Chemical Education Journal (CEJ), Vol. 19 / Registration No. 19-101 / Received March 1, 2018.
URL = http://www.edu.utsunomiya-u.ac.jp/chem/cejrnlE.html

Titration of Acetic Acid and Glycine: Doing Does Not Always Lead to Understanding

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Abstract
The act of titrating does not necessarily lead to concrete understanding of chemical species amount/concentration nor the interaction between the solute/solvent species with the titrant. Our practical laboratories, at essentially two different academic levels, were with acetic acid and glycine titration. To ensure better perception of what goes on during titration, we have added an extra session where the instructor guides the students, albeit partially, toward a better understanding and grasp of tangibility of chemical species through the whole process. The guidance was complemented by titration curves showing the amounts of various species at different stages of titration. Students were required to interact (question/answer) with the instructor and their peers by focusing on the dynamics of the titrations. Their learning achievement was assessed by their ability to answer correctly three questions posed to them, *i.e.* (i) what the buffer solution contains in terms of chemical species; (ii) what the added OH^- reacts with during titration; and (iii) how the buffer cushions the pH change.

Keywords: Titration dynamics, Buffering, Diprotic acid, Acetic acid, Glycine

Introduction

Doing titration of a weak acid by NaOH is routine for first- or second-year university or even some high school science-stream students. Unless students deviate widely from the protocol, an acceptable titration curve is usually obtained showing buffering as indicated by a near flat slope in a plot of pH change versus amount of base added. If titration of an aqueous solution of, say, 0.01 M acetic acid (mixed with HCl) starting from pH 2 to pH 12 using a pH meter yields a curve as expected, then not much is discussed in the class except that the buffering range centers around pH 4.76 and the pK_a value is where the slope is closest to zero.

The Problems

From our questionnaires about what actually goes on in terms of acid/base, water, and ionic species interacting during titration, we have found a crucial lack of thinking and understanding among students.

When asked why a compound can act as buffer, some students just say that it is because a weak acid or a weak base is involved. When the preceding question is followed by another about why a weak acid or a weak base can buffer (*i.e.* alleviate pH change), many just cite the

Le Châtelier principle, which is quite qualitative in explaining why concentration of chemical species on one side of the reaction arrows tends to drive the balance to the other side. Some of these students know the Henderson-Hasselbalch equation and some even have been exposed to the derivation of the thermodynamic equilibrium constant (forward rate constant / reverse rate constant). There are also students who think that the equilibrium constant applies only near the pK_a. When asked whether or not each drop of the base is neutralized equally by the acid at the steeper and the flatter parts of the titration curve, students find the question difficult to answer.

Because of the lack of insight into the species in the solution, both in terms of amount and concentration, many students cannot explain the flattening of the titration curve beyond the end point, which is due to difficult-to-attain higher pHs and to the logarithmic nature of the pH scale, not to buffering.

The titration curve of a strong acid like HCl by a strong base like NaOH, from pH 2 past the end point, has also quite a flat slope at lower pHs and the curve can be misconstrued as belonging to that of a weak acid by students who have never been exposed to it.

Biochemistry graduate students carry out the titration of 0.01 M glycine which has two pK_as: the process runs from pH 2 to pH 12. The students that carry out the exercise hands-on are graduates with backgrounds in chemistry, biology, biotechnology, biochemistry, agriculture, and health sciences. They all have done titration before coming to us. However, almost all of them have problems with the questions mentioned above about acetic acid.

From our experience with students' lack of understanding of what concretely happens in the titration, we thus wish to show here that the titration exercise, instead of being just a manipulative piece of training, can be supplemented to make them think in terms of tangibility/reality of chemical species reacting as amount as well as concentration. However, we also think that for the present purpose, there is no need to involve aspects such as H_2CO_3/HCO_3^- arising from the atmosphere, chemical activity, buffering capacity, or even limitations of the Henderson-Hasselbalch equation and the limitations of the pH meter. For a thorough review of *the problems*, see [1–2] and the references therein.

Readers are reminded that we can do a thought experiment using NaOH of infinite concentration so that there is no increase in volume during titration. In fact, with the micropipette delivering microliters of highly concentrated NaOH, we could virtually achieve complete titration with very little change in volume, therefore dilution, during titration.

Some of the problems above have been addressed [2–17]. Here we wish to illustrate that there are other problems that have to be rectified about student perception of species interaction and changes during titration. An extra session can lead to better thinking and understanding among students. (See the details in Appendix I.)

Solutions

Concentration and Amount

In an extra session after the manipulative exercise, students were partially guided by interactive questioning to come to correct answers or gradually appreciate the better answers. The instructor could eventually show them the amount and concentration of each species at different stages of titration as shown in Figure 1 for acetic acid titration and Figure 2 for glycine titration. These figures were produced using Mathematica version 10.3 (Wolfram

Research, Incorporated). The amounts of species were derived by simultaneously solving the relevant equilibrium equations, where the amount of water was included and the dissociation constants quoted in the literature were multiplied by the molar volume of water to obtain the proper unitless values. (See the details in Appendix II.) The students themselves did not necessarily have to work or understand at such a quantitative level.

By providing a semi-constructive guidance and demonstration to students, we have managed to correct the problems as follows. (i) Students usually ignore that the solvent's own hydronium ions, considered here to be different from those arising from the buffer, at various pHs and can participate distinctly in neutralization. At the end of the session, they could visualize more clearly what was participating in the neutralization during titration. (ii) Whereas the Henderson-Hasselbalch equation is based on concentration of species, by our guidance students could see that the NaOH added was diluted by the solution. The amount of NaOH added then had to neutralize the *amount of* acid species in the solution. The resulting concentration of these species then determined the change of pH and naturally the equilibrium pH of the solution. Starting with acetic acid or glycine at 0.01 M at pH 2, each buffer only helped to delay the increase in the slope of the titration curve of HCl added at the beginning to achieve pH 2. Students now understood that buffering should not be explained by just Le Châtelier principle because the *principle* was not quantitative enough to give a good prediction about the final pH. (iii) For each drop of NaOH added, the whole amount of OH^- was consumed by the hydronium ions before the end point, except in Figure 2 where the second pK_a was high and the hydronium ion concentration was very low. (iv) Because 0.01 M NaOH was diluted when added to the solution, its pH could not reach 12 (see Figure 1) and the flattening beyond the end point was due to the logarithmic nature of pH, not buffering.

Chemical Species

(i) Even in the presence of a fairly high level of solvent hydronium ions, the acidic buffer compound interacts with the OH^- even at pH values below the pK_a.

(ii) Relevant species to consider in the case of acetic acid titration are CH_3COOH, CH_3COO^-, H_3O^+, and OH^-. Relevant species to consider in the case of glycine titration are $H_3N^+CH_2COOH$, $H_3N^+CH_2COO^-$, $H_2NCH_2COO^-$, H_3O^+, and OH^-.

(iii) For both weak acids here, at higher pHs, the hydronium ions become fewer in amount, thus the OH^- added hardly neutralize the solution hydronium ions at all, unlike around pH 2.

Strong Acids

Most students think that strong acids have no pK_a, being 100% ionized in aqueous solution, regardless whether they are $HClO_4$, HCl, HNO_3, or H_2SO_4. They should be led to understand that dissociation of these acids is concentration dependent, as is dissociation of weak acids, and they actually have pK_as in the negative indicating how strong they are.

There are two more figures that help visualize the titration process. They are relevant but deemed peripheral and thus relegated to Appendix III for those interested in more subtle details.

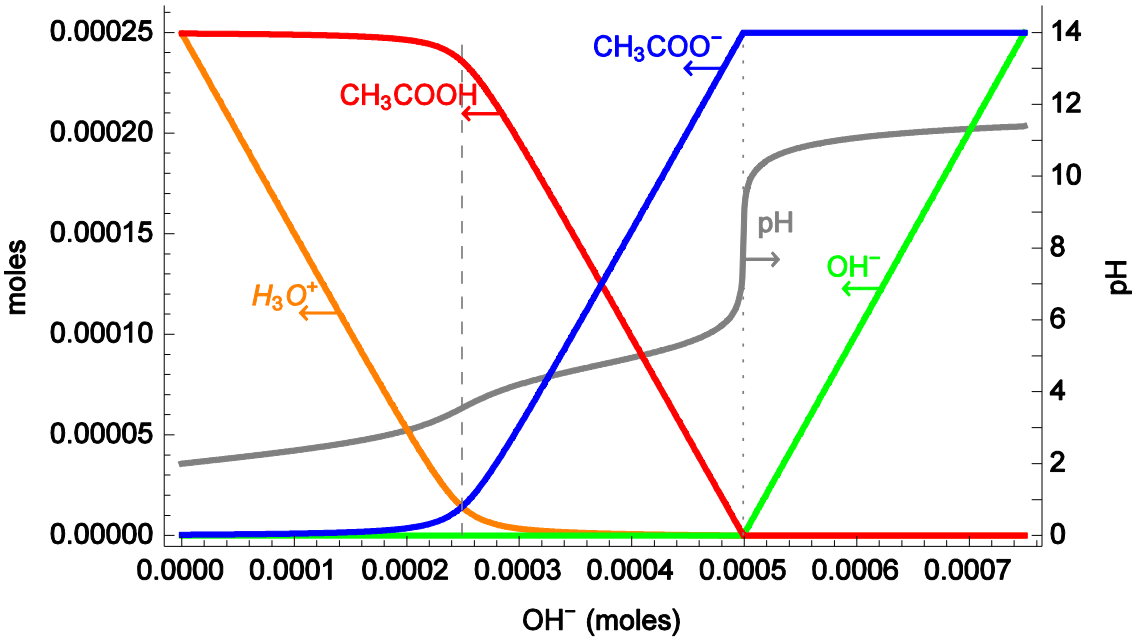

Figure 1. Titration curve of 0.01 M acetic acid by 0.01 M OH^- and amounts of different species. The initial volume of acetic acid solution is 25 mL. The horizontal axis represents the amount of OH^- added (in moles). The left vertical axis represents the amount of each species in the solution while the right one is the pH scale. Infinitely concentrated H_3O^+ is added (left of the vertical dashed line) until the pH of the solution is 2 before the titration with OH^- begins. The amount of OH^- (late increasing green line) is negligible before the end point, indicating that each drop of OH^- added is completely neutralized by H_3O^+ (early decreasing orange line) and CH_3COOH (red line decreasing in the middle). At the early stage of the titration, H_3O^+ decreases almost linearly while CH_3COOH is practically unchanged. At the dashed line, there are equal amounts of H_3O^+ and CH_3COO^-, signifying the start of the titration if H_3O^+ is not added. CH_3COOH plays a bigger role from this point on and turns into CH_3COO^- (blue line increasing in the middle) during this stage. Even though the amount of H_3O^+ changes smoothly and gradually around the dashed line, the pH curve (curvy increasing gray line) still exhibits a slight kink due to the logarithmic nature of pH. After the equivalence point (the vertical dotted line) where CH_3COOH has run out, pH jumps to a new level before entering a new flat stage even though the amount of OH^- increases linearly, illustrating the logarithmic nature of pH. (Recall that pOH = 14 – pH. So the graph of pOH is as flat as that of pH.) For a more detailed discussion about how each species participates in the neutralization around the dashed line, see Appendix III.

Conclusions

Manipulative experiments provide neuro-muscular coordination skills among others. But with more thinking effort under guidance of an instructor in an interactive session, students can gain more insights into the nanoscale, ionic, molecular, species realities of the chemical reactions. We have found that this extra session supplementing the simple hands-on titration exercise can enhance learning, especially about chemical species interacting in terms of kind, amount, concentration, and buffer capacity as well at the same time. This experience can lead to similar concrete thinking/understanding and beyond for students' future encounter with practical and theoretical chemistry (perhaps not so much the stereochemistry part).

The lesson(s) learned from this extra session should be applied by students studying changes of pH in body fluids to realize that there are H_3O^+/OH^- species in addition to weak acid buffering / conjugate base species to counteract pH change.

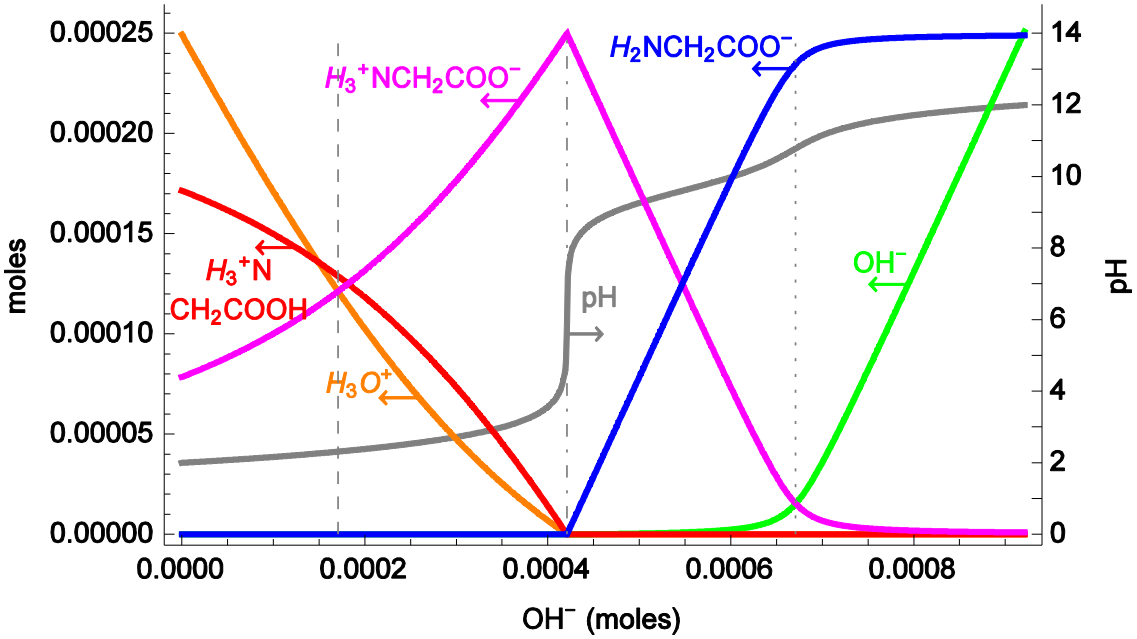

Figure 2. Titration curve of 0.01 M glycine by infinitely concentrated OH^- and amounts of ionic species. The initial volume of glycine solution is 25 mL and infinitely concentrated H_3O^+ is added (left of the vertical dashed line) until the pH of the solution is 2 before the titration with OH^- begins. Because the starting pH is close to the first pK_a of glycine (2.34), the titration begins in the middle of the first buffering stage (left of the vertical dash-dotted line) during which each drop of OH^- added is neutralized by both H_3O^+ (due to relatively low pH and concentration, early concave-up orange line) and the carboxylic group of $H_3N^+CH_2COOH$ (early concave-down red line), the latter of which turns into $H_3N^+CH_2COO^-$ (concave-up then decreasing magenta line), which, in turn, neutralizes added OH^- after the first equivalence point (the dash-dotted line). The second equivalence point (the dotted line) is relatively hard to find due to the high second pK_a (9.6) and low concentration. A significant amount of $H_3N^+CH_2COO^-$ is present in the solution well after the second equivalence point because the fewer the amount of $H_3N^+CH_2COO^-$, the higher the concentration of OH^- required to neutralize them. At this point, there is practically no H_3O^+ left to neutralize OH^-. If the last pK_a is even higher (for example, 10.53, the last pK_a of ε-NH_3^+ of lysine), then we can observe the amount of OH^- that is more or less the reverse of the amount of H_3O^+ around the dashed line in this figure which means that there are plenty of OH^- during the last buffering stage (just like there are a lot of H_3O^+ during the first buffering stage). Notice that around the dotted line, the titration curve and amounts of species are the reverses of those around the dashed line in Figure 1 and the kink in the pH curve is also due to its logarithmic nature. It should be noted that interacting with ε-NH_3^+ by OH^- species at higher pHs would be much slower than with H_3O^+.

References

1. Demerouti, M.; Kousathana, M.; Tsaparlis, G., *Chem. Educator*, **9**, 122–131 (2004). DOI 10.1333/s00897040769a
2. Heck, A.; Kędzierska, E.; Rogers, L.; Chmurska, M., *Chem. Educator*, **14**, 164–174 (2009). DOI 10.1333/s00897092217a
3. Clark, R. W., White, G. D., Bonicamp J. M., Watts, E. D. *J. Chem. Educ.*, **72**, 746–750 (1995). DOI 10.1021/ed072p746
4. de Levie, R. *Chem. Educator*, **1**(3) (1996). DOI 10.1333/s00897960033a
5. Barnum, D. *J. Chem. Educ.*, **76**, 938–942 (1999). DOI 10.1021/ed076p938
6. Cardellini, L. *Chem. Educ. Res. Pract.*, **1**, 151–160 (2000). DOI 10.1039/A9RP90016K
7. Eaker, C. W. *Chem. Educator*, **5**, 329–334 (2000). DOI 10.1333/s00897000426a
8. Po, H. N., Senozan, N. M. *J. Chem. Educ.*, **78**, 1499–1503 (2001). DOI: 10.1021/ed078p1499
9. Curtright, R.; Emry, R.; Heaton, R. M.; Markwell J. *Biochem. Mol. Biol. Educ.*, **32**, 71–77 (2004). DOI 10.1002/bmb.2004.494032020314
10. Drechsler, M., Schmidt, H.-J. *Chem. Educ. Res. Pract.*, **6**, 19–35 (2005). DOI 10.1039/B4RP90002B
11. Carvalho, E. O.; Nantes, I. L. *Biochem. Mol. Biol. Educ.*, **36**, 189–195 (2008). DOI 10.1002/bmb.20176
12. Orgill, M. K., Sutherland, A. *Chem. Educ. Res. Pract.*, **9**, 131–143 (2008). DOI 10.1039/B806229N
13. Barrette-Ng, I. H. *Biochem. Mol. Biol. Educ.*, **39**, 332–338 (2011). DOI 10.1002/bmb.20512
14. Cartrette, D. P., Mayo, P. M. *Chem. Educ. Res. Pract.*, **12**, 29–39 (2011). DOI 10.1039/C1RP90005F
15. Smith, G. C.; Hossain, M. M.; MacCarthy, P. *J. Chem. Educ.*, **91**, 225–231 (2014). DOI 10.1021/ed400297t
16. Baeza-Baeza1, J. J., Pérez-Pla, F. F., García-Álvarez-Coque, M. C. *World J. Chem. Educ.*, **6**, 127–133, (2015). DOI 10.12691/wjce-3-6-1
17. Easson, M. *Educ. Chem.* (23 May 2016). Retrieved from https://eic.rsc.org/cpd/acids-and-bases/2000001.article
18. Hassanali, A.; Prakash, M. K.; Eshet, H.; Parrinello, M. *Proc. Natl. Acad. Sci.*, **108**, 20410–20415 (2011). DOI 10.1073/pnas.1112486108

Appendix I: Post Laboratory Session: A Classroom Observation

This post laboratory session in the classroom is to ensure better perception (in light of absence of an animation) among students (graduates numbering 15–20; undergraduates divided into groups of 30–40 students) of what happens before, during, and at the end of titration process concerning: (i) what the buffer solution contains in terms of chemical species (amount and concentration); (ii) what the added OH^- reacts with from the beginning to the end of titration; and (iii) how mechanistically the buffer helps in cushioning pH change. Achievements were assured when students gave correct answers to these three questions. A typical session proceeded as follows:

(1) Each group of three students had with them their titration curves worked out previously for references. The instructor began by asking them to calculate the amounts of H^+ and OH^- (in mmol) in, say, 25 mL of H_2O at 0.25 pH intervals from pHs 2–12. Some students had to be reminded that $pH = -\log_{10}[H^+]$ and pH + pOH = 14 (the amount of $H^+ = 25 \times 10^{-pH}$ mmol), and, more importantly, they had to work out the amount of OH^- in each, say, 0.1 mL drop of 0.01 M NaOH solution. (These and other calculations can be done easily in a spreadsheet.) They all did that, albeit at their own pace. (Students saw for themselves that there was enough H^+ to neutralize added OH^- at lower pHs, in this case lower than 4.3.)

(2) If a question was raised about the rate of neutralization, students needed to be informed that OH^- reacted with H^+ almost instantaneously. And although the hydrogen bonded to the oxygen in the COOH group (or nitrogen in the case of glycine's second pK_a) ionized more slowly, the reaction with OH^- was faster (with stirring) than the time taken for the pH electrode measurement. (Students realized that OH^- reacted with H^+ first if possible.) At this stage students generally had no idea about the kinetics of neutralization.

(3) Students were asked to calculate using the Henderson-Hasselbalch equation the conjugate base to acid ratios at the same pH intervals as those in (1). (The ratio is 10^{pH-pKa}.) Some students might need help in the calculation but, because of their prior knowledge, it did not take much assistance for all of them to obtain the correct numbers. Students saw that most ionization happened around pK_a and the higher the pH, the more complete the ionization. In addition, pK_a governed the ionization at every pH level.

(4) The instructor asked students to discuss among themselves what would happen if H^+ was removed from the solution at different pHs. Students saw that because of the equilibrium constant, removing H^+ from the solution would increase the pH which would drive the acid to ionize more, thus reintroducing H^+ and decreasing the pH until the equilibrium was reached. Once again, the whole process was governed by the constant pK_a value. Students could see that the acid was converted to the conjugate base without having to calculate algebraically exactly what amount was changed. This step was thus not totally quantitative.

(5) The instructor then asked students to say which species (H^+ or buffer) predominated in neutralizing the OH^- added at different stages (pHs) of titration. Students saw that as long as there was an abundance of H^+, it would predominate and the buffer would ionize to maintain the pH as much as possible.

(6) The instructor then asked students to compare the role played by the solvent H^+ versus H^+ derived from the buffer in neutralizing the OH^- added at ±1 pHs from the pK_a.

(7) The instructor asked students to discuss among themselves what and where the buffer actually did in lowering the impact of the OH^- added on the pH. The question of buffer capacity was raised here; students could, without much effort, say that more concentrated buffers could better cushion pH change upon addition of OH^-.

(8) Students realized by now that by the time the pH reached 7 and beyond, the original H^+ (from pH 2) played a small role relative to H^+ provided by the ionization of the solvent H_2O because of K_w of water.

(9) Now students should see that in the titration of the glycine -NH_3^+ group's hydrogens at the alkaline range near the pK_a of 9.6, the added OH^- reacted very little with the H^+ from H_2O, *i.e.* the OH^- added was neutralized by the -NH_3^+ hydrogens. Now the buffering was done mostly by the glycine's NH_3^+, unlike when its COOH group (pK_a of 2.34) was titrated, solvent H^+ participated a great deal. (COOH was completely converted to carbonate at about the time solvent H^+ was insufficient to neutralize each drop of added OH^-.)

(10) By now students had grasped the main ideas of our entire post laboratory session, *i.e*. to see chemical species in action (neutralization and ionization) in a solution. Even though they had to perform several calculations, the idea was for them to take home a qualitative understanding.

(11) The instructor had to remind students that concentration was important for species to react and ionize, hence the emphasis on relationships among various chemical species. One big surprise was that ionization of the acid occurred earlier (at a lower pH) than expected by them. If possible, for graduate students, it would be helpful to show that K_{eq} is derived from forward and reverse kinetic constants time concentration(s).

(12) Now the instructor showed the quantitative titration curves (Figures 1 and 2) while asking what students thought happened at various stages in terms of the amount of chemical species and concentration. Students then discussed among themselves again. The majority of the students could follow what their more perceptive peers said. Then the instructor did a debriefing session to ensure whole class understanding by asking three students to present their understanding of the process in front of the class and asking their peers to comment. The instructor guided them in their discussion if necessary.

(13) We realize that all students did not learn equally but they achieved what we set out for them to learn, *i.e*. to see chemical species in the solution at different stages of titration rather than just the Henderson-Hasselbalch equation with the buffer as the sole agent in reacting with the OH^- added. This interactive session allowed them to reach their full potential.

(14) Students voiced their satisfaction with the way they were guided towards an understanding and none thought that this extra session was a waste of time. Their responses appeared genuine and were not out of politeness.

Finally, because they were life science students, we asked them about pH change in whole organisms, cells, tissues, organs, and body fluids, whether only the buffers did the buffering of any pH disturbances, their answers were no (to our satisfaction). We did not forget to ask them about cases where pH disturbances came from H^+ injected into the system to ensure student understanding of the equilibrium constant of the buffer and the role of bases introduced into the system also.

Most of our students entered our programs through a highly selective process but they had never been asked to think analytically. However from our guidance, most of them ended up able to perceive the chemical species reacting and ionizing very well without any animation clip shown to them. Obviously, some teachers may want to measure students' learning achievement more quantitatively than ours.

Naturally, with a small class of 15–20 graduate students, we were sure that everyone got the gist of what we asked them to achieve. However, for an undergraduate class of 30–40 students, teaching assistants might have to help, if only to speed up their calculations and to explain certain aspects more closely. Fortunately, there were not too many different aspects to consider in this exercise. Most importantly, teaching assistants did not help students in drawing conclusions about the concrete perception of the molecular species nor about how they interacted in the buffering process.

Appendix II: Derivation of the Amounts of Species during Titration

Figure 1 illustrates a typical titration curve and the amounts of different species during the titration of a monoprotic acid. These are the amounts after the solution has reached equilibrium where added hydroxide ions have been neutralized. Thus these amounts have to satisfy both the water self-ionization reaction

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad (1)$$

and the acid dissociation reaction

$$H_2O + HA \rightleftharpoons H_3O^+ + A^- \quad (2)$$

where A in this case is CH_3COO. The equilibrium constant for the former can be expressed as

$$K_w = [H_3O^+][OH^-]/[H_2O]^2$$

while that for the latter can be expressed as

$$K_a = [H_3O^+][A^-]/([H_2O][HA]).$$

Notice that concentration is the amount of species per volume of solution. Since all the species in both reactions are in the same solution, all the volume terms cancel out and one can use amounts instead of concentrations in the equation. Let $\{\cdot\}$ denote the amount (instead of $[\cdot]$ for the concentration) of a species, the equations above can be rewritten as

$$K_w\{H_2O\}^2 = \{H_3O^+\}\{OH^-\} \quad (3)$$

and

$$K_a\{H_2O\}\{HA\} = \{H_3O^+\}\{A^-\}. \quad (4)$$

It can be easily seen that these equilibrium constants are unitless. However, the equivalent equilibrium constants in the literature are for the equations

$$K_w = [H_3O^+][OH^-]$$

and

$$K_a[HA] = [H_3O^+][A^-]$$

whose corresponding units are $(mol/L)^2$ and mol/L respectively. Since amounts are primary quantities while concentrations are secondary, the equilibrium constants in the literature have to be multiplied (twice and once) by the molar volume of the solvent (water) to obtain the workable equilibrium constants.

There are 5 chemical species but only 2 equations: (3) and (4). Fortunately, if we focus on reactions (1) and (2) instead of equations (3) and (4), there are only 2 unknowns: the net amount of self-ionization in reaction (1) and the net amount of dissociation in reaction (2). Starting from any amounts of the 5 species, denoted by $\{\cdot\}$ for corresponding species, and let $2w$ be the net amount of self-ionization and a be the net amount of dissociation to reach equilibrium from these starting amounts, equation (3) becomes

$$K_w(\{H_2O\} - 2w - a)^2 = (\{H_3O^+\} + w + a)(\{OH^-\} + w) \quad (5)$$

and equation (4) becomes

$$K_a(\{H_2O\} - 2w - a)(\{HA\} - a) = (\{H_3O^+\} + w + a)(\{A^-\} + a). \quad (6)$$

Solving equations (5) and (6) for w and a yields the required amounts of the 5 species in equilibrium. For example, to start titration with 2 mol of water and 0.001 mol of acetic acid, the starting amounts of the 5 species (in mol) can be found by solving the system of equations

$$K_w(2 - 2w - a)^2 = (0 + w + a)(0 + w)$$
$$K_a(2 - 2w - a)(0.001 - a) = (0 + w + a)(0 + a).$$

Here, the starting amount of water is $2 - 2w - a$ mol, that of hydronium ions is $w + a$ mol, that of acetic acid is $0.001 - a$ mol, and so on. As another example, adding 0.00001 mol of infinitely concentrated OH^- during the titration of a monoprotic acid yields the system of equations

$$K_w(\{H_2O\} - 2w - a)^2 = (\{H_3O^+\} + w + a)(\{OH^-\} + 0.00001 + w)$$
$$K_a(\{H_2O\} - 2w - a)(\{HA\} - a) = (\{H_3O^+\} + w + a)(\{A^-\} + a)$$

where $\{\cdot\}$ denotes the amount before adding OH^-. The function `FindRoot` in Mathematica can be used to find the solutions (w and a) to these systems of equations.

For a diprotic acid, in addition to the water self-ionization reaction, 2 acid dissociation reactions are involved:

$$H_2O + H_2A \rightleftharpoons H_3O^+ + HA^-$$

and

$$H_2O + HA^- \rightleftharpoons H_3O^+ + A^{2-}.$$

If K_{a1} and K_{a2} are the respective equilibrium constants, the corresponding system of equations would consist of equation (3) and 2 more equations:

$$K_{a1}\{H_2O\}\{H_2A\} = \{H_3O^+\}\{HA^-\}$$

and

$$K_{a2}\{H_2O\}\{HA^-\} = \{H_3O^+\}\{A^{2-}\}.$$

Now, there are 6 species but all we have to do is solve for w, a, and b in the system of equations

$$K_w(\{H_2O\} - 2w - a - b)^2 = (\{H_3O^+\} + w + a + b)(\{OH^-\} + w)$$
$$K_{a1}(\{H_2O\} - 2w - a - b)(\{H_2A\} - a) = (\{H_3O^+\} + w + a + b)(\{HA^-\} + a - b)$$
$$K_{a2}(\{H_2O\} - 2w - a - b)(\{HA^-\} + a - b) = (\{H_3O^+\} + w + a + b)(\{A^{2-}\} + b)$$

where all the symbols can be interpreted in the ways similar to those in equations (5) and (6).

Appendix III: Geometric (Area) Representation of Acid Dissociation

During the titration of a monoprotic acid, due to the extremely fast (diffusion controlled) recombination reaction between hydronium and hydroxide ions (see, for example, [18]), as long as there are enough hydronium ions in the solution, they will neutralize each drop of hydroxide ions added completely. The resulting disequilibrium will cause the acid in the solution to dissociate in order to bring the solution back into equilibrium. The equilibrium under consideration is reaction (2) in Appendix II with the dissociation constant in equation (4). Since the amount of water changes insignificantly if infinitely concentrated hydroxide ions are used, it can be taken to be constant, so is the product of the dissociation constant and the amount of water. Thus one can rewrite the equation as

$$K_a\{HA\} = \{H^+\}\{A^-\}$$

where K_a is the product of the original dissociation constant and the (constant) amount of water and H^+ is a shorthand for H_3O^+. Figures A1 and A2 represent this equation at the start and midpoint of titration respectively.

Figure A1. Dissociation of acid at the start of titration. The horizontal axis represents the amounts of acid and its conjugate base. The amounts of acid and its conjugate base always add up to the original amount of acid. The left vertical axis represents the amount of hydronium ions while the right vertical axis represents acid dissociation constant. Solid lines represent the amounts of different species at the start of titration where the amounts of conjugate base and hydronium ions are equal and they result from the dissociation of original acid. The distance between the horizontal dotted line and the top solid line represents the amount of hydronium ions neutralized by the added hydroxide ions (which is the same as the amount of hydroxide ions added). The dashed lines represent the amounts of species in the new equilibrium.

In Figure A1, before adding a drop of hydroxide ions, the area of the solid-perimeter (mostly blue) square, representing $\{H^+\}\{A^-\}$, equals the area of the solid-perimeter (mostly red) rectangle, representing $K_a\{HA\}$. Adding hydroxide ions decreases the amount of hydronium ions to the level indicated by the dotted line, prompting the acid to dissociate so that the amount of hydronium ions rises to the level indicated by the dashed line which also increases the amount of conjugate base by the same amount. The new equilibrium is represented by the equality between the areas of the blue and red rectangles (demarcated by the dashed lines). Notice that acid dissociation helps to reinstall the equilibrium by increasing both the amounts of hydronium ions and conjugate base. The increase in the amount of hydronium ions alone compensates for about half the disequilibrium (the green rectangle between the dotted and dashed lines) and the increase in the amount of conjugate base does the rest (the area of the part of the blue rectangle to the right of the original square). As can be seen from Figure A1, the two rectangles have the same width and slightly different lengths, indicating that the two effects are about the same. So, only about half the amount of hydroxide ions added is required for the acid to dissociate in order to bring the solution back to equilibrium. As the amount of hydroxide ions added approaches zero, the dissociation approaches half that amount. Figure A2 shows acetic acid dissociation around the vertical dashed line in Figure 1.

Figure A3 illustrates the phenomenon at the midpoint of titration where the amounts of acid and its conjugate base are equal. Here, disequilibrium is compensated mostly by the increase in the amount of hydronium ions (the area of the green rectangle versus the area of the part of the blue rectangle right of the original midpoint) which means that the amount of acid dissociation almost equals the amount of hydroxide ions added. So, the amount of acid

dissociation rises from half the amount of hydroxide ions added at the beginning to almost the full amount by the midpoint of titration.

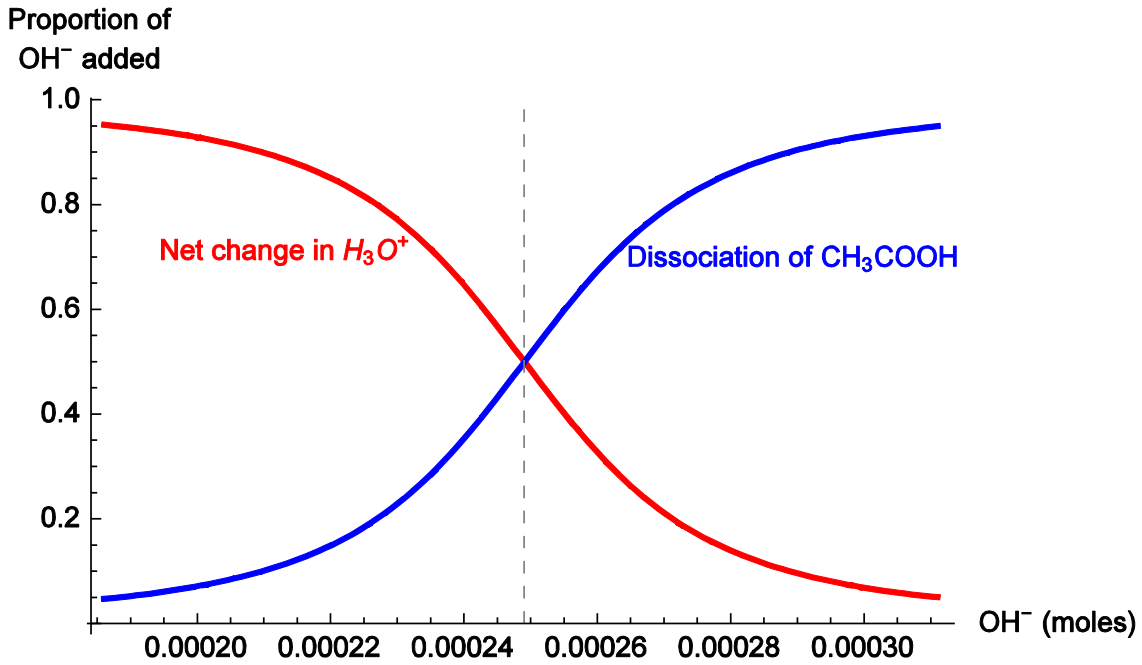

Figure A2. Dissociation of acetic acid as a proportion of each drop of added OH^- and its effect on net change in H_3O^+ (also as a proportion of each drop of OH^-) in the early stage of titration. In the early stage of acetic acid titration (around the vertical dashed line in Figure 1) where there is enough H_3O^+ in the solution to completely neutralize each drop of added OH^-, CH_3COOH will dissociate (increasing blue line) to keep the dissociation reaction

$$H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$$

in equilibrium after H_3O^+ is neutralized by added OH^-. At the dashed line where the amounts of H_3O^+ and CH_3COO^- are equal, CH_3COOH will dissociate about half the amount of OH^- added (H_3O^+ neutralized).

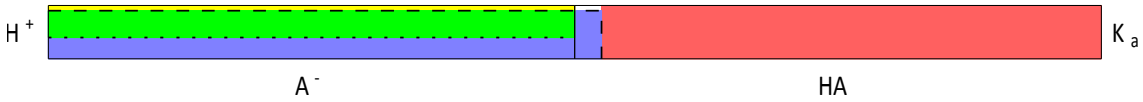

Figure A3. Dissociation of acid at the midpoint of titration. Solid line represents the amounts of different species at the midpoint of titration where the amounts of acid and its conjugate base are equal. The dotted and dashed lines have meanings similar to those in Figure A1.