

Research Article

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A simple theoretical, quantitative approach to help understand the titration of weak acids and bases

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Abstract: What happens at the very beginning of the titration of a weak acid or base is a question sometimes asked by undergraduate students when introduced to the concept of buffer solution. To attempt to answer this question, a simple quantitative approach is developed, which also allows explaining more general properties of the weak acid or weak base titration process, while serving as well as an introduction to the theoretical, quantitative treatment of this subject. Using this approach, it can be shown that, at the beginning of the titration, the reaction between a weak acid (base) and a strong base (acid) does not occur on a one to one ratio when very small amounts of the strong base (acid) are added.

Keywords: chemical education; titration; weak acid.

Introduction

Buffer solutions and the titration of weak acids and bases can be intuitively explained using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \quad (1)$$

where HA is the weak acid, and A[−] is the conjugate base. For example, we can consider the titration of a weak acid with a strong base. A central assumption is that the strong base will react on a one to one ratio with the weak acid. Therefore, when a small amount of strong base is added, an equal amount of weak acid will convert to its conjugate base. In the buffer zone, where the concentration of weak acid is in the same range as its conjugate base, the conversion of a small amount of weak acid to its conjugate base will not shift appreciably the ratio of conjugate base to weak acid. Therefore, from the Henderson-Hasselbalch equation it can be seen that, in the buffer zone, the pH will change little when a small amount of strong base is added.

However, the Henderson-Hasselbalch equation has limitations, in particular in regions of the titration curve far from the buffer zone (Pardue, Odeh, & Tesfai 2004; Po & Senozan, 2001). An alternative approach is to make an exact calculation for [H⁺], taking into account the dissociation of HA, the ionization of water and the hydrolysis of the conjugate base (de Levie, 1993; Po & Senozan, 2001). However, a more simple approach is to obtain an approximate expression for [H⁺] or [OH[−]], which allows to gain insight into the processes that occur at the beginning of the titration of a weak acid or a weak base, respectively.

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An approximate expression for $[H^+]$ or $[OH^-]$

The first assumption we make to obtain approximate expressions for $[H^+]$ or $[OH^-]$ is that initial concentrations of HA or A^- are high, although not higher than 0.1 M (Po and Senozan, 2001). Therefore, at the beginning of the titration of the weak acid we can assume that $[H^+] \gg [OH^-]$, whereas at the beginning of the titration of the weak base we can assume that $[OH^-] \gg [H^+]$. The second assumption is that the strong base or strong acid used in the titration (NaOH or HCl, respectively) are very concentrated, so that only small amounts are used during the titration, and therefore changes in the total volume of the solution are negligible. Third, for simplicity, the total volume of the solution is assumed to be 1 L, so that changes in the number of moles are equivalent to changes in molarity. Finally, the initial solution of the weak base A^- is formed from its sodium salt, NaA.

The equilibrium expressions for the weak acid and the weak base are, respectively:

$$K_a = \frac{([A^-] \times [H^+])}{[HA]} \quad (2)$$

$$K_b = \frac{([HA] \times [OH^-])}{[A^-]} \quad (3)$$

where K_a and K_b are the equilibrium constants for the dissociation of HA and the hydrolysis of A^- , respectively. It can be seen that $K_a \cdot K_b$ equals 10^{-14} , a well known relation (McEvoy, 2020). The mass balance equation is:

$$C_i = [HA] + [A^-] \quad (4)$$

where C_i is the initial concentration of the weak acid or weak base. In the case of the weak base, we also have:



Therefore, in the titration of the weak base, $[Na^+]$ equals C_i . Finally, we have the charge balance equations. For the weak acid, which is titrated with NaOH, we have:

$$[Na^+] + [H^+] = [A^-] + [OH^-] \quad (6)$$

Rearranging, we have:

$$[Na^+] + [H^+] - [OH^-] = [A^-] \quad (7)$$

and, because $[H^+] \gg [OH^-]$, we can write:

$$[Na^+] + [H^+] \approx [A^-] \quad (8)$$

For the weak base, which is titrated with HCl, we have:

$$[Na^+] + [H^+] = [A^-] + [OH^-] + [Cl^-] \quad (9)$$

Replacing $[Na^+]$ with C_i , and rearranging, we have:

$$C_i = [A^-] + [OH^-] - [H^+] + [Cl^-] \quad (10)$$

because $[OH^-] \gg [H^+]$, we can write:

$$C_i \approx [A^-] + [OH^-] + [Cl^-] \quad (11)$$

For the weak acid, we use Eqs. (4) and (8) to express $[HA]$ and $[A^-]$ in terms of $[H^+]$ and $[Na^+]$, the latter representing the amount of strong base added. Then, we replace $[HA]$ and $[A^-]$ in Eq. (2), to obtain:

$$K_a = \frac{(([Na^+] + [H^+]) \times [H^+])}{C_i - ([Na^+] + [H^+])} \quad (12)$$

Rearranging, we obtain:

$$[H^+]^2 + ([Na^+] + Ka) \times [H^+] + Ka \times ([Na^+] - C_i) = 0 \quad (13)$$

This is a quadratic equation, which has a positive and a negative solution. The positive solution is:

$$[H^+] = \frac{-([Na^+] + Ka) + \sqrt{([Na^+] + Ka)^2 + 4Ka \times (C_i - [Na^+])}}{2} \quad (14)$$

This is the approximate expression for $[H^+]$. Similarly, by using Eqs. (3), (4) and (11) and solving the resulting quadratic equation, we obtain:

$$[OH^-] = \frac{-([Cl^-] + Kb) + \sqrt{([Cl^-] + Kb)^2 + 4Kb \times (C_i - [Cl^-])}}{2} \quad (15)$$

This is the approximate expression for $[OH^-]$. Here, $[Cl^-]$ represents the amount of strong acid added.

Approximate values of $[H^+]$, $[HA]$ and $[A^-]$ at the beginning of the titration

The initial concentrations of $[H^+]$ or $[OH^-]$ are obtained when NaOH or HCl, respectively, have not been added to the solution yet. Therefore, replacing $[Na^+]$ with 0 in Eq. (14), we obtain:

$$[H^+] = \frac{-Ka + \sqrt{Ka^2 + 4Ka \times C_i}}{2} \quad (16)$$

For a weak acid, $Ka \ll 1$. Also, we are considering a high initial concentration of HA (but not higher than 0.1 M), so that $Ka \ll C_i$, and therefore $Ka^2 \ll 4Ka \times C_i$. We can then omit the term Ka^2 inside the $\sqrt{}$, obtaining:

$$[H^+] \approx \frac{-Ka}{2} + \sqrt{Ka \times C_i} \quad (17)$$

This is the approximate expression for the initial concentration of $[H^+]$ we will use. However, considering that $Ka \ll \sqrt{Ka}$, we could also omit the term $-Ka/2$, which gives

$$[H^+] \approx \sqrt{Ka \times C_i} \quad (18)$$

and, therefore:

$$pH \approx \frac{1}{2}pKa + \frac{1}{2}pC_i \quad (19)$$

which is a well known relation (Gordus, 1991). Next, using Eqs. (4), (8) and (17), and replacing $[Na^+]$ with 0 in Eq. (4), we obtain:

$$[A^-] \approx \frac{-Ka}{2} + \sqrt{Ka \times C_i} \quad (20)$$

and

$$[HA] \approx C_i + \frac{Ka}{2} - \sqrt{Ka \times C_i} \quad (21)$$

We can then ask what happens when we add a small amount of strong base. In Eq. (14), the two variables are $[Na^+]$ and Ka . To further simplify this expression, we can consider the situation where the amount of strong base added equals Ka . Therefore, substituting $[Na^+]$ for Ka in Eq. (14), we obtain:

$$[H^+] = -Ka + \sqrt{Ka \times C_i} \quad (22)$$

Therefore, comparing Eqs. (17) and (22), we find that, when we add an amount of strong base equal to K_a , $[H^+]$ decreases by an amount of $K_a/2$. Then, using Eqs. (4), (8) and (22), and replacing $[Na^+]$ with K_a in Eq. (4), we obtain:

$$[A^-] \approx \sqrt{K_a \times C_i} \quad (23)$$

and

$$[HA] \approx C_i - \sqrt{K_a \times C_i} \quad (24)$$

Comparing Eqs. (20) and (23), and Eqs. (21) and (24), we find that, when we add an amount of strong base equal to K_a , $[HA]$ decreases by an amount of $K_a/2$, whereas $[A^-]$ increases by an amount of $K_a/2$. This is an important result, because it shows that, at the beginning of the titration of a weak acid, the strong base will not react on a one to one ratio with the weak acid. However, the OH^- produced by the dissociation of the strong base will react on a one to one ratio with the H^+ present in solution. That is, in this example, an amount of OH^- equal to K_a will consume a similar amount of H^+ . This decrease in H^+ will cause a shift in the equilibrium towards the dissociation of HA , but HA will only dissociate by an amount equal to $K_a/2$. Based on these results, we can then try to answer in chemical terms what happens at the very beginning of the titration of a weak acid: in these conditions, $[H^+]$ is high enough that small amounts of strong base will only cause minor shifts in the equilibrium towards the dissociation of HA . At the same time, however, the strong base will consume the H^+ present in solution, giving rise to a faster increase in pH than that which occurs in the buffer zone. It is important to consider altogether that even in this initial pH range far from the buffer zone there is a certain buffering capacity (Urbansky & Schock, 2000). If the pK_a of the weak acid is low, the initial high $[H^+]$ will preclude a very fast rise in pH, whereas a higher pK_a will lead to a faster rise (see Figure 1).

A similar reasoning can be applied to the case of a weak base. Using Eqs. (4), (11) and (15), and considering first the case where $[Cl^-]$ is 0 and next the case where $[Cl^-]$ is equal to K_b , it can be shown that, when the amount of strong acid added is equal to K_b , $[A^-]$ decreases by $K_b/2$. That is, in this situation the strong acid does not react on a one to one ratio with the weak base. Therefore, at the very beginning of the titration of a weak base, small amounts of strong acid will only cause minor shifts in the equilibrium towards the hydrolysis of A^- , but at the same time the strong acid will consume the OH^- present in solution, giving rise to a faster decrease in pH than that occurring in the buffer zone (and, similarly to the weak acid case, the decrease will be faster the higher the pK_b of the weak base).

Approximate values of $[H^+]$, $[HA]$ and $[A^-]$ after the beginning of the titration process

After the beginning of the titration process, the amount of strong base added increases, whereas $[H^+]$ decreases steadily. Therefore, at some point after the beginning of the titration, we can assume that $[Na^+] \gg [H^+]$. We can then rewrite Eq. (12), obtaining:

$$K_a \approx \frac{([H^+] \times [Na^+])}{C_i - [Na^+]} \quad (25)$$

Comparing Eqs. (25) to (2), it can be seen that $[Na^+] \approx [A^-]$ and $[HA] \approx C_i - [Na^+]$. That is, when the amount of strong base added increases, the strong base reacts on a one to one ratio with the weak acid. We can then express the Henderson-Hasselbalch equation only in terms of the strong base added:

$$pH = pK_a + \log\left(\frac{[Na^+]}{C_i - [Na^+]}\right) \quad (26)$$

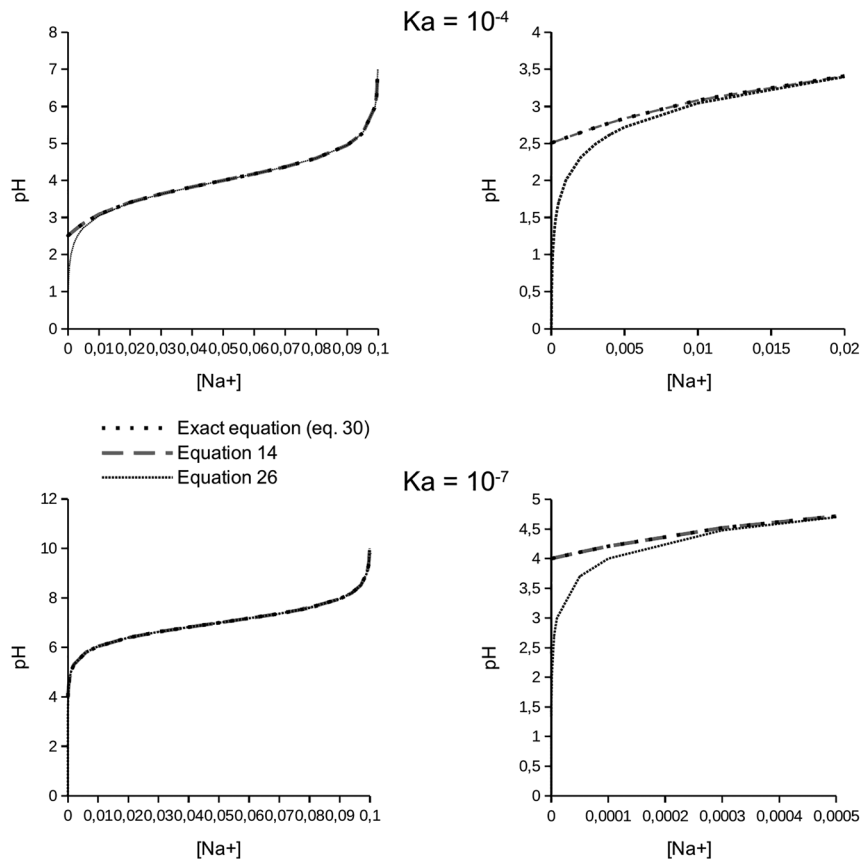


Figure 1: Titration curves based on the exact equations (30), (14) and (26). C_i is set at 0.1 M. The upper graphs correspond to $K_a = 10^{-4}$, and the lower graphs to $K_a = 10^{-7}$. The titration curves on the right correspond to initial values of $[Na^+]$.

From this expression, we can obtain fundamental properties of the titration process. We can begin by taking the derivative of pH:

$$\frac{dpH}{d[Na^+]} = \frac{1}{\ln 10} \left(\frac{1}{[Na^+]} + \frac{1}{C_i - [Na^+]} \right) \quad (27)$$

From Eq. (27), we can see that pH increases sharply either when the amount of strong base added approaches zero, or when this amount approaches C_i , that is, the starting concentration of weak acid. Therefore, in the titration of a weak acid, pH increases sharply either at the beginning or at the end of the process. However, as this equation is applicable after the beginning of the titration process, the initial increase in pH is not as sharp as predicted by it (see Figure 1). To find out what happens in the middle of the process, we can take the second derivative of pH:

$$\frac{\partial^2 pH}{\partial [Na^+]^2} = \frac{1}{\ln 10} \left(\frac{-1}{[Na^+]^2} + \frac{1}{(C_i - [Na^+])^2} \right) \quad (28)$$

Rearranging, we obtain:

$$\frac{\partial^2 pH}{\partial [Na^+]^2} = \frac{1}{\ln 10} \left(\frac{2[Na^+]C_i - C_i^2}{([Na^+]^2 \times (C_i - [Na^+])^2)} \right) \quad (29)$$

From Eq. (29), we can see that, when $[Na^+] = C_i/2$, the second derivative of pH equals zero, and therefore the derivative of pH reaches a minimum. That is, in the titration of a weak acid, the pH change reaches its

minimum when the strong base added equals half the starting concentration of weak acid, that is, when $\text{pH} = \text{pK}_a$. Therefore, by using Eq. (26) and its first and second derivatives we can obtain fundamental properties of the titration process of a weak acid. By using Eqs. (3), (4) and (11), we can obtain an equation similar to Eq. (25) for the titration of the weak base, in the condition when the strong acid added is much greater than $[\text{OH}^-]$. Therefore, the same analysis and its conclusions are also applicable to the titration of a weak base.

Supporting evidence for the values of $[\text{H}^+]$, $[\text{HA}]$ and $[\text{A}^-]$ at the beginning of the titration using an expression for exact $[\text{H}^+]$ and numerical solutions

As shown in (Po & Senozan, 2001), it is possible to obtain an equation for the titration process without any simplification, where the only variable is $[\text{H}^+]$, termed “an expression for exact $[\text{H}^+]$ ”. For the titration of a weak acid, we combine Eqs. (2), (4) and (6), and we replace $[\text{OH}^-]$ by $10^{-14}/[\text{H}^+]$, obtaining:

$$[\text{H}^+]^3 + ([\text{Na}^+] + \text{K}_a) \cdot [\text{H}^+]^2 + ([\text{Na}^+] \cdot \text{K}_a - C_i \cdot \text{K}_a - 10^{-14}) \cdot [\text{H}^+] - \text{K}_a \cdot 10^{-14} = 0 \quad (30)$$

Setting the values of C_i and K_a , we can find numerical solutions for this equation with different values of $[\text{Na}^+]$, by using online equation solvers such as <https://www.wolframalpha.com>. That is, we can find exact values for $[\text{H}^+]$, and therefore exact values for $[\text{HA}]$ and $[\text{A}^-]$, for different amounts of strong base added. For instance, setting the value of C_i to be 0.1 M and K_a to be 10^{-3} , we find that, adding an initial amount of $[\text{Na}^+]$ equal to K_a , $[\text{HA}]$ decreases by 0.488 K_a , that is, $\approx \text{K}_a/2$, similar to what we found previously. As shown in Table 1, larger K_a values give initial decreases in $[\text{HA}]$ even closer to $\text{K}_a/2$. If, however, an increase in $[\text{Na}^+]$ of K_a is set for example at the half equivalence point (when an amount of strong base equal to $C_i/2$ has already been added), the decrease in $[\text{HA}]$ is $\approx \text{K}_a$. That is, the weak acid does not react on a one to one ratio with the strong base at the beginning of the titration, but as the titration advances and pH increases the reaction proceeds on a one to one ratio, as we found previously.

We can then plot pH as a function of $[\text{Na}^+]$ using both the exact equation (Eq. 30), the approximate expression for $[\text{H}^+]$ at the beginning of the titration (Eq. 14) and the Henderson-Hasselbalch equation expressed only as a function of $[\text{Na}^+]$ (Eq. 26). Figure 1 shows plots for values of K_a of 10^{-4} and 10^{-7} . In both cases, Eq. (14) gives the same results as Eq. (30) for the whole titration range. Equation (26) gives the same results as Eq. (30) except at the very beginning of the titration, as shown in the plots focusing on the initial values of $[\text{Na}^+]$, where large deviations between the two titration curves can be seen. The initial pH rise is faster for $\text{K}_a = 10^{-7}$, and in this case, at lower values of $[\text{Na}^+]$ we will have $[\text{Na}^+] \gg [\text{H}^+]$, the assumption used to obtain Eq. (26). As shown in Figure 1, when $\text{K}_a = 10^{-7}$, Eq. (26) starts producing the same results as Eq. (30) at lower $[\text{Na}^+]$ than when $\text{K}_a = 10^{-4}$. Therefore, for weak acids with larger pK_a s, the reaction with the strong base begins to occur on a one to one ratio earlier in the titration process than for weak acids with lower pK_a s.

Table 1: The table shows variations in $[\text{HA}]$ when $[\text{Na}^+]$ goes from 0 to K_a , and from $C_i/2$ to $\text{K}_a + C_i/2$.

K_a	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}
$([\text{HA}]_0 - [\text{HA}]_{\text{K}_a})/\text{K}_a$	0.487515	0.496286	0.4988	0.49921	0.49975
$([\text{HA}]_{C_i/2} - [\text{HA}]_{\text{K}_a + C_i/2})/\text{K}_a$	0.963581	0.996176	0.998098	1.00006	1.000002

That is, when an amount of $[\text{Na}^+]$ equal to K_a is added. The variation in $[\text{HA}]$ is close to $\text{K}_a/2$ when initial $[\text{Na}^+]$ is 0, whereas the variation in $[\text{HA}]$ is close to K_a when initial $[\text{Na}^+]$ is $C_i/2$.

Conclusions

The quantitative approach shown here allows to obtain approximate expressions for $[H^+]$, $[HA]$ and $[A^-]$ at the beginning of the titration of a weak acid, and to obtain $[OH^-]$, $[HA]$ and $[A^-]$ at the beginning of the titration of a weak base. Using these expressions, it is possible to show that, in theory, a strong base will not react on a one to one ratio with a weak acid at the very beginning of the titration, and the same will occur for a strong acid and a weak base in this condition. Furthermore, numerical results using an expression for exact $[H^+]$ support this finding. While it will be important to further validate these results experimentally, it is interesting to consider the insight they provide into the process that occurs at the very beginning of the titration of a weak acid or base: in this situation, the chemical equilibrium is highly displaced towards the reverse of the dissociation of the weak acid, or highly displaced towards the reverse of the hydrolysis of the weak base, respectively. This equilibrium will only be shifted slightly by the addition of small amounts of a strong base or a strong acid, respectively. Therefore, the H^+ consumed by the strong base or the OH^- consumed by the strong acid will not be replenished by shifts towards the dissociation of the weak acid or towards the hydrolysis of the weak base, respectively. Hence, at the very beginning of the titration of a weak acid or a weak base, the pH will change faster than in the buffer zone with small additions of a strong base or a strong acid, respectively. Next, as the amount of strong base or strong acid added increases, the equilibrium of the weak acid is displaced towards dissociation or the equilibrium of the weak base is displaced towards hydrolysis, respectively. In this situation, the strong base or the strong acid reacts on a one to one ratio with the weak acid or the weak base, respectively. For the weak acid, this allows the pH to be expressed by a Henderson-Hasselbalch equation in which the amount of strong base added is the only variable (Eq. 26). Using the first and second derivatives of this expression, it is straightforward to show that the change in pH is greater at the beginning or the end of the titration, whereas it reaches a minimum at the half equivalence point.

From a teaching standpoint, this quantitative approach to weak acid and weak base titration might be helpful in two ways: first, even without a detailed development in the classroom, this approach gives a picture of the titration of a weak acid or a weak base that is centered in the increasing shift towards dissociation of the weak acid or hydrolysis of the weak base as greater amounts of strong base or strong acid are added, respectively. This perspective might help students to develop a clearer insight of the titration of weak acids and bases. Secondly, the approach presented here is quantitative but relatively simple, and therefore it could also be useful as an introduction to the theoretical, quantitative treatment of this subject.

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