelines such as the NRW-state media competence framework [37].

The modeling process presented here can be structured according to a model from mathematics education. The model of a modeling process according to Blum and Leiss [38] consists of three domains: reality, the chemical model (for a chemical application), and the mathematical domain. They summarize reality and the chemical model as “the rest of the world” in contrast to mathematics. There are a total of seven steps that represent transitions between the areas. Beck et al. [24] have already applied this model to individual chemical questions. The modeling discussed here can be assigned to the model steps in a similar way. The first step is about understanding the problem, i.e., clarifying the topic. Here, for example, this would be the measurement of a titration curve. The second step involves simplifying and structuring the problem. Here, the question of the course of a titration curve is raised, as well as the search for a description of the pH value as a function of the added base volume. It is clarified which variables are relevant and whether they are measured or calculated. This also includes the treatment of the underlying particle model and the balancing of the relevant variables. The possibility of approximations can be taken into account here, even if they are only applied later. Finally, the third step is mathematization, i.e., the transition from the chemical model to the mathematical model. The basic equation is established on the basis of the balances in combination with the particle model. The fourth step is the internal mathematical processing of the problem. Here, this involves deriving the equation for the titration curve by means of algebraic manipulations. However, this also requires references back to chemistry. For example, the question of the sign in the pq formula can only be clarified chemically. The fifth step is the interpretation of the results, which here refers to the recognition of the peculiar course of a titration curve and the identification of special points. This step is the transition back to the chemical problem. The sixth step of validation involves comparing the calculation with experimental results. In addition, different titrations can be simulated by varying the input parameters in the programs. This verifies the chosen solution approach. The seventh step of the presentation is to reconnect the chemical model to the real world. It is clarified whether the model describes reality sufficiently well and whether improvements are necessary. Among other things, possible deviations in the approximation of the infinitely diluted solution [32] can be discussed here.

Appendix

The individual algebraic manipulations that lead to a quadratic equation in the oxonium ion concentration are listed below. It has been found that substituting the variable $c(\text{H}_3\text{O}^+)$ with the variable x commonly used in mathematics is helpful for students. This aids both in further algebraic manipulation and in recognizing the quadratic equation. In principle, the order of transformations is irrelevant, so that one can respond flexibly to the students' suggestions. The order given here was suggested by students. First, the x in the denominator was removed.

$$x + \frac{c_b V_b}{V_a + V_b} = \frac{c_a V_a}{V_a + V_b} + \frac{K_w}{x} \quad | \cdot x$$

Once the students have discovered the quadratic form, the conversion to the pq form $x^2 + px + q = 0$ is achieved by subtracting the terms on the right-hand side:

$$\begin{aligned} x^2 + x \cdot \frac{c_b V_b}{V_a + V_b} &= x \cdot \frac{c_a V_a}{V_a + V_b} + K_w \quad | - x \cdot \frac{c_a V_a}{V_a + V_b} - K_w \\ x^2 + x \cdot \frac{c_b V_b}{V_a + V_b} - x \cdot \frac{c_a V_a}{V_a + V_b} - K_w &= 0 \end{aligned}$$

Then x is excluded. Students who recognize that the denominators are identical arrive at the pq form in one step:

$$x^2 + x \cdot \frac{c_b V_b - c_a V_a}{V_a + V_b} - K_w = 0$$

The solution to this equation, which students have been familiar with since 9th grade and which is used repeatedly in subsequent grades, is:

$$x_{1,2} = -\frac{p}{2} \pm \sqrt{\left(\frac{p}{2}\right)^2 - q}$$

At this point, back substitution should be performed, as the chemical significance of $x = c(\text{H}_3\text{O}^+)$ is required for the following argument. It must be taken into account that only the root with a positive sign is meaningful. Since the first term on the base side beyond the EP is negative, the sign of the root must be positive, otherwise the molar concentration of the oxonium ions would inevitably become negative. It makes sense to clarify the question of the sign at this point and not only mathematically after logarithmization, as it is easy for students to understand that a concentration cannot become negative. The equation for $c(\text{H}_3\text{O}^+)$ follows:

$$c(\text{H}_3\text{O}^+) = -\frac{c_b V_b - c_a V_a}{2(V_a + V_b)} + \sqrt{\frac{(c_b V_b - c_a V_a)^2}{4(V_a + V_b)^2} + K_w}$$

with which the pH value can be calculated $\text{pH} = -\lg(c(\text{H}_3\text{O}^+))$.

References

- [1] Denny, R. T. (1971). The Mathematics Skill Test (MAST) for Chemistry. *J. Chem. Edu.* **48**, 845 – 846.
- [2] Pienta, N. J. (2003). A Placement Examination and Mathematics Tutorial for General Chemistry. *J. Chem. Edu.* **11**, 1244 – 1246.
- [3] Leopold, D. G., Edgar, B. (2008). Degree of Mathematics Fluency and Success in Second-Semester Introductory Chemistry. *J. Chem. Edu.* **85**, 724 – 731.
- [4] Thoms, L.-J., Strahl, A., Müller, R., Formeln im Physikunterricht – eine Lehrerbefragung, Didaktik der Physik. Beiträge zur DPG-Frühjahrstagung in Münster 2011.
- [5] Woest, V., Vischer, S. (1998). Mathematik für das Lehramt Chemie. *CHEMKON* **5**, 118 – 120.
- [6] Parchmann, I., Sieve B. (Hrsg.) Mathematisieren. *Unterricht Chemie*, 24, Heft 134, 2013.
- [7] Reiners, Ch. S., Struve, H. (2011). Gleichungen – Didaktische Implikationen aus der Sicht des Chemie- und Mathematikunterrichts. *PdN-ChiS*, **60**, 35 – 40.
- [8] Eilks, I., Flintjer, B., Krilla, B., Möllencamp, H., Wagner, W. (2004). Computer und Multimedia im Chemieunterricht heute. *CHEMKON* **11**, 121 – 126.
- [9] Gräber, W., Lindner, M., Interessenstudie Chemieunterricht – Vergleich 1990 - 2009. In: Höttecke, D. (Hrsg.) *Chemie- und Physikdidaktik in der Lehramtsausbildung*. Lit-Verlag, Berlin, 92 – 94, 2009.
- [10] Christen, H. R. (1997). Chemie - faszinierend oder ein Horrorfach? *CHEMKON* **4**, 175 – 180.
- [11] Sheppard, K. (2006). High school students' understanding of titrations and related acid-base phenomena. *Chem. Edu. Res. Prac.* **7**, 32 – 45.
- [12] Kimpel, L., Sumfleth, E., Chemieaufgaben: Mathematisierung als schwierigkeits-erzeugender Faktor, In: *Authentizität und Lernen - das Fach in der Fachdidaktik: Gesellschaft für Didaktik der Chemie und Physik: Jahrestagung in Berlin 2015 / GDCP-Jahrestagung*, 14. bis 17. September 2015, Berlin; / Maurer, Christian (Hrsg.), 521 – 523, 2016.
- [13] Goldhausen, I., Mathematische Modelle im Chemieunterricht. Dissertation, ISBN 978-3944072494, Uni-Edition Berlin, 2015.
- [14] Hinrichs, G., Modellierung im Mathematikunterricht. ISBN 978-3-8274-1938-5, Springer, 2008.
- [15] Cox Jr., C. T., Schwartz Poehlmann, J., Ortega C., Lopez, J. C. (2018). Using Writing Assignments as an Intervention to Strengthen Acid-Base Skills. *J. Chem. Educ.* **95**, 1276 – 1283.
- [16] Elcock, A. H. (1999). Realistic Modeling of the Denatured States of Proteins Allows Accurate Calculations of the pH Dependence of Protein Stability. *J. Mol. Biol.* **294**, 1051 – 1062.
- [17] Batstone, D. J., Puyol, D., Flores-Alsina, X., Rodriguez, J. (2015). Mathematical modelling of anaerobic digestion processes: applications and future needs. *Rev. Environ. Sci. Biotechnol.* **14**, 595 – 613.
- [18] da Costa Fo, M. V. A., Normey-Rico, J. E., Modeling, Control and Optimization of Ethanol Fermentation Process. Preprints of the 18th IFAC World Congress Milano (Italy) August 28 - September 2, 2011.
- [19] Pons, M. N., Garrido-Sanchez, L., Dantigny, P., Engasser, J.M. (1990). pH modelling in fermentation broths. *Bioprocess Engineering* **5**, 1 – 6.
- [20] Bothe, D., Waatsack, T., Warnecke H.-J. (2000). Kinetic Modeling of Simultaneous Phosphate Precipitation in Municipal Sewage Treatment Plants. *Chem. Eng. Technol.* **8**, 670 – 674.

- [21] Vieira, J., Fonseca, A., Vilar, V. J. P., Boaventura, R. A. R., Botelho, C. M. S. (2013). Water quality modelling of Lis River. Portugal, Environ. Sci. Pollut. Res. **20**, 508 – 524.
- [22] Strahl, A., Grobe, J., Müller, R., Was schreckt bei Formeln ab? - Untersuchung zur Darstellung von Formeln - Didaktik der Physik Beiträge zur DPG-Frühjahrstagung in Hannover, 2010.
- [23] Blum, W., Modellierungsaufgaben im Mathematikunterricht – Herausforderung für Schüler und Lehrer. In A. Büchter u. a. (Hrsg.) Realitätsnäher Unterricht – vom Fach aus für die Praxis, Hildesheim: Franzbecker, 8 – 23, 2006.
- [24] Beck, U., Markic, S., Eilks, I. (2010). Modellierungsaufgaben im Chemieunterricht. PdN-ChiS **59**, 5 – 9.
- [25] Nakhleh M. B. (1994). Students' Models of Matter in the Context of Acid-Base Chemistry. J. Chem. Edu. **71**, 495 – 499.
- [26] Smith, K. J., Metz, P. A. (1996). Evaluating Student Understanding of Solution Chemistry through Mikroskopische Representations. J. Chem. Edu. **73**, 233 – 235.
- [27] de Levine, R. (1993). Explicit Expressions of the General Form of the Titration Curve in Terms of Concentration. J. Chem. Edu. **70**, 209 – 217.
- [28] Mercier, P. H. (2018). Applying Le Châtelier's Principle To Model Strong Acid-Strong Base Titration. J. Chem. Edu. **95**, 521 – 527.
- [29] Waser, J. (1967). Acid-Base Titration and Distribution Curves, J. Chem. Edu. **44**, 274 – 276.
- [30] Morales, D. A. (2002). Mathematical modeling of titration curves. J. Chemometrics **16**, 247 – 260.
- [31] Heil, G., Schäfer, H. (2002). Modeling and Graphic Presentation of Acid-Base Titration Curves. Presentation of an Alternative Method. Chem. Educator **7**, 339 – 346.
- [32] The pH value is defined by the activity: $\text{pH} = -\lg(a(\text{H}_3\text{O}^+))$. In the limit of infinite dilution, the activity becomes the molar concentration. As customary in school chemistry, the approximation $\text{pH} \approx -\lg(c(\text{H}_3\text{O}^+))$ is used here, which is more accurate the lower the oxonium ion concentration is. When comparing measured values (see Online Supporting Information)
- [33] Gran, G. (1950). Determination of the Equivalent Point in Potentiometric Titrations. Acta Chem. Scand. **4**, 559 – 577.
- [34] Brewersdorf, J., Algebra für Einsteiger. Springer, 5. Auflage, ISBN 978-3-6580-2261-7, Springer Vieweg, 2013.
- [35] Glaister, P. (1994), A titration model an analysis and solution. Int. J. Math. Educ. Sci. Tech. **25**, 399 – 406.
- [36] One might assume that the product $K_W \cdot K_S$ is so small that one could neglect q under the root of the formula, which would lead to $c(\text{H}_3\text{O}^+) = -p$ after factoring out the quadratic equation. In fact, neglecting q leads to a sign change under the root at the equivalence point.
- [37] Medienkompetenzrahmen des Landes NRW, Herausgeber: Medienberatung NRW, Münster / Düsseldorf, 2. Auflage 2018, <https://www.medienpass.nrw.de/de>
- [38] Blum, W., Leiss, D., (2005). Modellieren im Unterricht mit der „Tanken“-Aufgabe. mathematik lehren **128**, 18 – 21.

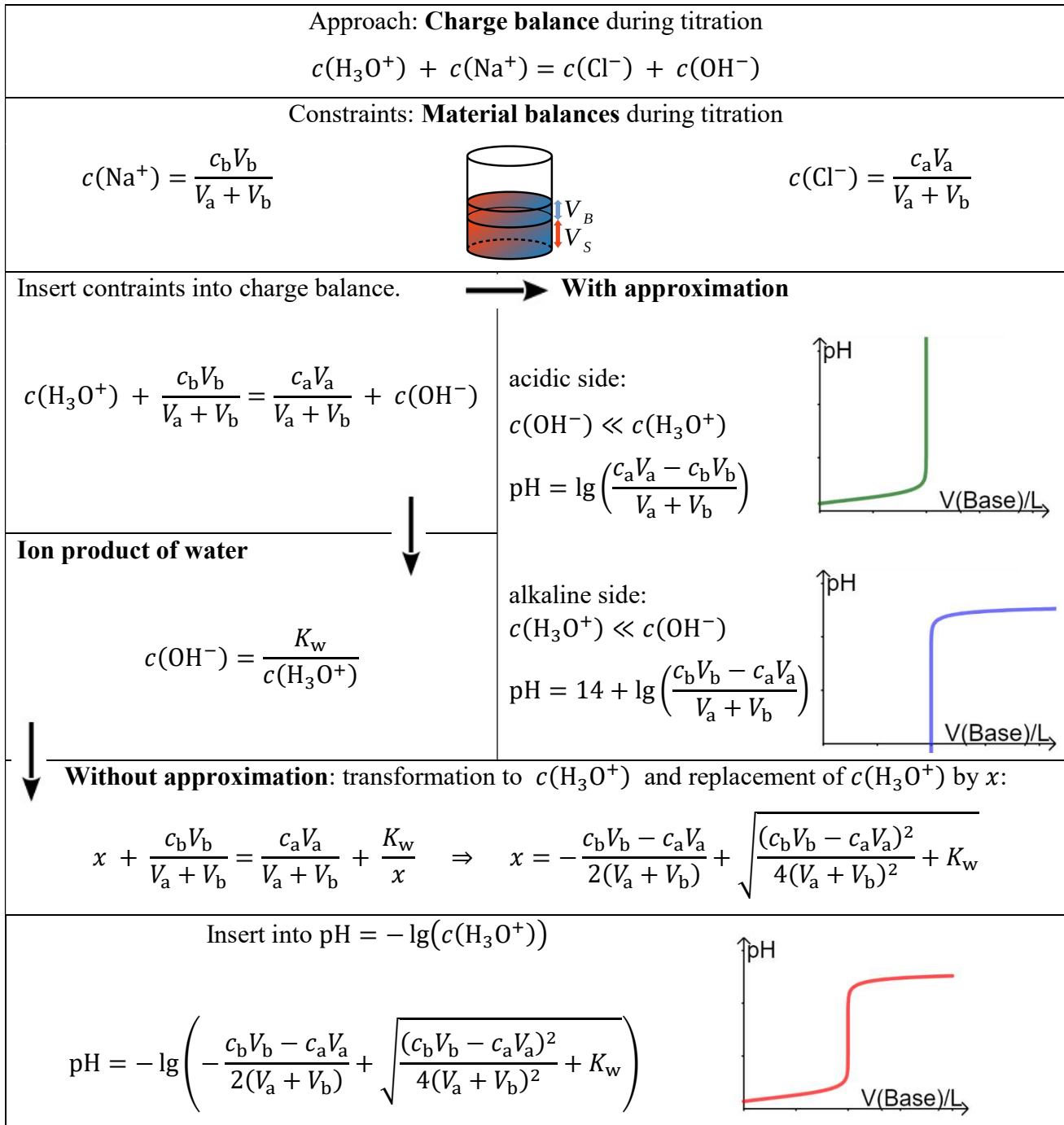


Diagram 1: Overview of the derivation of the pH-equation for the titration of a strong acid with a strong base. The diagram also contains the approximations for both sides of the titration curve. In the case of a weak acid, the mass action law must be introduced in the secondary conditions.