

Henderson Hasselbalch relationship and weak acid titration

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Abstract

Henderson-Hasselbalch relation is generally the simplified theoretical framework used to introduce students to acid-base titration. However, it is not always valid and its limitations should be made clear to chemistry students. The appropriate parameter to evaluate its validity is K_a/C_0 , in connection with Ostwald dilution law. For more advanced students, it is possible to deduce analytical expressions that always fit accurately acid-base titrations and allow an evaluation of Henderson Hasselbalch relation. Gran plot appears as a particularly sensitive technique to the breakdown of Henderson Hasselbalch relation.

Introduction

To first year chemistry students, weak acid titration is generally presented in a simplified way. First, it is often assumed that the only reaction to be considered is the reaction between

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the weak acid and hydroxide ions:



Considering the case of a solution of weak acid of initial concentration and volume respectively C_0 and V_0 , and a solution of sodium hydroxide of concentration C and poured volume V , it is then assumed that, as the equilibrium constant of that reaction is very high, $[\text{AH}] = (C_0V_0 - CV)/(V_0 + V) = C_a$ and $[\text{A}^-] = CV/(V_0 + V) = C_b$. Finally, via the dissociation constant K_a , it comes the Henderson-Hasselbalch relationship (HHR)¹:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{AH}]}\right) \approx \text{p}K_a + \log\left(\frac{C_b}{C_a}\right) = \text{p}K_a + \log\left(\frac{x}{1-x}\right) \quad (2)$$

where $x = V/V_{eq}$ is the fraction titrated, where $V_{eq} = C_0V_0/C$ is the equivalent volume.

As de Levie¹ reminded, Henderson equation is an *approximation* based on hypothesis that will be reminded below. However, it is used to model the weak acid titration for $V_{eq} > V > 0$. Generally, this is enough for a first year chemistry class.

Po and Senozan² have presented a detailed and critical history of this equation, in connection, notably, with the history of the notion of pH and of Ostwald's law of dilution. They showed that Henderson-Hasselbalch relationship is not reliable to model acid-base titration curves when $\text{p}K_a$ becomes too low or too high. They did so by comparing the predicted curve obtained by equation 2 with the curve obtained by modelling the full chemical system, without the assumptions (often implicitly) made when using Henderson-Hasselbalch

¹Po and Senozan wittily note that "many students of chemistry have wondered if the thought of taking the logarithm of both sides of an expression should warrant immortalization of these two scientists", we could maybe suggest that, beyond the role it played in understanding buffers as noted by Po and Senozan, it also provides us with the great benefit of having a name for that very useful equation, which, in and of itself, in our opinion, is a great service to the community.

relationship. The full resolution involves the following equations:

$$\left\{ \begin{array}{l} K_e = [H^+][OH^-] \\ K_a = \frac{[A^-][H^+]}{[AH]} \\ C_0^* = [A^-] + [AH] = C_0V_0/(V_0 + V) \\ C^* = [Na^+] = CV/(V_0 + V) \\ 0 = [H^+] + [Na^+] - [OH^-] - [A^-] \end{array} \right. \quad (3)$$

As it is well known, it comes, for $[H^+]$:

$$[H^+] = K_a \frac{[AH] - [H^+] + [OH^-]}{[A^-] + [H^+] - [OH^-]} \quad (4)$$

which has the great advantage to show the conditions that must be satisfied so that Henderson-Hasselbalch relation be a good approximation, namely:

$$[H^+] \ll [AH], [H^+] \ll [A^-], [OH^-] \ll [AH], [OH^-] \ll [A^-] \quad (5)$$

However, the titration curve is often obtained by determining the roots of the third order polynomial that can be deduced from the set of equations 3 and which is able to account for the whole titration curve, even for $V = 0$ or $V > V_{eq}$ and that's how Po and Senozan evaluated the quality of HHR. It would be more satisfactory to be able to propose an analytical solution to that question as well as – at the same time – an improved (although more complicated) version of HHR. That is what we propose to examine here.

Study of HHR at low pH/beginning of titration

Satisfying fit at low pH

At low pH, Henderson-Hasselbalch relation may break down, when $[H^+]$ cannot be neglected in 4, (but $[OH^-]$ can then safely be neglected). It comes:

$$[H^+] = K_a \frac{[AH] - [H^+]}{[A^-] + [H^+]} \quad (6)$$

This leads to an improved relation (iHHR1):

$$pH = -\log \left(\frac{-(K_a + [A^-]) + \sqrt{(K_a + [A^-])^2 + 4K_a[AH]}}{2} \right) \quad (7)$$

However, one may wonder what should be used for $[A^-]$ and $[AH]$ in such a case? The development of 6 as a polynomial leads to:

$$[H^+]^2 + ([A^-] + K_a)[H^+] - K_a[AH] = 0 \quad (8)$$

and the set of equation 3, when $[OH^-]$ is neglected, produces the polynomial:

$$[H^+]^2 + (K_a + C^*)[H^+] - K_a(C_0^* - C^*) = 0 \quad (9)$$

By identification between equations 8 and 9, it comes $[A^-] = C^*$ and $[AH] = C_0^* - C^*$, which is equivalent to $[A^-] = C_b$ and $[AH] = C_a$, as in the Henderson-Hasselbalch relation. Hence, equation 7 should provide a satisfying fit to titration curves before the equivalence and as long as $[OH^-]$ may be neglected, using C_a and C_b exactly as it is done when using the simpler Henderson-Hasselbalch relation.

Figure 1 presents the fit to titration curves obtained using equation 7 compared to curves obtained by solving the full exact system for various pK_a – we used the same conditions as

in,² i.e. the titration of 100 mL of solution of weak acid, with pK_a ranging from 3 to 11 and with $C_0 = 0.01$ M by NaOH 0.01 M. Obviously, relation 7 is very satisfying to predict $pH = f(V)$ for small values of V , whereas it behaves exactly like Henderson-Hasselbalch relation when V goes to V_{eq} , as in this case $[OH^-]$ cannot be neglected and is then the reason why HHR breaks down: it applies strictly in the same way to HHR and iHHR1.

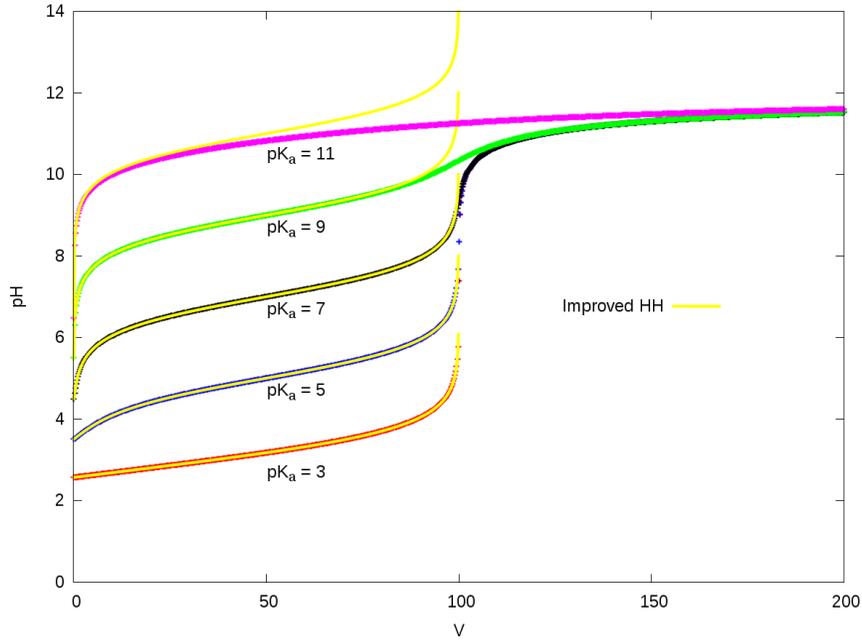


Figure 1: Approximate and exact pH as a function of base volume during titration of 100 mL of 0.010 M acid. Base concentration is also 0.010 M. pK_a of the acid is identified near the curve corresponding to it. The thick lines correspond to the exact solution and the thinner yellow lines to equation 7.

Knowing $[H^+]$ from 7, it is then possible to determine the dissociation rate of the weak acid, $\alpha = [A^-]/([AH] + [A^-]) = [A^-]/C_0^*$. One gets:

$$\alpha = \frac{K_a}{K_a + [H^+]} \quad (10)$$

Figure 2 presents the case of a solution of weak acid with $pK_a = 3$ and compares the dissociation rates for three approaches: the full solution, the improved HHR and HHR. As it can be seen on the graph, the iHHR1 agrees perfectly with the exact solution from $V = 0$

almost up to V_{eq} , and the dissociation rate of the acid predicted by the iHHR1 approach is also excellent. On the other hand, for these conditions, the HHR does a poor job until $0.1 < V < 0.2$. Hence, the iHHR1 may be considered an excellent approximation at least in the beginning of the titration curve.

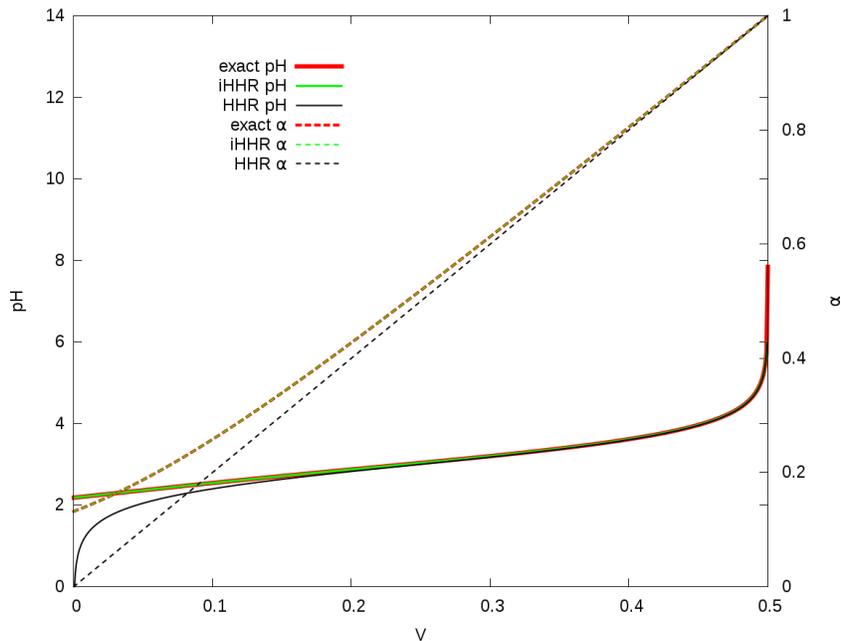


Figure 2: Titration modeled by the three approaches for $pK_a = 3$, along with the corresponding dissociation rates of the weak acid, with $pK_a = 3$, $C_0 = 0.05$ M, $V_0 = 10$ mL, $C = 1$ M.

In figure 2, the variation of the dissociation rate of the acid, in the beginning of the titration, increases more slowly than assumed by the HHR model. This is because the OH^- ions react with the H^+ already present in the solution and – at first – only marginally with the weak acid AH. Hence the reaction that occurs is:



which has a larger equilibrium constant than reaction 1 (here 10^{14} vs. 10^{11}), so that reaction 1 becomes prominent only gradually and the dissociation rates of the HHR and exact solution finally converge.

The advantage of this approach is that it allows an estimate of HHR validity using only analytical expressions, based on a controllable assumption² and there is no need for numerical resolution. This is then a pertinent analysis for an intermediate chemistry class that encourages reasoning on hypothesis, before introducing students to numerical modeling techniques in an advanced course. It can very beneficially be used in group projects where students are asked to analyse weak acid titrations for which HHR is not satisfactory, preferably with a little guidance.

Analytical expression of the onset of validity of Henderson-Hasselbalch relation

We propose here to study in greater details the breakdown of Henderson-Hasselbalch relationship in the beginning of the titration curve.

By considering that relation 7 remains very close to the exact solution in the beginning of the titration, one may study the validity of Henderson-Hasselbalch relation by calculating ΔpH , the difference between equation 7 and the Henderson-Hasselbalch relationship 2. It writes:

$$\Delta pH = \log \left(\frac{2}{-(K_a + C_b) + \sqrt{(K_a + C_b)^2 + 4K_a C_a}} \right) + \log \left(\frac{K_a C_a}{C_b} \right) \quad (12)$$

and, with $\beta = 10^{-\Delta pH}$, it comes:

$$\beta^2 K_a C_a + \beta K_a C_b + \beta C_b^2 - C_b^2 = 0 \quad (13)$$

Then, by writing $C_a = C_0^*(1 - x)$ and $C_b = xC_0^*$, we finally have a second degree polynomial whose roots include the fraction titrated x_β at which the Henderson-Hasselbalch relation

²when $[OH^-]$ becomes too large, neither HHR nor iHHR1 can be used anymore

differs from relation 7 by $\Delta pH = -\log(\beta)$:

$$x^2 - x \frac{K_a}{C_0^*} \beta - \frac{\beta^2}{1 - \beta} \frac{K_a}{C_0^*} = 0 \quad (14)$$

By neglecting the dilution, i.e. assuming that $C_0^* \approx C_0$, 14 has the following solution³:

$$x_\beta = \frac{\beta \frac{K_a}{C_0} + \sqrt{\beta^2 \frac{K_a^2}{C_0^2} + 4 \frac{\beta^2}{1 - \beta} \frac{K_a}{C_0}}}{2} \quad (15)$$

We see that x_β is a function of K_a/C_0 , i.e. the parameter that controls Ostwald's dilution law for weak acids and allows an estimate of the dissociation rate of the acid when $x = 0$, which is intuitively pertinent. Indeed, when we stated that Henderson-Hasselbalch relation was not satisfying in the beginning of the titration curve if $[H^+]$ could not be neglected, it meant that we were confronted with a very dissociated acid that is to say for which K_a/C_0 is large. Hence, this extends the study of Po and Senozan concerning the onset of applicability of Henderson-Hasselbalch relationship during a titration: it is not merely controlled by K_a alone but by K_a/C_0 .

Figure 3 presents the evolution of x_β as a function of K_a/C_0 for $\Delta pH = 0.1$ and 0.01 . As it can be seen, the fraction titrated x_β at which the Henderson-Hasselbalch relationship becomes satisfying increases with K_a/C_0 or as the dissociation rate of the acid *prior* to titration increases. As it has already been discussed, it is because the assumption behind the HHR is that only reaction 1 occurs, whereas for dissociated acids reaction 11 occurs first⁴.

³It is possible to derive a solution when not neglecting the dilution, it is however rather cumbersome and does not add anything significant to the result. In this case, the polynomial writes:

$$x^2 \left(1 - \beta \frac{K_a}{C}\right) - x \left(\beta \frac{K_a}{C_0} + \frac{\beta^2}{1 - \beta} \frac{K_a}{C}\right) - \frac{\beta^2}{1 - \beta} \frac{K_a}{C_0} = 0$$

and the root would be a pain to calculate analytically.

⁴to the limiting situation where the (weak) acid would be almost completely dissociated beforehand, leading to the titration of a strong acid by a strong base and the HHR would not be relevant at all – this situation corresponds to $x_\beta \rightarrow 1$.

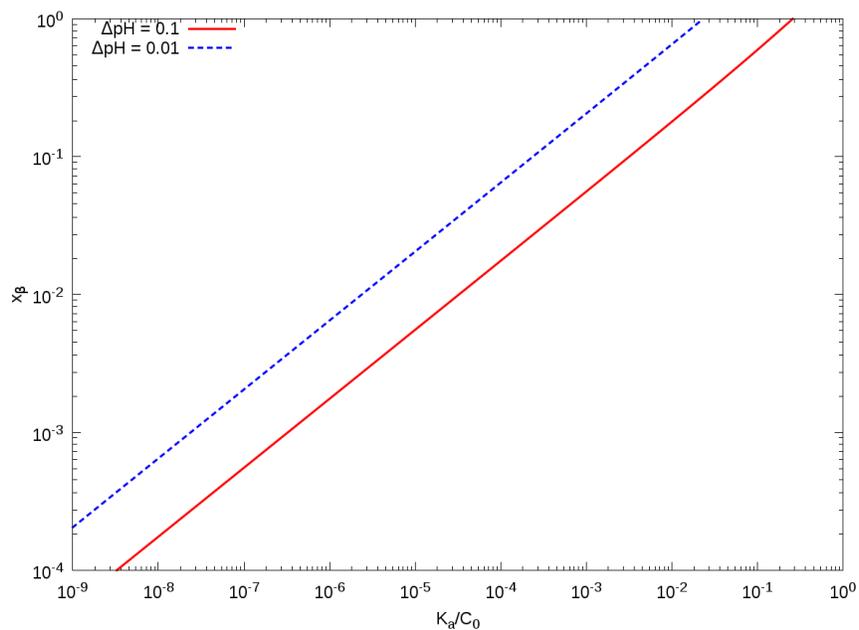


Figure 3: Variation of the onset of validity of Henderson-Hasselbalch relationship as a function of K_a/C_0 . Here, validity means that ΔpH , the difference between the pH predicted by HHR and the exact solution – the latter being correctly modeled by relation 7 – falls below some critical value (here, 0.1 – for which the error in $[H^+] \approx 25\%$ – or 0.01 – for which the error in $[H^+] \approx 3\%$).

To illustrate the importance of considering K_a/C_0 rather than K_a , figure 4 presents the behaviour of iHHR1 and HHR in the case of the titration of a solution of weak acid with $pK_a = 4$ and various initial concentrations. It appears clearly that when C_0 varies, HHR predicts the exact same $pH = f(x)$ behaviour in each case and does a poorer and poorer job when the initial concentration decreases, i.e. when K_a/C_0 increases and the weak acid, following Ostwald's dilution law, behaves more and more like a strong one. Red bars in figure 4 denote the point at which $\Delta pH = 0.05$. It is interesting to note that the later this point is reached, the slower the convergence between iHHR1 and HHR, up to the point of the lowest concentration considered here ($C_0 = 0.001$ M) for which HHR never fully agrees with iHHR1. It is an opportunity for the chemistry students to understand that the relation $pH = pK_a$, often stated for $x = 0.5$, is not always true and depends also on K_a/C_0 , something they should be aware of.

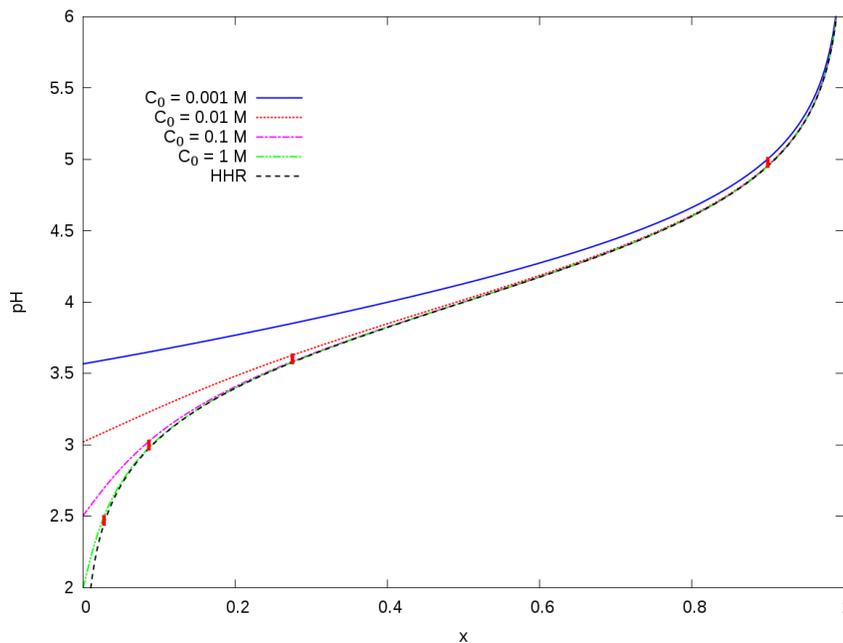


Figure 4: Comparison of titration curves obtained *via* iHHR1 or *via* HHR. The weak acid has $pK_a = 4$, its initial concentration is indicated on the figure and $[\text{NaOH}] = 1$ M. Red bars (0.05 pH unit in length) indicate $x_{\Delta pH=0.05}$ according to relation 15.

Gran plot

A convenient way to visualize whether HHR applies for the considered titration or not, is to use Gran's plot.³ In this case, if HHR applies, the following linear relation is expected to hold:

$$10^{-pH}x = K_a(1 - x) \quad (16)$$

Otherwise, if there is a loss of linearity, it means that Henderson-Hasselbalch relation does not apply. Figure 5 shows the Gran plots of the titration curves presented figure 4. In this way, the extent of validity of HHR becomes rather obvious : the more dilute the acid (the more strongly it behaves) the later its Gran representation reaches HHR Gran plot. In the case of the most dilute solution considered here, there never is a convergence between HHR and iHHR1.

This advocates to teach Gran's plot to students as a mean to determine K_a , but also as a tool to evaluate the validity of Henderson-Hasselbalch relation.

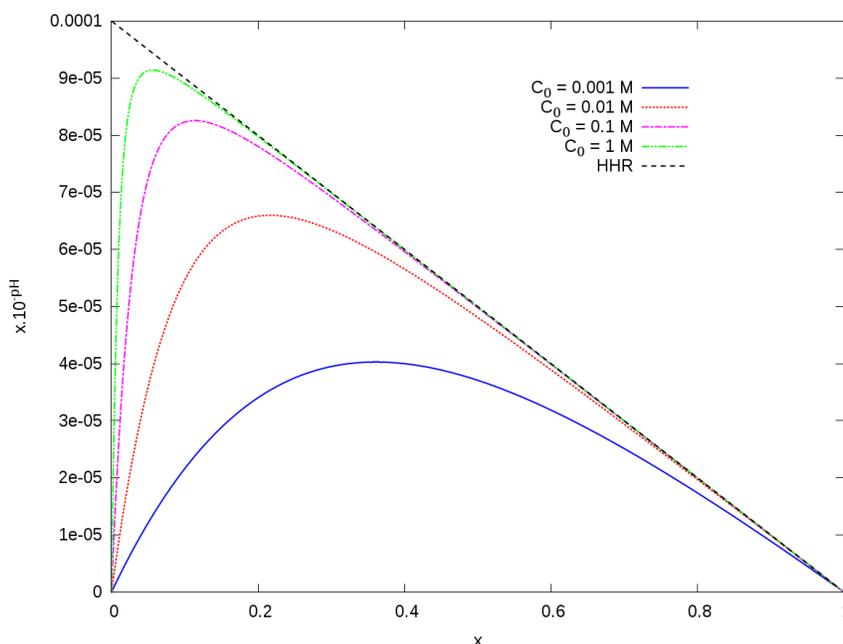


Figure 5: Comparison of Gran plots obtained *via* iHHR1 or *via* HHR. The weak acid has $pK_a = 4$, its initial concentration is indicated on the figure and $[\text{NaOH}] = 1 \text{ M}$.

Study of HHR at high pH/close to equivalence

Satisfying fit at high pH

A very similar treatment can be proposed close to equivalence. In this case, however, $[H^+]$ must be neglected in the equation of electroneutrality in the set 3, which leads to the following polynomial:

$$C^*[H^+]^2 - (K_e + K_a(C_0^* - C^*)) [H^+] - K_e K_a = 0 \quad (17)$$

whose roots allow calculating the pH:

$$pH = -\log \left(\frac{K_e + K_a(C_0^* - C^*) + \sqrt{(K_e + K_a(C_0^* - C^*))^2 + 4K_e K_a C^*}}{2C^*} \right) \quad (18)$$

where the relationship between C_a , C_b , C^* and C_0^* is the same as in the case of the low pH approximation. We propose to call that approximation "iHHR2". Figure 6 presents the comparison between the exact solution (third order polynomial) and iHHR2. As a matter of fact, this approximation behaves like HHR at low pH but works better and better when the pH increases and is in perfect agreement at equivalence and beyond.

Analytical expression of the end of validity of Henderson-Hasselbalch relation

Using the same approach as in the case of the onset of HHR validity, we now study the difference $\Delta pH = pH(HHR) - pH(iHHR2)$, and we neglect dilution. It comes the following polynomial:

$$K_a^2 C_a^2 \chi^2 - K_e K_a C_a \chi - K_a^2 C_a^2 \chi - K_e K_a C_b = 0, \text{ with: } \chi = 10^{\Delta pH} \quad (19)$$

that can be rewritten:

$$\chi^2 - \frac{K_b}{C_a} \chi - \chi - \frac{K_b C_b}{C_a C_a} = 0 \quad (20)$$

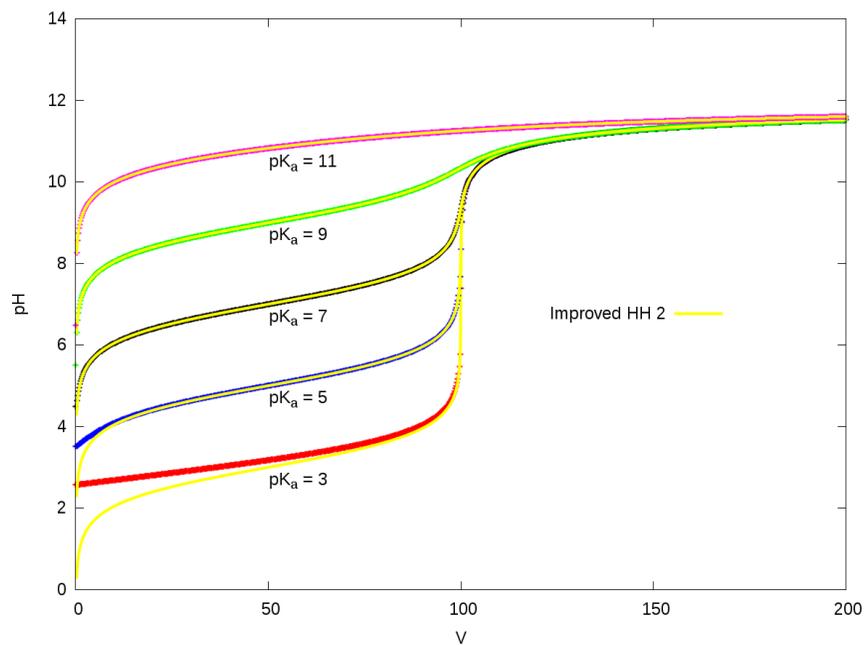


Figure 6: Approximate and exact pH as a function of base volume during titration of 100 mL of 0.010 M acid. Base concentration is also 0.010 M. pK_a of the acid is identified near the curve corresponding to it. The thick lines correspond to the exact solution and the thinner yellow lines to equation 18.

where $K_b = K_e/K_a$. Here, it is convenient to use the following change of variable: $y = 1 - x$, hence it comes $C_a = C_0(1 - y)$ and $C_b = yC_0$. We finally find:

$$y^2\chi(\chi - 1) - y\frac{K_b}{C_0}(\chi + 1) - \frac{K_b}{C_0} = 0 \quad (21)$$

whose solution of interest is:

$$y_\chi = 1 - x_\chi = \frac{-\frac{K_b}{C_0}(\chi + 1) + \sqrt{\left(\frac{K_b}{C_0}(\chi + 1)\right)^2 + 4\frac{K_b}{C_0}\chi(\chi - 1)}}{2\chi(\chi - 1)} \quad (22)$$

Here, it is interesting to note that the natural variable of interest is K_b/C_0 , which is analogous to K_a/C_0 that appeared in the case of the onset of validity, and we can expect to find similar results: the stronger the base, the sooner the end of validity of the HHR will intervene.

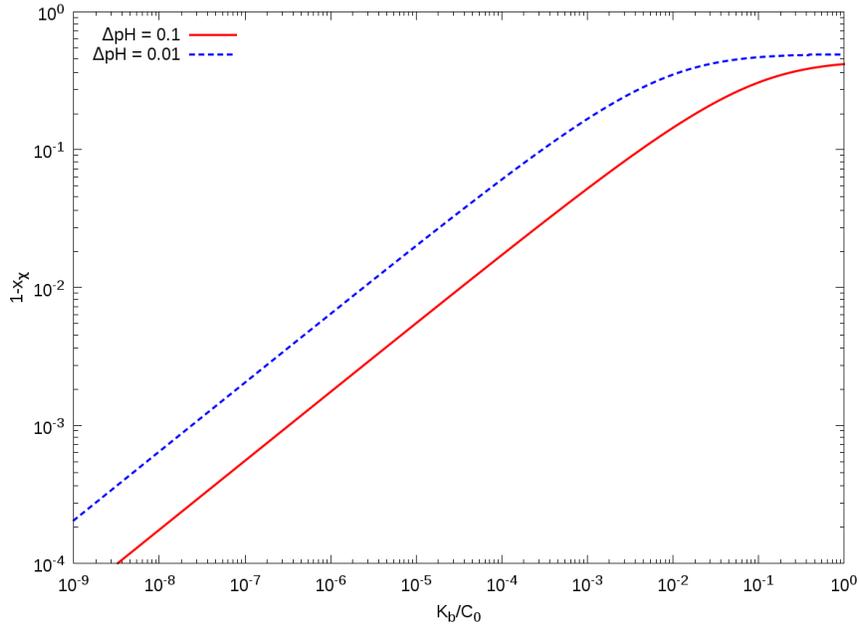


Figure 7: End of validity of HHR as a function of K_b/C_0 or $K_e/(K_aC_0)$. For high values of K_b/C_0 , the HHR ceases to be valid sooner and sooner, i.e. for $1 - x_\chi$ going to larger values.

Figure 7 represents the evolution of $y_\chi = 1 - x_\chi$ as a function of K_b/C_0 . As we expected, the smaller K_b/C_0 , the weaker the base and the closer to equivalence HHR is valid (i.e. for y

small or x close to 1). Another way to understand this point is to realize that weaker bases correspond to stronger acids, hence a situation where the pH jump at equivalence is large and very steep, which corresponds to a greater validity of HHR that diverges at equivalence and is there a very steep function.

On the other hand, when K_b/C_0 increases, that is to say for stronger bases, HHR ceases to be valid further and further away from equivalence with what looks like a horizontal asymptote at $y \approx 0.6$ or $x \approx 0.4$ for $\Delta pH = 0.01$. Another way to look at this situation is to see that the pH jump at equivalence gets smaller and smaller as the base gets stronger, and the HHR vertical divergence disagrees faster and faster with the actual titration. For the strongest bases, however, HHR is always valid in the beginning of the titration curve up to $x_\chi \approx 0.5$.

All this is qualitatively visible in figure 1.

In the classroom

The elements presented here are used during the first two years (first and second-year undergraduate) of the chemistry degree at Université Paris-Est Créteil, in the class dealing with acid-base titration – these students are destined to major in chemistry up to the graduate level.

First-year undergraduate

To first year undergraduates, resolution of equilibria is presented in a simplified way that does not include electroneutrality and mass conservation equations. The acid base calculations begin with calculating the pH of simple solutions and, in this framework, Ostwald's dilution law is presented for the calculation of the pH of a solution of weak acid. Hence the students know the K_a/C_0 parameter.

When acid base titrations are introduced, at this level, the Henderson-Hasselbalch rela-

tion is used to explain weak species titration, without discussing its validity in great details. Arguments are only provided on a semi qualitative basis that there should be a transition in the behaviour of the titration curve from that of a weak species to that of a strong species as K_a/C_0 evolves. At this point in the class, figures 3, 4 and 7 are used to illustrate this idea. The only way in which the understanding of students is controlled is through simple questions in exercises and exams. Overall, most students understand clearly the difference between a strong and a weak species behaviour via the slope of the curve at small values of x and the connection with K_a/C_0 is rather easily assimilated... for those that understand Ostwald's law in the first place!

Second-year undergraduate

Very oddly, until two years ago, there was no advanced equilibrium course in our chemistry degree, as our university has a great emphasis on organic chemistry, biochemistry and some environmental chemistry, which apparently could function without more advanced notions on equilibria. At the second-year undergrad level, student were only exposed to an almost purely experimental 30 hours course of titration, in the lab. It included acid-base titration, redox titration, precipitation titration and pH-potential diagrams. This class was very intense but met a great success with the students, as the objectives were clear and a systematic method was presented on how they were supposed to deal with the curve modeling. They were asked to arrive with fully modeled titration curves – they were given the exact concentration of the various solutions, but had to find other data on their own (pK_a , E_0 , etc.) and were asked to compare their modeling with their experimental results. The modeling only involved Henderson-Hasselbalch relation and the Gran plot method was introduced.

Then, as the curriculum of the chemistry degree was reevaluated (this happens every 5 years in the French system) it was considered important that future chemists should go through a more advanced theoretical class on equilibria. Hence, a 30 hours course (15 hrs lecture + 15 hrs tutorials) was introduced, which now coexists with the 30 hrs lab module.

The aim of the theoretical module is to teach various techniques to determine equilibria in a rigorous manner or to simplify complicated equilibria in a rational way. This course begins by introducing the full system that must be solved to determine the exact solution in the ideal solution approximation (equilibrium constant, mass conservation and electroneutrality), and how it can be made simpler thanks to hypothesis that must be verified. This method is first applied to various pH calculations and then to acid-base titrations.

Typically, to calculate the pH of a solution containing a weak species, the students are asked 1) to write the whole nonlinear system to be solved for determining the pH of a weak acid or a weak base solution, 2) to write the third degree polynomial without assumption, then 3) to make the proper assumption (i.e. $[OH^-]$ and $[H_3O^+]$ can be neglected in the electroneutrality equation, respectively, for the weak acid or the weak base solution) 4) produce the second order polynomial and 5) determine the root that corresponds to the equilibrium, determine the pH and validate the assumption.

Then, moving on to titration, students are asked to derive relations 7 and 18 and plot them for comparison with Henderson-Hasselbalch relation in a similar way: 1) set the whole nonlinear system 2) write the full polynomial 3) make the proper assumption ($[OH^-]$ can be neglected in the beginning of titration curve of a weak acid, $[H_3O^+]$ can be neglected once pH is large enough and until the end of weak acid titration) 4) determine the second order polynomial and the root that solves the system 5) plot that solution and compare it with the Henderson-Hasselbalch relationship – discuss the validity of the various relations – and compare it with experimental results.

Students are encouraged to use these more elaborate modeling techniques in the experimental module as they see fit, but this is not mandatory and gives extra-credit (only one student went on and applied these methods to model his titration curves in a promotion of 32 – not quite surprisingly, he is head of the class...).

Finally, it could also be possible to lead them into the analysis presented here (i.e. deriving equations 14 and 22 and plotting figures 3 and 7), however the arithmetic is rather

cumbersome and enough time and guidance should probably be proposed if one were to take its class along these lines... with rather limited added value in my opinion.

Conclusion

The weak acid titration is an extremely rich technique from a pedagogical viewpoint. It can be treated in a variety of ways, from the initial introduction of first year students that can understand the main ideas behind titration (titration reaction and equivalence point, mainly) to numerical calculations of the full system. In the first case, Henderson-Hasselbalch relation is the main tool used to interpret titration curves, in the latter, the student will generally have the opportunity to compare exact results with experiment but will seldom analyse the chemical system itself.

Hence, there is room for an intermediate analysis, that remains analytical and represents an opportunity to handle hypothesis and compare the simple Henderson-Hasselbalch relation to a better approximation. It is an opportunity to check the quality of an approximation and realize that it is possible to increase only gradually the complexity of the system, with the benefit of preserving analyticity.

Moreover, from a chemical standpoint, it is possible for the student to grasp that Henderson-Hasselbalch relation is not satisfying initially when the weak acid is too dissociated and that the proper parameter to evaluate that is the ratio K_a/C_0 that intervenes in Ostwald's dilution law. In an analogous manner, the end of validity of Henderson-Hasselbalch relation depends on K_b/C_0 and intervenes sooner for stronger bases or weaker acids.

A study of Gran plot is also a convenient way to visualize clearly when Henderson-Hasselbalch relation is not satisfying, and care must be taken when using this tool to evaluate K_a . A good discussion and the preferred approaches when HHR is not valid on how to improve Gran plot has been provided by Schwartz and is worth reading.⁴

References

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