Acid-Base Titration Curves in an Integrated Computer Learning Environment

André Heck[1], Ewa Kędzierska[1], Laurence Rogers[2], Małgorzata Chmurska[3]

[1] AMSTEL Institute, Universiteit van Amsterdam, The Netherlands,
heck@science.uva.nl, miodus@science.uva.nl
[2] School of Education, University of Leicester, United Kingdom, lto@leicester.ac.uk
[3] Ośrodek Edukacji Informatycznej i Zastosowań Komputerów (OEIiZK), Warsaw, Poland,
mchmur@oeiizk.waw.pl

Abstract

The topic of acid-base reactions is a regular component of many chemistry curricula that requires integrated understanding of various areas of introductory chemistry. Many students have considerable difficulties understanding the concepts and processes involved. It has been suggested and confirmed by research that students may be benefit from computer-supported activities such as data logging, simulation and modeling. In this paper we review the different methods of using computer acquisition and modeling to examine acid-base titration and we discuss how a versatile, integrated computer learning environment can be successfully applied to this end. The environment integrates, amongst other things, measurement, a control tool, and a modeling tool: using an inexpensive step-motor buret, automated pH measurement in acid-base titration can be realized and measured data can then be compared graphically and in tabular form with data computed via the (text-based or graphical) system dynamics modeling tool. In this paper we discuss concrete examples, taken from an in-service teacher training course and culminating in the student practical investigation of analysis of acid in soft drinks. We also show how computer algebra can assist to find the mathematical formulas needed for computing a titration curve. We discuss the design of instructional materials and the didactical approach of integrating data logging and modeling in acid-base chemistry education.

Introduction

The topic of acid-base reactions is a regular component of many chemistry curricula. This topic requires integrated understanding of various areas of introductory chemistry. Many students have considerable difficulties understanding concepts and processes involved in this topic. For example, students often have difficulties in understanding

- and distinguishing between different acid-base models (at phenomenological level as properties of substances, at phenomenological and particulate level by the Arrhenius model, and at particulate level via the Brønsted-Lowry model and the more advanced Lewis model)[1-3], models which may be treated in the chemistry textbooks for grade 12 and university chemistry students in an incoherent way[4,5] that leads the teacher's pedagogical content knowledge in the wrong direction;[6]
- amphoteric substances and in particular understanding water as an acid or a base depending on reaction conditions;[7]
- the difference between acid strength and concentration;[8,9]
- the pH scale, e.g., understanding the inverse and logarithmic nature of the pH scale;[8]
- the change of the value of pH during a titration;[8]
- the meaning of neutralization;[9-11]
- the difference between 'equivalence point' and 'neutral point' (pH = 7) in acid-base titration.[1,11-13] Students assume that acid-base reactions always result in a neutral solution;

- the calculation of a single curve via separate calculations for different stages of titration, using different sets of simplifying assumptions;[14-16]
- the acid-base terminology and distinguishing between scientific and everyday language;[10]
- chemical change and equilibrium.[3,12,17]

Many of the referred research papers about the students' difficulties in understanding of titration and related acid-base phenomena contain the suggestion that students can benefit, at secondary school level and beyond, from computer-supported activities ranging from computer-assisted instruction[18], data logging (MBL & CBL)[*] [19-24] and spreadsheet calculations[25-29] to simulations and computer modeling[30,31]. Sheppard[8] stated it explicitly as follows: *"This research suggest that MBLs, with their real time display of results and almost immediate feedback, when used with prediction – observation – explanation (POE) techniques can provide a powerful tool for probing student conceptual understanding of a variety of topics. Student understanding of other areas of chemistry could be similarly investigated."* Nakhleh and Krajik[32,33] investigated how different levels of information, presented by various technologies, affected the focus of high school students' observations during the process of titration and how they influenced the students' understanding of acid-base and pH concepts. They found that students using MBL focused primarily on the pH titration graph, whereas other groups exhibited multiple foci, and that the order of the influence of technology on understanding was MBL > chemical indicator > pH meter. However, Suits, Kunze and Diack[23] found that even successful chemistry students possess misconceptions regarding the particulate level in titration experiments and they noted that use of MBL technology does not automatically conjure up images of interactions of ions at the particulate level. They identified the need to complement MBL technology with interactive multimedia simulations that represent the phenomenon being studied with MBL in the laboratory. Thomas *et al* [34] reported that students from a typical secondary school in Hong Kong who studied acid-base equilibrium via MBL identified similar benefits for their learning as MBL advocates. But they also identified issues related to (a) lack of technical familiarity with the MBL, (b) differences between using computers at home and the MBL, and (c) the nature of learning occurring through the use of MBL. What is clear from this and other studies is that it should not be assumed that students would instantly be competent and confident in the use of MBL and have a nice range of understanding of its benefits. What strikes us is that in these studies, the possibility of using system dynamics simulation and modeling software like STELLA or Powersim for the calculation of titration curves and for the comparison of real data with modeling results seems to have been overlooked or not promoted. In this paper we pay attention this.

Another point of discussion is that we think that, despite the continuous growth of ICT use in chemistry education, still insufficient light has been shed on the several layers of complexity of scientific instrumentation and software when it comes to real use by secondary school teachers and students in the classroom. Computer-based laboratory experiments can only be realized when students and teachers get ample opportunities to acquaint themselves with equipment and software. But time is a limited resource in education, especially at secondary school level. Here every subject taught competes with others that may come from completely different fields. One better spends time and effort on learning to work with tools that can be re-used over and over again in a variety of teaching and learning circumstances, including many science fields. This could also contribute to the realization of transfer of knowledge and skills between the sciences.

With this in mind, the use of graphical calculators, augmented with measurement tools, and the use of spreadsheets combined with data collection programs on a computer have been

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[*] MBL (Microcomputer-Based Laboratory) and CBL (Calculator-Based Laboratory) are devices that collect data with various probes and then store the data into a computer or calculator for data representation and analysis.

advocated. But from our point of view, these tools form more or less a grab bag of equipment and software that do only part of the job, do not work well together, are still limited in scope, cannot be easily adjusted to the appropriate level of the students, and provide students an inadequate picture of what is in reality used on the shop floor of laboratories. What is more beneficial is an affordable suite of adjustable tools that match well with one another, or even better an integrated computer workplace that can be used in all mathematics and science disciplines at various levels of education – from primary school up to university – so that a growth path for students can be realized. Such suites of tools and more complete learning environments exist at present.[35]

In this paper we discuss what can be realized in a single computer learning environment that integrates many tools. We will use Coach,[36] which is widely used at secondary schools in the Netherlands and in other countries, with extensions towards primary education and higher education. It has been developed for educational purposes, offering students genuine scientific experiences, but as we will see it has strong resemblance with present-day professional tools. Coach can be briefly described as a versatile learning and authoring environment for mathematics, science, and technology education that integrates tools for

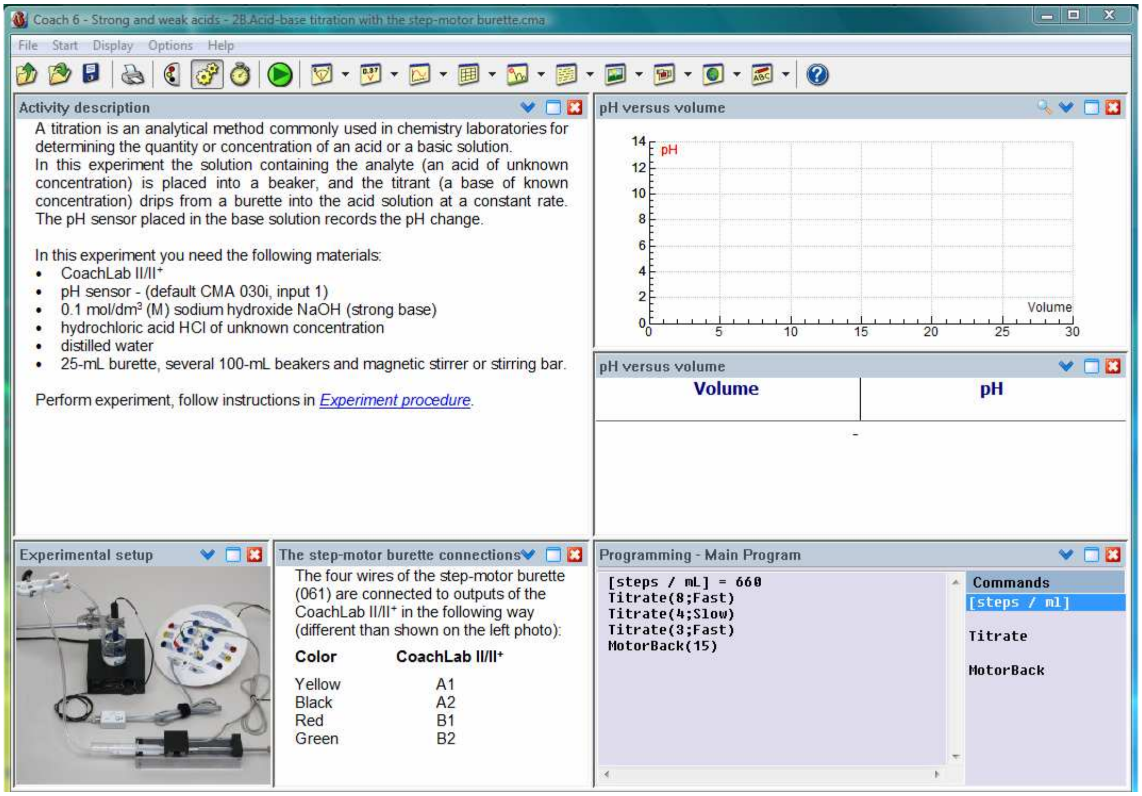
- Measurement – online and offline with interfaces, data loggers, and sensors;
- Control of devices (e.g., motors) and processes (e.g., automated titration);
- Data video – measurement on digital video clips (capturing of own movies included) and digital images;
- Processing and analysis of data (e.g., data smoothing, differentiation, regression analysis);
- Modeling (text-based, equation-based, and graphical approach to system dynamics;
- Simulation and animation of modeled phenomena;
- Representation of measured data and computed results (graphs, tables, meters, etc.);
- Authoring by instructors and students (formatted texts, multimedia components, hyperlinks to external resources, etc.).

The instructional module presented in this paper offers activities in which students mainly use measurement, control, data processing, modeling, and authoring tools to analyze acid-base reactions and differences in behavior of strong and weak acids in solution. The work was developed during the Socrates Comenius project ‘IT for US – Information Technology for Understanding Science’. This project[37] took place between 2005 and 2008 and aimed to design a modular in-service training course for science teachers and to create the supporting courseware materials. The distinctive feature of this project was that it brought together teacher trainers, science education researchers and curriculum developers with extensive experience in innovations with information and communication technology (ICT). The project was founded on the belief that there is an unfulfilled need for teacher training materials to promote the implementation of ICT tools that serve for constructing new information and understanding. The ICT tools concerned are mainly those involving data logging, simulation and modeling. The purpose of this approach was explicitly to promote teachers' and students' thinking about the meaning of data, employing the principle of social constructivism.

Data Logging with an Automated pH Titration System

Traditionally, in a laboratory experiment of acid-base titration performed with a buret – pH meter system, a student delivers small increments, dropwise at times, from a buret, records pH as a function of titrant volume (perhaps CBL-based), and constructs the pH versus volume plot for further analysis to determine the unknown concentration of the sample and/or the ionization constant of the substance in the sample. The data analysis can be done by pencil-and-paper, with the help of a graphing calculator, or via a spreadsheet. However, doing both the data logging and data analysis on a computer in a single environment has the following pedagogical advantages: it eliminates tedious and repetitious operations, allowing the students to concentrate on data analysis, on design of experiments, and on comparison of measured data with predictions from a chemical model. In addition, use of an automated pH titration system offers students the opportunity to work directly with high-quality data in much the same way as is practiced in professional chemistry laboratories. They learn then how a computer is not only used to measure data via sensors, but also can simultaneously control addition of reagents. Last but not least, in an integrated computer environment students can process and analyze their collected data and report their findings. All this is not still in the future at secondary school level, but already available. For example, Witteck and Eilks[38] presented a field tested lesson plan that follows a new and innovative approach to learning acid-base chemistry through an instructional model based on an idealized company, Max Sour Ltd, in which students learn besides chemistry how processes in a company occur. In this 'learning company' approach students' learning takes completely place via simulations of practical, profession-oriented tasks in business. This puts more emphasis on student activity in the planning, evaluating and reporting phases of experiments. In this instructional setting it is natural that students' laboratory techniques would be similar to professional laboratory methods. The Coach learning environment would be suitable for this approach.

Figure 1 is a screen shot of a Coach activity, in which an inexpensive step-motor buret is used to control accurately titration of a strong acid with a strong base. We show the activity in the format as it was prepared for students' use by the author of the activity. This author could have been a developer of curriculum materials, a teacher, or even a student. This screen shot shows several multimedia components: a picture of the equipment and the experimental set-up, text frames for explanations and instructions, a frame with the initial computer program to control the step-motor buret, a table window, and a graph window.



A titration is an analytical method commonly used in chemistry laboratories for determining the quantity or concentration of an acid or a basic solution.
In this experiment the solution containing the analyte (an acid of unknown concentration) is placed into a beaker, and the titrant (a base of known concentration) drips from a burette into the acid solution at a constant rate. The pH sensor placed in the base solution records the pH change.

In this experiment you need the following materials:
- CoachLab II/II$^+$
- pH sensor - (default CMA 030i, input 1)
- 0.1 mol/dm^3 (M) sodium hydroxide NaOH (strong base)
- hydrochloric acid HCl of unknown concentration
- distilled water
- 25-mL burette, several 100-mL beakers and magnetic stirrer or stirring bar.

Perform experiment, follow instructions in *Experiment procedure*.

Volume	pH
-	

The four wires of the step-motor burette (061) are connected to outputs of the CoachLab II/II$^+$ in the following way (different than shown on the left photo):

Color	CoachLab II/II$^+$
Yellow	A1
Black	A2
Red	B1
Green	B2

```
[steps / mL] = 660
Titrate(8;Fast)
Titrate(4;Slow)
Titrate(3;Fast)
MotorBack(15)
```

```
Commands
[steps / ml]

Titrate

MotorBack
```

Figure 1. Screen shot of a Coach activity on titration with an automated pH titration system.

Modeling

We discuss in this section both the mathematical modeling of acid-base titration and the computer modeling with a system dynamics simulation and modeling tool.

Mathematical Modeling

Typically, an acid-base titration curve is dissected into two segments, namely, before and after the equivalence point has been reached. In addition, separate calculations are done for the different segments in one of the following three ways:

1. Via approximate formulas that hold at certain stages of titration;
2. Via exact or approximate methods to compute the pH for a given titrant volume. This leads to the problem of solving a polynomial equation in [H_2Slv^+], where the solvent is denoted by HSlv and its autoionization is $2\mathrm{HSlv} \rightleftarrows \mathrm{H_2Slv^+} + \mathrm{Slv^-}$;
3. As the inverse of the progress curve, that is, the graph showing the titrant volume as function of pH, determined with or without making approximations. In this case we compute for a given pH what the corresponding titrant volume should be.

In the first method, which is still the common textbook treatment, separate approximate formulas are used for the starting point of the titration curve, for the equivalence point, and for points in between. Autoionization of the solvent is in most cases ignored. For acid-base titration in water, within a maximum error of 1%, autoionization may be ignored for pH less than 6 and greater than 8. Other approximations are also possible under certain conditions.[39-41] For example, for titration of a monoprotic weak acid with a strong base one commonly uses the following equations to calculate pH at several stages of titration:

1. At the starting point: $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{a} - \frac{1}{2}\log C_\mathrm{a}$, where C_a is the initial acid concentration and pK_a is the negative logarithm (base 10) of the acid ionization constant K_a.
2. After addition of the base, but before the equivalence point is reached, one uses the Henderson-Hasselbalch equation: $\mathrm{pH} = \mathrm{p}K_\mathrm{a} - \log\left(\frac{[\mathrm{acid}]}{[\mathrm{base}]}\right)$. Halfway to the equivalence point, when the current molar concentrations of acid and the salt formed by the reaction (acting as a base) are equal, $\mathrm{pH} = \mathrm{p}K_\mathrm{a}$.
3. At the equivalence point: $\mathrm{pH} = \frac{1}{2}\mathrm{p}K_\mathrm{a} + \frac{1}{2}\mathrm{p}K_\mathrm{Slv} + \frac{1}{2}\log S$, where p$K_\mathrm{slv}$ is the negative logarithm of the solvent autoionization constant K_Slv and S is the molar concentration of the salt that is present after the reaction of the acid with a stoichiometrically equal amount of base.
4. Beyond the equivalence point: $\mathrm{pH} = \mathrm{p}K_\mathrm{Slv} + \log B$, where B is the concentration of the excess base present in the solution.

The only thing to take carefully into account in computations of the molar concentrations used in the above expressions is that during titration volume changes and therefore dilution takes place. The effect of dilution on the computed pH is small, but cannot be neglected if titrations are used to find the ionization constant pK_a.[42]

A drawback of the above method is that many a student gets confused by all those mathematical formulas and has no clear idea why one has to consider these distinct stages in titration and under what simplifying assumptions the formulas can be applied safely. For example, when the above formula for the starting point is applied with a very small acid concentration, one gets a much too high pH value, which may even indicate a basic solution instead of acidic solution. When the Henderson-Hasselbalch equation is applied with very small titrant volumes to compute the very first part of the titration curve, addition of the base leads first to a smaller pH before it rises again, which is of course very strange. These problems can only be solved by more robust mathematical methods. But these methods may be beyond the algebraic skills of many a student. In that case, as we will see, a computer algebra system could give a helping hand.

Explicit expressions for the shape of several aqueous acid-base titration curves have been published before by Gordus[43] and de Levie.[44,45] We show how the Gröbner basis technique,[46,47] which is implemented in computer algebra systems like Maple or *Mathematica*, can be used to derive the required polynomial equation in $[H_3O^+]$. In order to make formulas more readable we write henceforth $[H^+]$ instead of $[H_3O^+]$. The Gröbner basis technique can also be applied to derive an explicit expression of the progress curve (graph of titrant volume against pH). In our example we treat only the titration of one monoprotic weak acid with an aqueous strong monoprotic base and we ignore activity coefficients, i.e., we use 'apparent' equilibrium constants. It is possible to derive unified titration formulas that embrace several types of titration[48]. Generalizations to titration of mixtures of acids or bases, to the polyprotic case, to general solvents, and to titration of bases with acids are not too complicated, and the same computer algebra supported approach can be extended to complexation, precipitation, and redox equilibria[49].

To introduce the use of the Gröbner basis package in the derivation of the relationship between pH and titrant volume, we consider the titration of a volume V_a of a weak monoprotic acid HA of concentration C_a with the volume V_b of an aqueous strong monoprotic base MOH of concentration C_b. In this case, the equilibrium $HA + H_2O \rightleftarrows H_3O^+ + A^-$ is constantly disturbed by adding a strong base: $HA + MOH \rightarrow H_2O + M^+ + A^-$. The exact formula for $[H^+]$ at any moment during the titration can be derived as follows from three conditions:

1. Charge balance: $[H^+]+[M^+]=[OH^-]+[A^-]$.

2. Mass balance: $[HA]+[A^-]=C_a\cdot\dfrac{V_a}{V_a+V_b}$ (partial ionization of weak acid).

$[M^+]=C_b\cdot\dfrac{V_b}{V_a+V_b}$ (complete ionization of strong base).

3.Equilibrium: $\dfrac{[A^-][H^+]}{[HA]}=K_a$ (chemical equilibrium of weak acid).

$[H^+]\cdot[OH^-]=K_w$ (autoionization of water)

To make upcoming formulas more readable and comparable with formulas found in the literature we introduce the following 'apparent initial concentrations' of acid and base:

$$a_{HA}=C_a\cdot\frac{V_a}{V_a+V_b}\ \text{and}\ a_{MOH}=C_b\cdot\frac{V_b}{V_a+V_b}.$$

These are the acid and base concentrations during titration when no reaction would have taken place, but only dilution is taken into account. In addition, it turns out to be convenient to introduce the concentration fraction α_{A^-} as $[A^-]=\alpha_{A^-}\cdot a_{HA}$. It can be shown that

$$\alpha_{A^-}=\frac{[A^-]}{[HA]+[A^-]}=\frac{K_a}{[H^+]+K_a}.$$

All we have to do now is to rewrite the above system of equations as a system of polynomial equations. The defining polynomials are shown in the below snapshot of a Maple session. The Gröbner basis package of Maple contains the procedure UnivariatePolynomial that returns for a system of polynomial equations under some suitable assumptions a univariate polynomial in one of the variables. In our case, we ask for a polynomial in $[H^+]$ and write the computer-generated answer in its simplest form: a univariate polynomial of degree 3 is obtained. The assumption that autoionization of water can be ignored is realized by substituting $K_w = 0$ in the univariate polynomial. This leads to a simpler polynomial of degree 2.

```
> WeakAcidStrongBaseSystem := < H_plus+M_plus-A_min-OH_min,
   (HA_+A_min)*(Va+Vb)-Ca*Va,M_plus*(Va+Vb)-Cb*Vb,
   A_min*H_plus-Ka*HA_, H_plus*OH_min-Kw, a_HA*(Va+Vb)-Ca*Va,
   a_MOH*(Va+Vb)-Cb*Vb,(HA_+A_min)*alpha_A_min-A_min >;
```

$$\mathit{WeakAcidStrongBaseSystem} := \langle [A^-]\,[H^+] - K_a\,[HA],\ [H^+]\,[OH^-] - K_w,$$
$$[M^+]\,(V_a+V_b) - C_b\,V_b,\ a_{HA}\,(V_a+V_b) - C_a\,V_a,\ a_{MOH}\,(V_a+V_b) - C_b\,V_b,$$
$$([HA]+[A^-])\,\alpha_{A^-} - [A^-],\ ([HA]+[A^-])\,(V_a+V_b) - C_a\,V_a,$$
$$[H^+] + [M^+] - [A^-] - [OH^-]\rangle$$

```
> UnivariatePolynomial(H_plus, WeakAcidStrongBaseSystem,
    {Ca,Cb,OH_min,A_min,M_plus,HA_,alpha_A_min,H_plus});
```

$$-K_w\,K_a + [H^+]\,a_{MOH}\,K_a + [H^+]^2\,K_a + [H^+]^2\,a_{MOH} - K_a\,a_{HA}\,[H^+] - [H^+]\,K_w + [H^+]^3$$

```
> polynomial := collect(%, [H_plus,Ka], factor);
```

$$\mathit{polynomial} := [H^+]^3 + (K_a + a_{MOH})\,[H^+]^2 + ((a_{MOH} - a_{HA})\,K_a - K_w)\,[H^+] - K_w\,K_a$$

```
> approximation := collect(eval(%, Kw=0)/H_plus, H_plus, factor);
```

$$\mathit{approximation} := [H^+]^2 + (K_a + a_{MOH})\,[H^+] - (-a_{MOH} + a_{HA})\,K_a$$

The positive root of this polynomial of degree 2 can be found by standard methods:

$$[\mathrm{H}^+] = \frac{-(a_{\mathrm{MOH}} + K_{\mathrm{a}}) + \sqrt{(a_{\mathrm{MOH}} + K_{\mathrm{a}})^2 + 4K_{\mathrm{a}}\cdot(a_{\mathrm{HA}} - a_{\mathrm{MOH}})}}{2}$$

Using this formula for the various stages in acid-base titration, a student can derive simpler formulas, sometimes under additional assumptions. For example, prior to the equivalence point, if $K_a \cdot (a_{\mathrm{HA}} - a_{\mathrm{MOH}}) << (a_{\mathrm{MOH}} + K_a)^2$, the above formula can be approximated by computing a low-order Taylor series in $a_{\mathrm{HA}} - a_{\mathrm{MOH}}$:

$$[\mathrm{H}^+] \approx \frac{(a_{\mathrm{HA}} - a_{\mathrm{MOH}})\cdot K_{\mathrm{a}}}{(a_{\mathrm{MOH}} + K_{\mathrm{a}})}$$

In other words, when K_a is small compared to the added amount of base, we can take

$$\mathrm{pH} \approx pK_{\mathrm{a}} - \log\left(\frac{a_{\mathrm{HA}} - a_{\mathrm{MOH}}}{a_{\mathrm{MOH}}}\right).$$

So, the Henderson-Hasselbalch equation is found with the help of a computer algebra system as a special case of a more general formula.

In summary, the Gröbner package of a modern computer algebra system can support the derivation of general mathematical formulas required for acid-base reactions. We think that this approach is feasible for chemistry students at university level. For secondary school students however, it focuses in our opinion too much on mathematical concepts and techniques instead of on chemical concepts. At this level, students will learn more when they first determine experimentally in laboratory sessions some titration curves to get a feeling for what a titration curve is, how it is created, what is its shape in general, and how it can be interpreted. After this practical experience students can use computer models to explore titration curves in more detail without having the need to calculate themselves pH by mathematical formulas that are actually meaningless to them. With the computer models they can compare, for example, experimental titration curves with theoretical curves, determine ionization constants from real data, or explore buffer solutions.

The same computer algebra supported approach can be applied to find the defining polynomial equation of the progress curve. The below snapshot of a Maple session shows the computation of a third degree polynomial in [H$^+$]; the result is equal to Formula (8) in reference [20] and it is equivalent to the formula previously found in this paper. The titrant volume V_b is linear in this mathematical formula and this is the reason that it is so easy to compute the titrant volume as a rational function in [H$^+$].

```
> WeakAcidStrongBaseSystem := < H_plus+M_plus-A_min-OH_min,
    (HA_+A_min)*(Va+Vb)-Ca*Va, M_plus*(Va+Vb)-Cb*Vb,
     A_min*H_plus-Ka*HA_, H_plus*OH_min-Kw >;
```

$$\mathit{WeakAcidStrongBaseSystem} := \langle [A^-]\,[H^+] - K_a\,[HA], [H^+]\,[OH^-] - K_w, [M^+]\,(V_a + V_b) - C_b\,V_b, ([HA] + [A^-])\,(V_a + V_b) - C_a\,V_a, [H^+] + [M^+] - [A^-] - [OH^-]\rangle$$

```
> UnivariatePolynomial(H_plus, WeakAcidStrongBaseSystem,
   {OH_min,A_min,M_plus,HA_,H_plus});
```

$$-[H^+]\,V_a\,K_w - [H^+]\,K_a\,C_a\,V_a + V_a\,[H^+]^3 + V_a\,K_a\,[H^+]^2 - V_a\,K_a\,K_w + [H^+]^3\,V_b + [H^+]\,C_b\,V_b\,K_a - [H^+]\,V_b\,K_w - K_w\,K_a\,V_b + [H^+]^2\,K_a\,V_b + [H^+]^2\,C_b\,V_b$$

```
> polynomial := collect(%/(Va+Vb), [H_plus,Ka], factor);
```

$$\mathit{polynomial} := [H^+]^3 + \left(K_a + \frac{C_b\,V_b}{V_a + V_b}\right)[H^+]^2 + \left(-\frac{(C_a\,V_a - C_b\,V_b)\,K_a}{V_a + V_b} - K_w\right)[H^+] - K_a\,K_w$$

```
> Vb = collect(solve(polynomial,Vb), H_plus, factor);
```

$$V_b = \frac{\left(-[H^+]^3 - K_a\,[H^+]^2 + (C_a\,K_a + K_w)\,[H^+] + K_a\,K_w\right)V_a}{[H^+]^3 + (K_a + C_b)\,[H^+]^2 + (K_a\,C_b - K_w)\,[H^+] - K_a\,K_w}$$

It can be shown that this formula is equivalent to Formula (13) published by de Levie:[50]

$$\frac{V_\mathrm{b}}{V_\mathrm{a}} = \frac{\dfrac{K_\mathrm{a}}{[\mathrm{H}^+] + K_\mathrm{a}}C_\mathrm{a} - \left[\mathrm{H}^+\right] + \dfrac{K_\mathrm{w}}{\left[\mathrm{H}^+\right]}}{C_\mathrm{b} + \left[\mathrm{H}^+\right] - \dfrac{K_\mathrm{w}}{\left[\mathrm{H}^+\right]}},$$

Thus, given pH and therefore given [H$^+$], one can use the above formula to compute a corresponding titrant volume V_b. The computed pair (pH, V_b) can be used either to plot the progress curve (graph of V_b as function of pH) or the titration curve (graph of pH as function of V_b). It is true that the titration curve is the inverse of the progress curve, but the understanding of this kind of relationship between graphs is at secondary school level, in our point of view, more an issue to be discussed in a mathematics lesson than in a chemistry lesson. Chemistry education at secondary school better focuses on chemical concepts and contexts than on mathematical applications in chemistry labs. Some may say that the above type of mathematical analysis is beyond the scope of freshmen level chemistry as well, and that it is only suitable for an analytical chemistry course, in which use the more complicated, albeit complete, mathematical formulas to estimate the error of approximate methods. Anyway, computer models, which are based on this mathematical analysis of acid-base titration, do the job of allowing students to compare measured titration curves with theoretical curves and to further explore model titration curves.

Computer Modeling

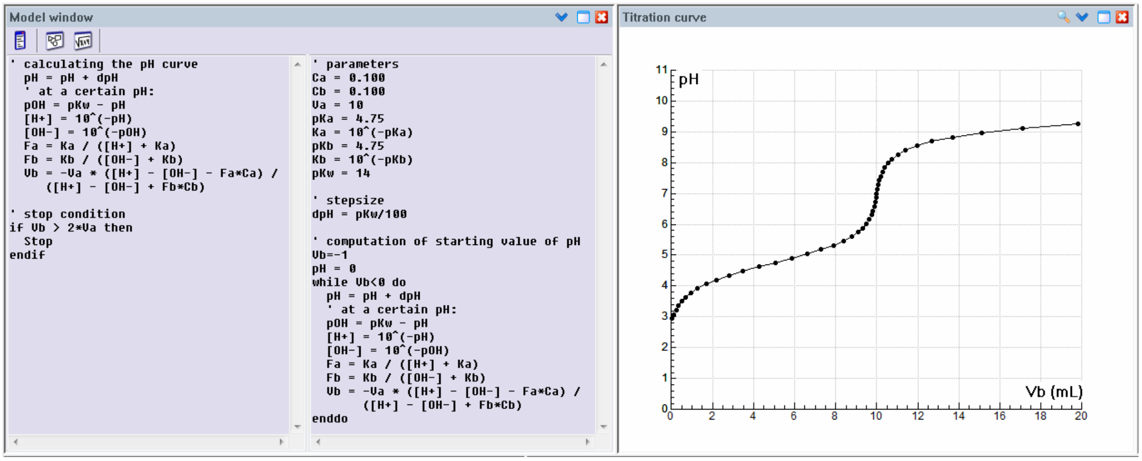
We think that the main reason for overlooking system dynamics simulation and modeling software like STELLA or Powersim for the calculation of titration curves is that when one concentrates on mathematical formulas of titration, system dynamics does not easily come into mind because this mathematical field is linked with differential equations. Thus, use of such software seems more appropriate for studying chemical kinetics.[51-53] However, these packages are nothing more, nor less than computer programs that can also be used to specify relationships between variables and to compute how these relationships evolve. We illustrate this by two computer models that compute the progress curve and the titration curve. For this we use the Coach 6 environment, but the work can also be done with other system dynamics modeling tools. The first model is a text-based and shows all details of the computer code for titration of a monoprotic acid with a monoprotic base. The second one is a graphical model for titration of a diprotic acid with an aqueous strong monoprotic base. The calculation of the progress curves for a titration of a sample of volume V_s and concentration C_s with a titrant volume V_t and titrant concentration C_t is based on Equation (8) of reference [49], stated in the following general form with details hidden in functions F_s and F_t of [H$^+$] and coefficients K_a:

$$V_\mathrm{t} = -V_\mathrm{s} \cdot \frac{\left[\mathrm{H}^+\right] - \left[\mathrm{OH}^-\right] + \sum F_\mathrm{s} C_\mathrm{s}}{\left[\mathrm{H}^+\right] - \left[\mathrm{OH}^-\right] + \sum F_\mathrm{t} C_\mathrm{t}} \,.$$

Here $F = -F_a = F_b$ for each species participating in the titration (index “a” refers to acid and “b” to base). The summation is only needed for mixtures, where each component contributes its own F and its own concentration C.

In case of titration of a monoprotic acid with a monoprotic base we have to take into account the following chemical equilibria $2\mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{OH^-}$, $\mathrm{HA} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+} + \mathrm{A^-}$ and $\mathrm{H_2O} + \mathrm{B} \rightleftarrows \mathrm{BH^+} + \mathrm{OH^-}$. We have

$$F_\mathrm{s} = -F_\mathrm{a} = -\alpha_{\mathrm{A}^-} = -\frac{K_\mathrm{a}}{[\mathrm{H}^+] + K_\mathrm{a}} \text{ and } F_\mathrm{t} = F_\mathrm{b} = \alpha_{\mathrm{BH}^+} = \frac{K_\mathrm{b}}{[\mathrm{OH}^-] + K_\mathrm{b}} = \frac{[\mathrm{H}^+]}{[\mathrm{H}^+] + K_\mathrm{a}} \,.$$



```
' calculating the pH curve
  pH = pH + dpH
  ' at a certain pH:
  pOH = pKw - pH
  [H+] = 10^(-pH)
  [OH-] = 10^(-pOH)
  Fa = Ka / ([H+] + Ka)
  Fb = Kb / ([OH-] + Kb)
  Vb = -Va * ([H+] - [OH-] - Fa*Ca) /
     ([H+] - [OH-] + Fb*Cb)

' stop condition
if Vb > 2*Va then
  Stop
endif
```

```
' parameters
Ca = 0.100
Cb = 0.100
Va = 10
pKa = 4.75
Ka = 10^(-pKa)
pKb = 4.75
Kb = 10^(-pKb)
pKw = 14

' stepsize
dpH = pKw/100

' computation of starting value of pH
Vb=-1
pH = 0
while Vb<0 do
  pH = pH + dpH
  ' at a certain pH:
  pOH = pKw - pH
  [H+] = 10^(-pH)
  [OH-] = 10^(-pOH)
  Fa = Ka / ([H+] + Ka)
  Fb = Kb / ([OH-] + Kb)
  Vb = -Va * ([H+] - [OH-] - Fa*Ca) /
       ([H+] - [OH-] + Fb*Cb)
enddo
```

Figure 2. Computer model of weak acid - weak base titration

Figure 2 shows a screen shot of a text-based computer model that uses the above formulas to compute the progress curve (V_t as function of pH). The corresponding titration curve (pH as function of V_t) is drawn in the diagram next to the computer model. To make things more concrete, we consider here the titration of acetic acid (pK_a = 4.75 at 25°C) with aqueous ammonia (pK_b = 4.75 at 25°C), with concentrations $C_a = C_b = 0.100$ M.

You see in Figure 2 a model window that contains on the left-hand side the core of the text-based computer model and on the right-hand side parameters and initialization code. Text after an apostrophe is meant for explanation of the program and is not used during a simulation. You can look at the computer model as a sequence of instructions on the left-hand side that are repeatedly carried out until some stop condition is fulfilled or the maximum number of iterations has been reached. The instructions on the right-hand side of the model window are carried out only once: initial values of parameters are set and we compute in a repetition loop a starting value of pH that leads to a nonnegative titrant volume V_b. An alternative would be to estimate the initial H^+ concentration as $[H^+]_{\text{initial}} \approx \dfrac{-K_a + \sqrt{K_a{}^2 + 4K_a \cdot C_a}}{2}$.

The text-based model reveals all details of the program and all formulas used, but it gives students no visual clues of relationships between variables used in the model. This makes it more difficult for students to understand the model and to let them develop the computer model. A graphical modeling tool offers more support for a classroom discussion about relationships of variables and it may help visually oriented students to develop a computer model. Figure 3 shows a screen shot of a graphical model of titration of a weak diprotic acid with an aqueous strong monoprotic base. In this case we have to take into account the equilibria $2H_2O \rightleftarrows H_3O^+ + OH^-$, $H_2A + H_2O \rightleftarrows HA^- + H_3O^+$ and $HA^- + H_2O \rightleftarrows A^{2-} + H_3O^+$, and the ionization $MOH \rightarrow M^+ + OH^-$. We use the following formula to compute the progress curve (V_t as function of pH):

$$V_b = -V_a \cdot \frac{\left[H^+\right] - \left[OH^-\right] + F_a C_a}{\left[H^+\right] - \left[OH^-\right] + C_b},$$

where

$$F_a = -\alpha_{HA^-} - 2\alpha_{A^{2-}} = -\frac{K_{a1}[H^+] + 2K_{a1}K_{a2}}{[H^+]^2 + K_{a1} \cdot [H^+] + K_{a1}K_{a2}}$$

To make it more concrete we consider, as in reference [25], the titration of sulfurous acid (pK_{a1} = 1.91, pK_{a2} = 7.18 at 25°C) with a strong base (sodium hydroxide), with concentrations $C_a = C_b = 0.100$ M.

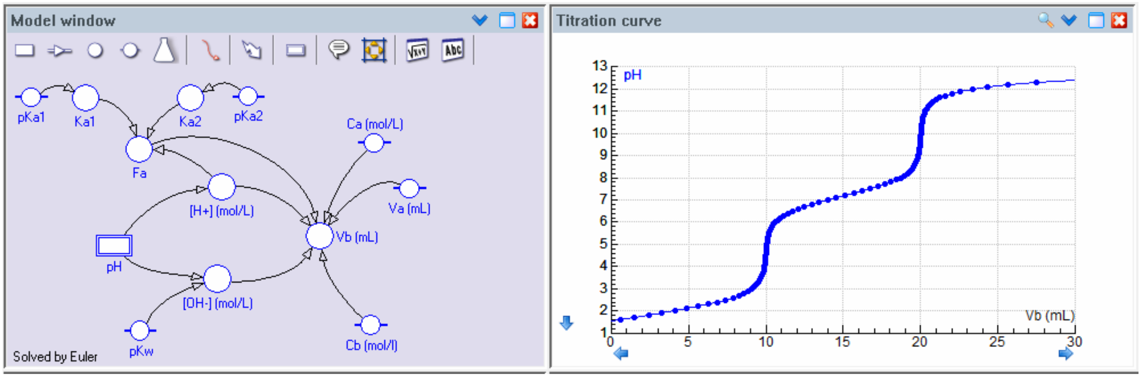


Figure 3. Screen shot of a graphical model of diprotic acid - monoprotic strong base titration.

The model window on the left-hand side of the above screen shot illustrates what graphical modeling is all about: an author (curriculum designer, teacher, or student) literally ‘draws’ variables representing physical quantities or mathematical entities and the relations between them. An arrow explicitly indicates a dependency between variables: for example, the arrow from pK_{a1} to K_{a1} means that the author of the model wanted to express that K_{a1} depends on

$\mathrm{p}K_{\mathrm{a1}}$. By clicking on the icon of K_{a1} a dialog window appears in which the mathematical formula $\mathrm{p}K_{\mathrm{a1}} = 10^{-\mathrm{p}K_{\mathrm{a1}}}$ can be entered. An arrow ensures that connected variables are available in the formula editor, but in Coach you may enter any variable. The reason for not having the strong requirement that every connection must be visible is that the software designers wanted to avoid an incomprehensible spaghetti structure of arrows in a graphical model; they wanted to leave it up to the user to decide which relationships between variables are considered so crucial in the model that they must be shown via arrows in the model window. In Figure 3 all relationships are shown: for example, the arrows with endpoint V_{b} come from all variables that are present in the mathematical formula for V_{b} mentioned before.

There are three types of variables present in the graphical model and they are represented by different icons: (1) constants ($\mathrm{p}K_{\mathrm{a1}}$, $\mathrm{p}K_{\mathrm{a1}}$, $\mathrm{p}K_{\mathrm{w}}$, C_{a}, C_{b}, V_{a}, V_{b}), which are parameters that users can easily change in the user interface via a slider bar or directly by entering a value, (2) auxiliary variables (V_{b}, F_{a}, $[\mathrm{H}^+]$, $[\mathrm{OH}^-]$), which depend on other variables via mathematical formulas, and (3) the independent variable (pH). The presence of the independent variable has to do with the kind of modeling language that underpins the graphical model. To date, modeling languages can be divided into three kinds: (1) so-called aggregate modeling languages (e.g. STELLA, Powersim, Model-it, Coach), also referred to as system dynamics modeling languages, (2) object-based modeling languages (e.g., StarLogo), and (3) agent-based modeling languages (e.g., NetLogo, AgentSheets). Aggregate modeling tools use accumulations (commonly called stocks or containers), flows and other graphical descriptors of changing dynamics to describe a system that is in mathematical terms represented by a (system of) differential equation(s) or finite difference equations. In most cases, time is the independent variable, but it can be anything, e.g., in our model pH. The only thing that happens when you run the above model is that pH is repeatedly incremented with a user-defined step size dpH, as shown in the text-based model of Figure 2. By the way, in Coach 6 you can always show the text-based or equations-based model that is equivalent to the graphical model. It is actually a matter of choice whether one prefers the text-based or graphical modeling approach, although research[54] indicates that graphical modeling tools support novice modelers in constructing their own models and in understanding other people's models. Anyway, an important didactic point of graphical modeling is the active choice of relations made by the modeler: the role of the modeling engine is only to perform the calculation of the instructions received and to display results in the form of graphs, tables, and/or animations. The chemical relevance of the value of parameters in the titration model is rapidly visualized: for example, a student can easily investigate the relation between the shape of the titration curve and the values of ionization constants of the acid and base involved.

The system dynamics approach is more apparent in the graphical model shown in Figure 4. It is a computer model of a titration of a weak acid with a strong base. In particular, it models the process of adding an aqueous sodium hydroxide solution to an acetic acid solution. This picture reveals more than the previous graphical model that the system dynamics modeling language builds on a simple metaphor that mainly consists of elements to control flow and containers to accumulate flow. There are three containers, each represented by a rectangular icon, present in the model: the variables nHAc and nNAOH represent the amount (in moles) of weak acid and strong base present during titration, respectively, and in the variable Volume is stored the volume of the solution during titration. The vertical double arrows represent rates of flow to and from containers. Time is the independent variable in the model, but in this case it is not shown in the graphical window anymore. The computer model repeatedly calculates at several times the flow rates and updates the values of the containers. A rough sketch of the calculations is as follows: As long as a sufficient amount of acetic acid is still present in the solution, the inflow and outflow of sodium hydroxide are equal. The equilibrium restores itself by dissociation of some acetic acid. At one point all the remaining acetic acid reacts to sodium acetate and hereafter there is an excess of sodium hydroxide that only gets bigger. The computation of pH during titration is divided into two parts, namely, before and after the equivalence point. After the equivalence point has been reached pH is derived from the OH^- concentration delivered by the strong base. In the calculations are used the mathematical formulas of de Levie,[45] simplified under the assumption that autoionization of the solvent may be ignored.

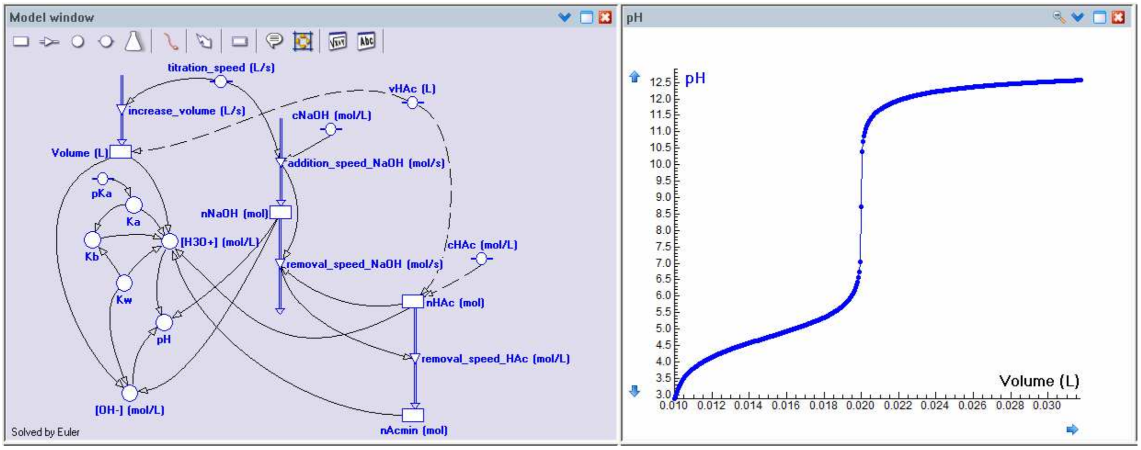


Figure 4. Screen shot of a graphical model of titration of acetic acid with sodium hydroxide.

The computed titration curve shows a region where the pH of the solution changes only a little regardless of the addition of sodium hydroxide (pH stays between 4 and 5.5 while 8 mL base is added). This is the buffer region. A student could also discover via computer experiments that halfway the titration the pH is always equal to pK_a and that buffering is best at that point. A more advanced practical investigation for students would be to apply the modeling tool and data analysis tools in Coach (e.g., the slope tool or numerical differentiation) to design an appropriate buffer solution at a particular pH and with a requested buffer capacity.

Design of the Instructional Materials and the Didactical Approach

The developed lab module consists of three types of Coach activities and is available on the project website.[37] The first type of activity concentrates on observing titration, recording pH curves and interpreting the changes of pH (or H_3O^+ concentrations) during the reactions. The second type of activity applies the titration method to find an unknown concentration of an acidic solution. Students determine titration curves by adding a titrant via a glass buret (a titration curve as function of time) and also via an automated pH titration system consisting of a step-motor buret (a titration curve as function of titrant volume). Optionally one could simultaneously record a video clip of the experiment. This would enable students to relate the color change of an indicator with the striking pH change in the titration curve. This activity concludes the data logging part of the module, which consists of real-time titration of strong and weak acids with a strong base. The third type of activity in the lab module offers graphical models of titration. The sole purpose is to use the models via simulation. Students can change the models and study the effects of changes by altering values of model parameters. In this way they could also determine ionization constants on the basis of real data that they have measured before.

We envision that the developed lab module consisting of data logging and modeling activities is used as an application module in a POE-approach to titration. Students use in the activities elementary acid-base concepts that have already been introduced and apply them to new situations, that is, to titration. The goal is to have students generalize the application of their knowledge. This application of the principles leads to enhanced understanding of the theories and models. But this only works when the data logging and modeling in classroom activities can be implemented successfully. Research[55-59] has shown that this is not straightforward, but worth the effort. For example, Newton[58,59] has identified via interviews with secondary school science teachers in the UK, who were experienced in data logging methods, some of the interacting factors which need to be addressed to manage successful implementation of data logging in chemistry education and which explain why data logging techniques appear to be underused. These factors include characteristics of the innovation itself, namely: goal clarity, complexity, and practicality of the innovation. Other features including teacher roles, teachers' beliefs on ICT in education, and external factors such as practical teachers' support, choice of contexts of use, assessment, textbooks used, and the current chemistry curriculum are also influential in successful innovation. In our experience, this means that for the developed activities to be effective for teaching and learning, it is helpful for teachers to consider two types of skills in using the computer learning environment:

- *Operational skills*, which concern the manipulation of the computer hardware and knowledge of the features in the software;
- *Procedural skills*, which concern the manner in which the software tools are employed in the lesson context for the purpose of achieving learning benefits. A dominant aspect of these skills is the development of an inquiry approach to the analysis and interpretation of data and to making links with previous knowledge. Understanding the basis of ICT via mathematical and computer programming is important for teachers who plan to use these in their teaching. This eliminates the teachers treating CBL/MBL and modeling tools as black-boxes and helps them to provide direction to data analysis.

Such skills are important for the preparation of students for the activities, and the activity sheets each contain indications of the skills needed for the particular activity. For the teacher, there are further *pedagogical skills*, which contribute to the effectiveness of the activities:

- Making clear the learning objectives for each activity;
- Understanding of the special value of the ICT method and exploiting its full potential in purposeful ways, i.e., integrating ICT-based activities meaningfully in lesson plans;
- Managing the activity in a way which promotes 'appropriate' rather than 'indiscriminate' use of ICT;
- Identifying of opportunities to exploit aspects of data logging and modeling for developing higher order interpretative skills in experimental science;
- Integrating the learning from each activity with previous knowledge and skills to enhance students' understanding of the acid-base topic and titration in particular.

The activities in the lab module have been specially selected to illustrate how integration might be achieved. Comparisons of the observations, predictions, and results of each activity form a central role in this integration process. For example, use of results from acid-base titration and/or from a computer model contributes to a discussion about reactions of an acid with a strong base. Here, the graph is a key tool in facilitating comparisons and interpretations. Skills with graphs generally provide a common thread in data logging and modeling activities. Teacher interventions in the classroom can prompt students' interpretations of computer generated graphical data. Skillful questioning of students by the teacher and encouragement of interaction between students to talk about data can assist the students in exploring data for scientific meaning.[60]

The management of the classroom setting also has an important influence on the successful integration of activities. When access to computer equipment is scarce it is likely that the teacher will wish to present the activity as a demonstration in a didactic manner. In this mode, the teacher can give strong guidance to students' thinking about the comparisons between the activities. Alternatively, students could perform the activities in small groups of three or four students, each group engaged on a different activity. Integration might then be achieved by having each group presenting their results to the whole class. In chairing these presentations the teacher can prompt discussion of the significant findings of each group.

It is worth considering that all the activities may be used in a variety of learning contexts. Although the activities have been designed to provide complementary experiences, it is not essential to use all of them; two or three activities might be chosen according to how well they suit the needs of teachers and students in a particular context. The lab module can also be extended, for example, to include titration of polyprotic acids and bases. In varying conditions between schools and within schools at different times of the year or different stages in the curriculum, needs and appropriateness are likely to change; for example, data logging equipment might not be available at the time of need, an individual student might need a revision or extension activity, an enrichment activity might be required to occupy some spare time, a quick activity might be needed if time is scarce. The overlapping features, such as graphical presentation, between the activities allow them to be used to a certain extent as alternatives, but their distinctive features also allow them to be used as complements to each other. Table 1 summarizes the distinctive potential learning benefits of each. It is a useful guide to the special value of each type of ICT-based activity.

Type of activity	*Potential learning benefits, 'ICT value'*
Data logging	o Graph of pH versus volume is displayed real-time during the experiment and it may be used as a starting point for student thinking or as a bridge between formal presentation of titration and the phenomenon investigated. o Shape of titration curve can be linked with the strength of acid or base, the use of polyprotic acids or base in titration, and the concept of buffer solution. In other word, it enhances students' interpretation of data-related graphs in acid-base chemistry. o The difference between 'equivalence point' and 'neutral point' is undoubtedly revealed in titration of a weak acid with a strong base. o Data processing and analysis tools facilitate a detailed investigation of the collected data and a discussion of the quality of the equivalence point determination. o Processing tools allow calculation of H_3O^+ ions concentrations. o The automated pH titration system provides high-quality data and illustrates genuine data acquisition with the computer similar to professional laboratory techniques.
Modeling	o The models calculate the $[H^+]$, $[OH^-]$ and pH changes. o Models are used as simulations, allowing students' explorations about the shape of the titration curve by changing parameter values. o The modeling results can be compared with the experimental data. o Modeling provides dynamic visuals to present abstract concepts of acid-base chemistry and investigate "What if" questions. o Simulation combined with data processing and analysis enhances the learning of concepts like buffer strength that would otherwise remain too abstract for many a student. o Students get an idea of the descriptive and predictive quality of models. o Students get a better view on the use of models in chemistry.

Table 1. Learning benefits of data logging and modeling in titration activities

A Practical Investigation: Analysis of Acid in Cola Drinks

As an example of a practical investigation for upper-level secondary school students we briefly describe results of an analysis of acid in various Cola drinks. Phosphoric acid is a common ingredient in cola drinks; it provides a taste that is both sweet and sour, but it does not compete with other flavors. There is some variability in both the amount and composition of the acid in Cola drinks. The composition is affected by the following equilibrium of this weak aqueous triprotic acid: $H_3PO_4 + H_2O \rightleftarrows HPO_4^- + H_3O^+$, $HPO_4^- + H_2O \rightleftarrows HPO_4^{2-} + H_3O^+$, and $HPO_4^{2-} + H_2O \rightleftarrows PO_4^{3-} + H_3O^+$, with equilibrium constants K_{a1}, K_{a2}, and K_{a3}, respectively. We investigate the acidic mixture of a sample of fresh Coca-Cola Light (also known as Diet Coke) through titration with a strong base (0.1M sodium hydroxide). Citric acid, which is also triprotic, is another common ingredient of soft drinks. It is certainly present in Coca-Cola Light because the product specification of the bottle mentions the presence of the nutritive acid E330 (the indication E338 reveals the presence of phosphoric acid). Since our drink is not de-carbonated, the diprotic carbonic acid will also be present in our sample of 30 mL. In addition to the previously mentioned formulas for F_a in case of a weak monoprotic or diprotic acid we need the following formula for a triprotic acid:[50]

$$F_a = -\alpha_{HA^-} - 2\alpha_{A^{2-}} - 3\alpha_{A^{3-}} = -\frac{K_{a1}[H^+]^2 + 2K_{a1}K_{a2}[H^+] + 3K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

to be used in the unified titration formula

$$V_t = -V_s \cdot \frac{\left[H^+\right] - \left[OH^-\right] + \sum F_s C_s}{\left[H^+\right] - \left[OH^-\right] + \sum F_t C_t}.$$

In the model we have three unknown parameters, namely, the concentrations of carbonic acid, phosphoric acid and citric acid. By trial-and-error a reasonable 3-tuple of parameter values can be found so that the titration curve computed with the model matches the measured titration curve. By the way, the measurement was carried out with the step-motor buret adding slowly the strong base to the sample while recording the pH of the solution. Figure 5 shows a screen shot with the graphical model and a graph window with the computed (blue line) and measured (red line) titration curves. The model is very useful for understanding the titration of complex solutions, with multiple polyprotic acids and bases.

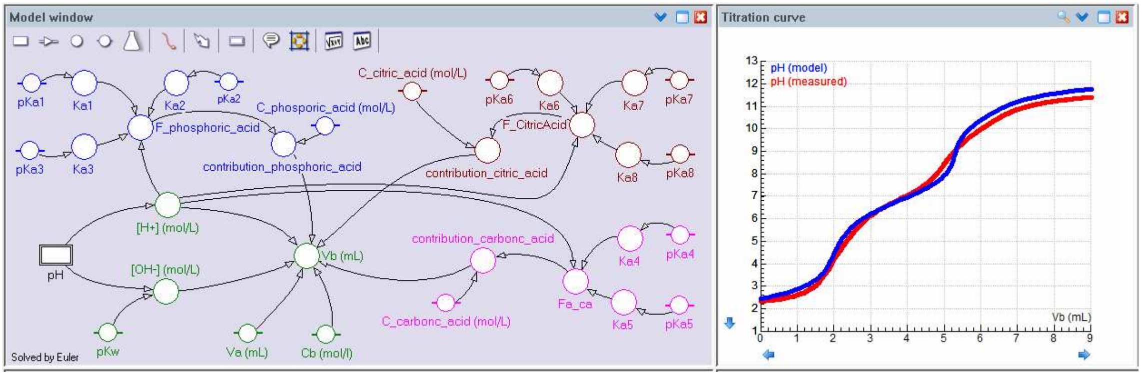
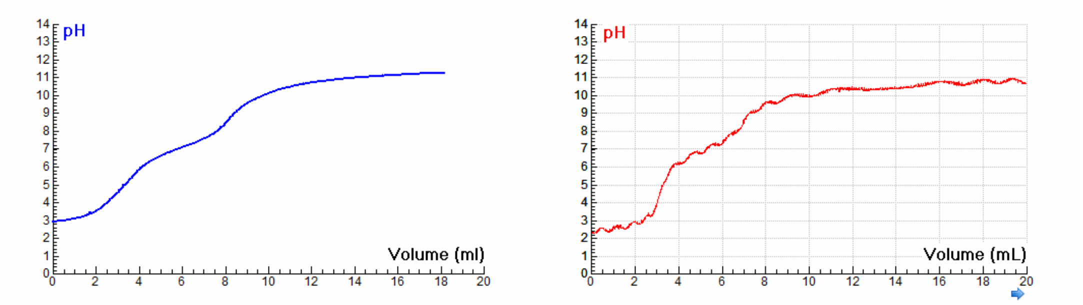


Figure 5. Screen shot of a graphical model of titration of Coca-Cola Light with a strong base and a comparison of the modeling results with a measured titration curve.

Our experience with students in the last form of pre-university education (age 17-18 years) is that they like this kind of practical investigations and get a good idea what the purpose of titration is, how polyprotic acids and bases can be recognized, how one can deal with mixtures of acids or bases in titration, and how titration is done in a reality in a chemistry laboratory.

The concepts of acid-base chemistry, pH, and titration come to life with this type of student activities.

These positive effects of practical work on students' understanding of acid-base reactions and titration do not occur as a matter of course, but are more or less orchestrated by the teacher. To ensure that students not just do their experiments and report their results without much reflection, it is wise to provide students with guidelines for the report and to emphasize the expected/required quality of both experimentation and reporting. Figure 6 illustrates that the quality of the titration experiment may indeed differ from one student team to another. This is not a big issue, at least when students pay attention to the quality of their experimental results, can figure out what went wrong during the experiments, and can formulate or make improvement.



(a) (b)

Figure 6. Titration curves obtained by two teams of students. The quality of diagram (a) is good, but diagram (b) was obtained under weaker experimental conditions: the speed of the step-motor buret was too fast and the rotational speed of the magnetic stir bar in the beaker was too slow.

In figure 7 are shown two fragments of the students' guidelines for the report. They concern (1) the theoretical background of the experiment and (2) the discussion of the obtained results and the conclusions drawn. These guidelines help to improve the quality of the students' learning and reporting process, and they increase the satisfaction with which both the teacher and the students look back at the practical investigation.

1. Theoretical Background

- Explain what is meant by a strong/weak acid, a strong/weak base, a polyprotic acid, a polyprotic base, acidity, pH, a pH-indicator, and by an acid-base reaction.
- Explain the principle of an acid-base titration.
- Explain which acid-base reaction(s) (at least) is (are) playing a role in the determination of concentration of phosphoric acid present in Cola drinks. Write down your explanation in plain words as well as in terms of chemical equilibria.
- Use these chemical equilibria to explain why the Cola drink must be boiled at the start of the experiment.

2. Conclusions and Discussion

- Explain why there are in the titration curves only two regions where the pH-curve is steeply increasing, despite the fact that phosphoric acid is a triprotic acid.
- Try to explain differences between various types of Cola (for example, between Coca-Cola Regular and Coca-Cola Light).
- Compare the concentrations of phosphoric acid that you found in Cola with data found in the literature and/or provided by the producer of the soft drinks.
- Discuss the reliability of the measured results
- Write down some options of further research and motivate your choices.
- Write down the answer to your own research question and possibly other conclusions that you could draw from the series of experiments.

Figure 7. Two fragments of the guidelines for the report.

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