

Mathematical modelling of acid-base titration

Brendan Mabbutt¹

Chemistry is, well, technically, chemistry is the study of matter. But I prefer to see it as the study of change.

– Walter Hartwell White [1]

1 Introduction

Over a year before writing this article, on the same day as my practical titration exam for Year 12 HSC Chemistry, I managed to come up with a formula for a weak acid – strong base titration curve and have been trying to improve it ever since. I focus this article on acid-base titrations where a known volume of titrant has been added and a chemical equilibrium is assumed to be established. I derive the mathematical relationship between the volume of acid and base present, the concentration said acids and bases and the pH of the mixture for multiple types of titration. It will employ equilibrium methods to derive such relations for monoprotic and polyprotic acids along with strong and weak acids and bases.

2 Theory

For anyone well versed in chemistry, this section can be easily skipped.

2.1 Acids and bases

The chemical procedure of titration [2] is used to determine the molar concentration an analyte by adding a measured volume of titrant with known concentration until the endpoint is reached such as the colour change of a natural indicator though other methods may be used. Molar consideration is determined though the endpoint indicating the completion of reaction between the analyte and titrant once the titrant has been added in sufficient amounts so as to use up all of the analyte. Note that this article considers the titrant as being added to the analyte, if the opposing method was used the calculations would still work with a simple reversal in (4) and (5). Particularly for acid-base titrations, a acid is used as the either the titrant or analyte and a base is used as the other. A sharp change in pH generally stands as the endpoint of such a titration as the excess of acid or base rapidly changes the pH of the solution once the other has been neutralised.

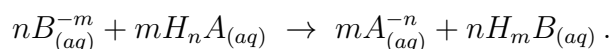
¹Brendan Mabbutt is a first year Aerospace Engineering student at UNSW Sydney.

2.2 Acids and bases

This article looks at acids and bases strictly under the Brønsted–Lowry theory [1] and restricts acid base reactions to aqueous (containing water) solutions. The theory defines acids and bases as proton (H^+ ion) donors and acceptors, respectively. Further, monoprotic acids are acids that can only donate one proton whilst polyprotic acids can donate more than one and do so in stages. It is similar with bases, with monoprotic bases only being able to accept one proton and polyprotic bases being able to accept more than one.

A weak acid is one that is only a partial proton donor in aqueous solution, and, similarly, a weak base is only a partial proton acceptor in aqueous solution. On the other hand, strong acids and bases donate and accept protons, respectively, to an almost complete extent in aqueous solution. Polyprotic and monoprotic acids may be strong or weak, and there are applications for both. On the other hand, monoprotic and polyprotic bases may be strong or weak but weak polyprotic bases are of the extremely weak variety and have little application, and thus I don't consider them.

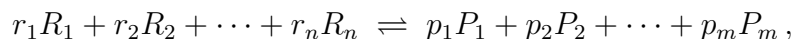
The basis of an acid base titration is this exchange of protons between an acid and base, called a naturalisation reaction, written for an arbitrary acid H_nA and arbitrary base B^{-m} in an aqueous solution as



However, the way I interpreted titration that lead to my derivations is that the reaction can be considered an equilibrium as opposed to one that goes to completion.

2.3 Equilibrium

This article uses the equilibrium constant formulae [2] as the basis of the mathematical. I outline it as follows. Suppose that we have a reversible chemical reaction



where lower cases denote stoichiometric ratios (a rational balancing number such that each side of the chemical equation has the same number of atoms of each element involved) and capitals denote chemical species. Now for a particular temperature, where square brackets denote concentration, at any state of chemical equilibrium, there is a constant K_i given by

$$K_i = \frac{\prod_{k=1}^m [P_k]^{p_k}}{\prod_{j=1}^n [R_j]^{r_j}}.$$

Note that chemical equilibrium is the state in which the concentrations of species don't change or, equivalently, in which the forward and reverse reacting rates are equal.

2.4 pH

pH is an inverse-logarithmic scale [3] related to the concentration hydronium ions (H_3O^+) by

$$pH = -\log[H_3O^+]. \quad (1)$$

Hence, pH is effected by the addition of acids and bases through their donation of protons to water and acceptance of protons from hydronium ions, respectively. Hence, fast changes in pH near the equivalence point, where acids and bases are present in molar ratios given by their neutralisation reaction, will occur in acid-base titrations that allow for the concentration analyte to be determined by system's response to this change, providing an endpoint that gives likely indication of where this equivalence point is.

2.5 Titration curves

For acid-base titrations, titration curves indicate the solution pH as a function of the volume of titrant added. These curves were the inspiration of this article, as I sought a formula for them in explicit form if possible and implicitly otherwise. These curves have particular use in determining the equivalence point of a titration by the vertical points of inflection representing them.

3 Assumptions

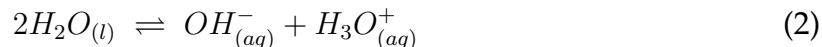
In this article, I will assume that, at equilibrium, the equilibrium constant K_i for a given reaction can be chosen to not include water due to its relatively constant concentration. Further, I will only consider reactions involving the acids, bases, hydroxide (OH^-) and hydronium (H_3O^+) ions in the aqueous solution of the mixture and will ignore any other possible reactions involved. Also, this article will be looking at shifts in equilibrium involving reactions that occur a discrete number of times, but will also assume that this number will vary with the high magnitude of reactions that occur. Finally, I will assume that all titrations performed allow time for the chemical equilibrium to be established at each arbitrarily small increment of titrant volume added.

4 Monoprotic acids

In this section, I only consider acids that are monoprotic and hence only contribute one proton to the equilibrium in dissociation. Similarly, all bases are assumed to be monoprotic in this section, despite leaving some room for generality in the later sections.

4.1 Strong base and strong acid

I will state here the self ionisation of water reaction [3] considered in this article and its corresponding equilibrium constant as



and

$$K_w = [OH^-][H_3O^+]. \quad (3)$$

Now, for a strong base and strong acid titration, it is only necessary to consider the above equilibrium, as both the acids and base would effectively completely ionise in solution. First with volume of titrant added as x , I will write

$$c_{N,I}(x) = \frac{V_{N,0}c_{N,0}}{x + V_{N,0}}$$

for the analyte and

$$c_{T,I}(x) = \frac{xc_{T,0}}{x + V_{N,0}}$$

for the titrant, to provide concatenations at a state denoted I such that they would be the concentration each species if they had been added into solution but without any reaction occurring at any particular x . Further, the subscript 0 denotes values at $x = 0$, N is for the analyte and T is for the titrant, c is concentration in standard units and V and x are volumes in standard units. Now, since we can choose the acid or base to be either the titrant of the analyte, I will denote, for all further reference,

$$c_A(x) = \begin{cases} c_{N,I}(x) & \text{if analyte} \\ c_{T,I}(x) & \text{if titrant} \end{cases} \quad (4)$$

as the concentration the Acid species in state I and

$$c_B(x) = \begin{cases} mc_{N,I}(x) & \text{if analyte} \\ mc_{T,I}(x) & \text{if titrant} \end{cases} \quad (5)$$

for the concentration the base in state I multiplied by the maximum number of protons that the base can accept, m . The reason that I multiply by m here is that it allows me to incorporate polyprotic bases into the next section. Note that when I talk about bases in this section, I refer to monoprotic bases, so $m = 1$.

Now, since the initial concentration hydroxide and hydronium are negligible ($\approx 10^{-7}$) in comparison to all other species, I choose to neglect them henceforth, choosing to consider the hydroxide and hydronium ions in solution as resulting strictly from acids' donation or chemical shift in the self ionisation of water equilibrium. Further, I will be denoting equilibrium shifts as Greek letters in this article, and note that although these shifts are functions of the volume x of titrant added, I will simply write

them as variables. For example, I only write ω , not $\omega(x)$, for the equilibrium shift of the self ionisation of water reaction. Hence, I may write from (3) that

$$K_w = (c_A(x) - \omega)(c_B(x) - \omega), \quad (6)$$

where

$$\begin{aligned} [OH^-] &= c_B(x) - \omega \\ \text{and } [H_3O^+] &= c_A(x) - \omega. \end{aligned}$$

Solving for ω gives

$$\omega = \frac{c_A(x) + c_B(x) \pm \sqrt{(c_A(x) + c_B(x))^2 - 4(c_A(x)c_B(x) - K_w)}}{2}.$$

Since $[OH^-] \geq 0$ and $[H_3O^+] \geq 0$, it follows that

$$\begin{aligned} \omega^+ &> \frac{c_A(x) + c_B(x) + \sqrt{(c_A(x) + c_B(x))^2 - 4c_A(x)c_B(x)}}{2} \\ &= \frac{c_A(x) + c_B(x) + \sqrt{(c_A(x) - c_B(x))^2}}{2} \\ &= c_A(x). \end{aligned}$$

Similarly,

$$\begin{aligned} \omega^- &< \frac{c_A(x) + c_B(x) - \sqrt{(c_A(x) + c_B(x))^2 - 4c_A(x)c_B(x)}}{2} \\ &= \frac{c_A(x) - c_B(x) + \sqrt{(c_A(x) - c_B(x))^2}}{2} \\ &= c_B(x). \end{aligned}$$

We must therefore choose ω^- since this always gives positive values for $[H_3O^+]$, whilst ω^+ will always give negative values for $[OH^-]$, and from (6) they both must have the same sign for any ω . Hence from (1), I get that

$$pH(x) = -\log\left(\frac{c_A(x) - c_B(x) + \sqrt{(c_A(x) + c_B(x))^2 - 4(c_A(x)c_B(x) - K_w)}}{2}\right). \quad (7)$$

Now since $[H_3O^+]$ and $x \geq 0$, it can be easily verified that this function is continuous and differentiable. In Figure 1, I give an example of the graph this function gives with an acid as the analyte (concentration 1 mol L^{-1} and initial volume 50 mL) and the strong base with concentration 1 mol L^{-1} .

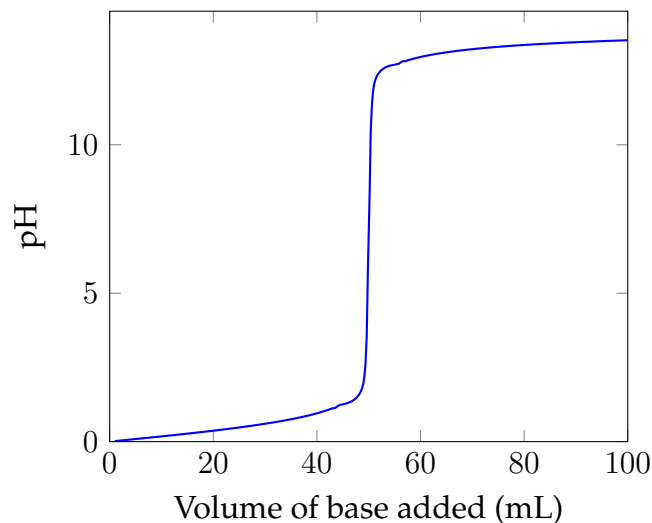
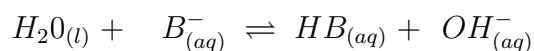
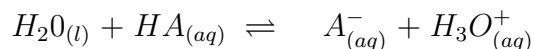


Figure 1: Strong acid - strong base titration

4.2 Weak and weak

Now, I introduce the procedure for when the ionisation of both acid and base are only partial. If that is the case, then we must consider two additional equilibrium reactions, that being the dissociation equilibrium of the acid and base. Following convention [3] for arbitrary monoprotic acid HA and arbitrary monoprotic base B^- , I write



and

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \quad \text{and} \quad K_b = \frac{[HB][OH^-]}{[B^-]}.$$

Now from (3) and (2), and following a similar method as before, I denote α as the shift in the acid dissociation equilibrium reaction, such that

$$K_a = \frac{\alpha[H_3O^+]}{c_A(x) - \alpha}, \quad (8)$$

where $c_A(x) > \alpha$ and so

$$\alpha = \frac{K_a c_A(x)}{K_b + [H_3O^+]}. \quad (9)$$

Similarly for a shift β for the base dissociation reaction, I write

$$K_b = \frac{\beta[OH^-]}{c_B(x) - \beta}.$$

and so

$$\beta = \frac{K_b c_B(x)}{K_b + [OH^-]}. \quad (10)$$

Now, since hydroxide and hydronium ions are involved in these reactions, and considering (3), I can see from (2) that

$$K_w = (\alpha - \omega)(\beta - \omega),$$

where ω is as in the previous section ($\alpha, \beta > \omega$) with

$$[OH^-] = \beta - \omega \quad \text{and} \quad [H_3O^+] = \alpha - \omega.$$

Therefore,

$$[OH^-] = \frac{K_w}{[H_3O^+]} \quad \text{and} \quad \omega = \beta - [OH^-],$$

so

$$[H_3O^+] = \alpha - \beta + \frac{K_w}{[H_3O^+]}. \quad (11)$$

By (9), (10) and (1), I get the relation

$$10^{-pH} = \frac{K_a c_A(x)}{K_a + 10^{-pH}} - \frac{K_b c_B(x)}{K_b + K_w 10^{pH}} + K_w 10^{pH}. \quad (12)$$

In Figure 2, I give an example of the graph that this relation gives with an acid as the titrant (concentration 1 mol L^{-1} and $K_a = 10^{-5}$) and the base with concentration 1 mol L^{-1} , initial volume 50 mL and $K_b = 10^{-5}$.

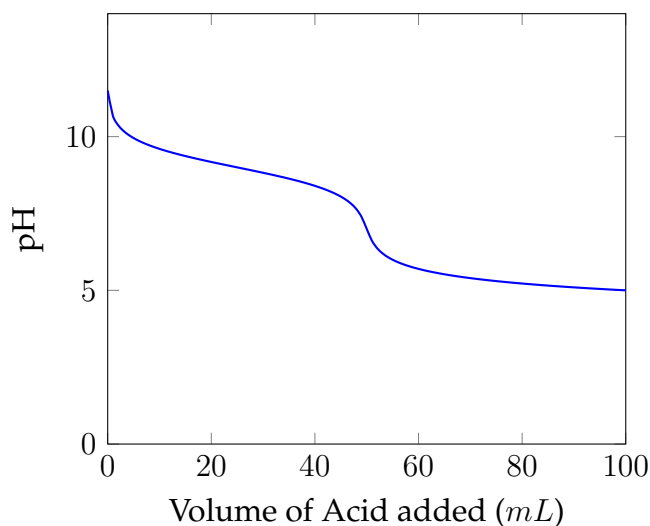


Figure 2: Weak Acid - Weak Base Titration

4.3 Strong and weak

Now if one of the bases or acids considered in the subsection above is weak, then we can simplify the relation. For instance, if we have a strong base, then α is approximately $c_A(x)$, and so from (11) we obtain

$$10^{-pH} = c_A(x) - \frac{K_b c_B(x)}{K_b + K_w 10^{pH}} + K_w 10^{pH} . \quad (13)$$

Similarly, if we have a strong acid, then β is approximately $c_B(x)$, so (11) implies that

$$10^{-pH} = \frac{K_a c_A(x)}{K_a + 10^{-pH}} - c_B(x) + K_w 10^{pH} . \quad (14)$$

In Figure 3, I give an example of the graph of this relation for the strong base case with an acid as the analyte (concentration 1 mol L^{-1} , initial volume 50 mL and $K_a = 10^{-8}$) and the base with concentration 1 mol L^{-1} . Note that it can be easily verified that, if we take both the acid and base to be strong, then (12) reduces to form of (7).

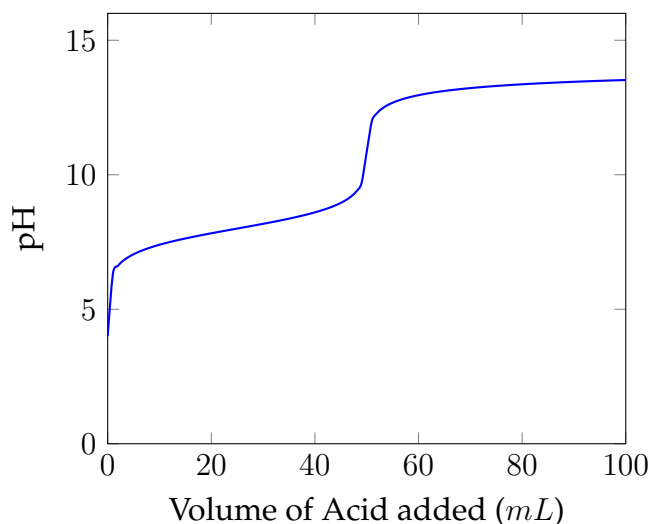


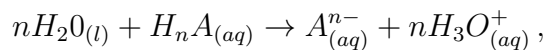
Figure 3: Strong Base - Weak Acid Titration

5 Polyprotic acids

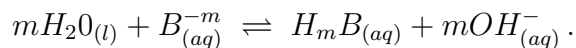
In this section, I consider titrations involving acids that dissociate in stages to produce more than one proton. I shall denote an acid that donates 2 protons diprotic, an acid that donates 3 protons triprotic and an acid that donates n protons n -protic.

5.1 Strong acid

For this first part, I assume that we are dealing with either a monoprotic or polyprotic strong base, along with a monoprotic or polyprotic strong acid. If an acid is n -protic and strong, then, for an arbitrary n -protic acid H_nA ,



and, for a arbitrary m -protic base B^{-m} , that



Note that the factor of m has already been incorporated into calculations through $c_B(x)$. Therefore,

$$K_w = (nc_A(x) - \omega)(c_B - \omega),$$

and so

$$pH(x) = -\log\left(\frac{nc_A(x) - c_B(x) + \sqrt{(nc_A(x) + c_B(x))^2 - 4(nc_A(x)c_B(x) - K_w)}}{2}\right). \quad (15)$$

Now if $m = 1$ and the base was weak, then I get from considering (3) that

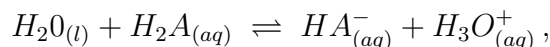
$$K_w = (nc_A(x) - \omega)(\beta - \omega).$$

Here, β is as in the section above. This will give the same result as (13) but with $nc_A(x)$ substituted for $c_A(x)$. Hence, for the case of a strong n -protic acid and a weak base, I get

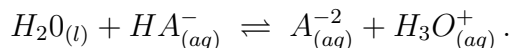
$$10^{-pH} = nc_A(x) - \frac{K_b c_B(x)}{K_b + K_w 10^{pH}} + K_w 10^{pH}.$$

5.2 Diprotic weak

Now, when we have a weak diprotic acid, there is an extra equilibrium to consider, since the acid dissociation for some arbitrary acid H_2A can be written as



and then



I write K_{a1} and K_{a2} as the equilibrium constants of the first and second equation, respectively, where

$$K_{a1} = \frac{[HA^-][H_3O^+]}{[H_2A]} \quad \text{and} \quad K_{a2} = \frac{[A^{2-}][H_3O^+]}{[HA^-]}.$$

Similarly, I write α_1 and α_2 as the equilibrium shifts such that

$$K_{a1} = \frac{(\alpha_1 - \alpha_2)[H_3O^+]}{c_A(x) - \alpha_1} \quad \text{and} \quad K_{a2} = \frac{\alpha_2[H_3O^+]}{\alpha_1 - \alpha_2}.$$

Note that

$$\alpha_2 = \frac{\alpha_1 K_{a2}}{[H_3O^+] + K_{a2}},$$

so

$$K_{a1}(c_A(x) - \alpha_1) = \alpha_1[H_3O^+] \left(1 - \frac{K_{a2}}{[H_3O^+] + K_{a2}} \right).$$

It follows that

$$\alpha_1 = \frac{K_{a1}c_A(x)}{\frac{[H_3O^+]^2}{[H_3O^+] + K_{a2}} + K_{a1}}.$$

I now follow a similar procedure as that for the monoprotic weak acid, only that now α becomes $\alpha_1 + \alpha_2$. So, from (11), I get

$$10^{-pH} = \frac{K_{a1}c_A(x)}{\frac{10^{-2pH}}{10^{-pH} + K_{a2}} + K_{a1}} \left(1 + \frac{K_{a2}}{10^{-pH} + K_{a2}} \right) - \frac{K_b c_B(x)}{K_b + K_w 10^{pH}} + K_w 10^{pH}. \quad (16)$$

In Figure 4, I give an example of the graph that this relation gives with an acid as the analyte (concentration 1 mol L^{-1} , initial volume 50 mL , $K_{a1} = 10^{-2}$ and $K_{a2} = 10^{-2.5}$) and the base being strong and with concentration 1 mol L^{-1} .

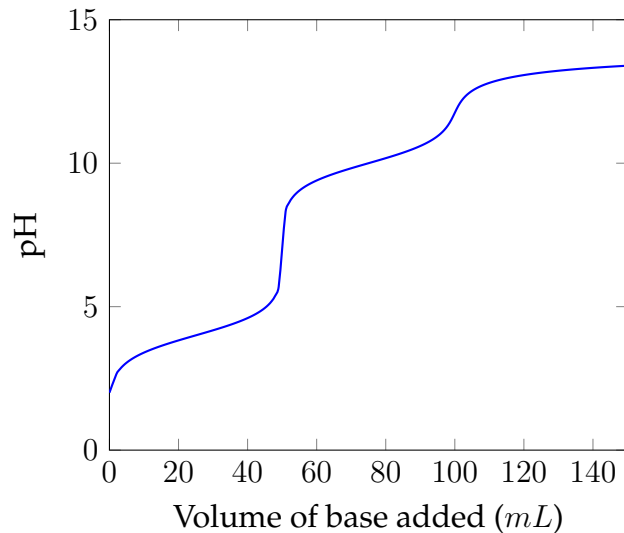
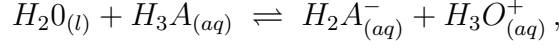


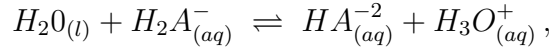
Figure 4: Weak diprotic acid - strong base titration

5.3 Triprotic weak

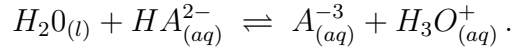
Similarly as above, I now write $\alpha = \alpha_1 + \alpha_2 + \alpha_3$, with the equilibrium for an arbitrary triprotic acid H_3A being



then



and finally



As before, I also write

$$K_{a1} = \frac{(\alpha_1 - \alpha_2)[H_3O^+]}{c_A(x) - \alpha_1} \quad \text{and} \quad K_{a2} = \frac{(\alpha_2 - \alpha_3)[H_3O^+]}{\alpha_1 - \alpha_2},$$

and

$$K_{a3} = \frac{\alpha_3[H_3O^+]}{\alpha_2 - \alpha_3}.$$

Now,

$$\alpha_3 = \frac{\alpha_2 K_{a3}}{[H_3O^+] + K_{a3}}, \quad (17)$$

so

$$K_{a2}(\alpha_1 - \alpha_2) = \alpha_2 \left(1 - \frac{K_{a3}}{[H_3O^+] + K_{a3}} \right) [H_3O^+],$$

giving

$$\alpha_2 = \frac{K_{a2}\alpha_1}{\frac{[H_3O^+]^2}{[H_3O^+] + K_{a3}} + K_{a2}}. \quad (18)$$

Finally,

$$K_{a1}(c_A(x) - \alpha_1) = \alpha_1 [H_3O^+] \left(1 - \frac{K_{a2}}{\frac{[H_3O^+]^2}{[H_3O^+] + K_{a3}} + K_{a2}} \right),$$

and so

$$\alpha_1 = \frac{K_{a1}c_A(x)}{[H_3O^+] \left(1 - \frac{K_{a2}}{\frac{[H_3O^+]^2}{[H_3O^+] + K_{a3}} + K_{a2}} \right) + K_{a1}}. \quad (19)$$

From (17), (18), (19) and (11), I conclude that, for a triprotic acid,

$$\begin{aligned} 10^{-pH} = & \frac{K_{a1}c_A(x)}{10^{-pH} \left(1 - \frac{K_{a2}}{\frac{10^{-2pH}}{10^{-pH} + K_{a3}} + K_{a2}} \right) + K_{a1}} \left(1 + \frac{K_{a2}}{\frac{10^{-2pH}}{10^{-pH} + K_{a3}} + K_{a2}} \left(1 + \frac{K_{a3}}{10^{-pH} + K_{a3}} \right) \right) \\ & - \frac{K_b c_B(x)}{K_b + K_w 10^{pH}} + K_w 10^{pH}. \end{aligned}$$

In Figure 5, I show a titration of a triprotic weak acid as the analyte (concentration 1 mol L^{-1} , initial volume as 50 mL , $K_{a1} = 10^{-1}$, $K_{a2} = 10^{-5}$ and $K_{a3} = 10^{-9}$) against a strong base with concentration 1 mol L^{-1} . Further in Figure 6, I show a variation of this graph by changing the value of K_{a1} to 10^{-3} , K_{a2} to 10^{-5} and K_{a3} to 10^{-6} .

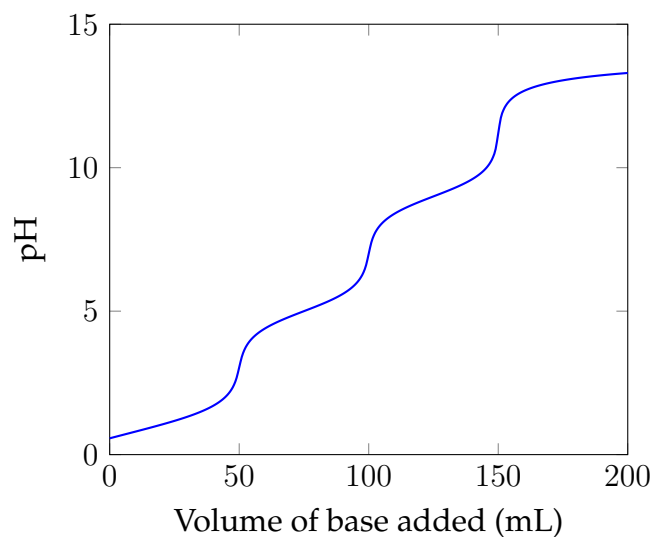


Figure 5: Weak triprotic Acid - strong base titration A

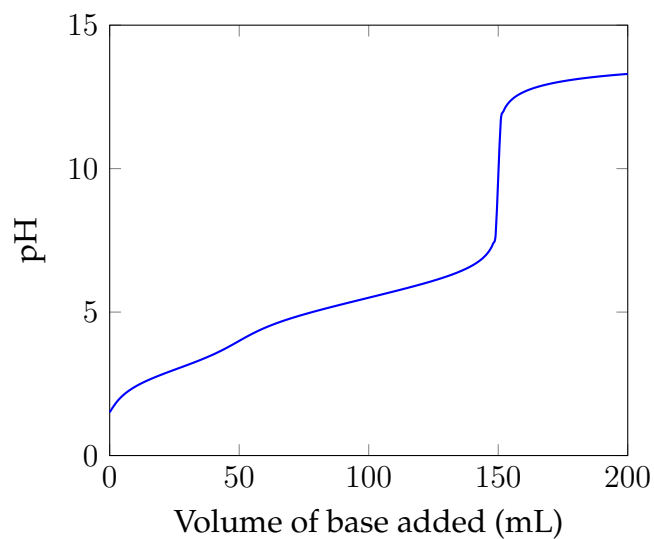
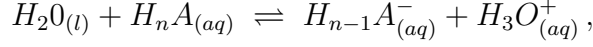


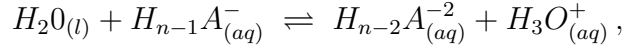
Figure 6: Weak triprotic acid - strong base titration B

5.4 n -protic weak

Now, for a n -protic weak acid, we have $\alpha = \alpha_1 + \alpha_2 + \dots + \alpha_n$. Further, the dissociation for an arbitrary n -protic acid H_nA can be given by

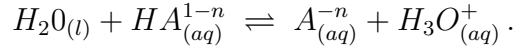


then



⋮

and finally



Further, I follow convention by setting

$$K_{a1} = \frac{(\alpha_1 - \alpha_2)[H_3O^+]}{c_A(x) - \alpha_1} \quad \text{and} \quad K_{an} = \frac{\alpha_n[H_3O^+]}{\alpha_{n-1} - \alpha_n},$$

and, for an integer i with $1 < i < n$,

$$K_{ai} = \frac{(\alpha_i - \alpha_{i+1})[H_3O^+]}{\alpha_{i-1} - \alpha_i}.$$

From the above, it can be seen that, for an integer i with $1 < i < n$,

$$\alpha_i = \frac{\alpha_{i-1}K_{ai}}{(1 - \frac{\alpha_{i+1}}{\alpha_i})[H_3O^+] + K_{ai}}.$$

Additionally, it can be seen that

$$\alpha_n = \frac{K_{an}\alpha_{n-1}}{[H_3O^+] + K_{an}} \quad \text{and} \quad \alpha_1 = \frac{c_A(x)K_{a1}}{(1 - \frac{\alpha_2}{\alpha_1})[H_3O^+] + K_{a1}}.$$

Therefore,

$$\alpha_i = c_A(x) \prod_{k=1}^i \frac{K_{ak}}{K_{ak} + [H_3O^+](1 - Q_k)},$$

where

$$Q_k = \frac{K_{ak}}{(1 - Q_{k+1})[H_3O^+] + K_{ak}}$$

and where $k \geq 1$ and $Q_{n+1} = 0$. Solving this recurrence gives the solution

$$Q_k = \frac{\sum_{j=1}^{n-k+1} [H_3O]^{n-k+1-j} \prod_{m=0}^{j-1} K_{a(m+k)}}{[H_3O]^{n-k+1} + \sum_{j=1}^{n-k+1} [H_3O]^{n-k+1-j} \prod_{m=0}^{j-1} K_{a(m+k)}}.$$

Thus, I can re-write α_i as

$$\alpha_i = c_A(x) \prod_{k=1}^i \frac{\sum_{j=1}^{n-k+1} [H_3O]^n [H_3O]^{-k+1-j} \prod_{m=0}^{j-1} K_{a(m+k)}}{[H_3O]^{n-k+1} + \sum_{j=1}^{n-k+1} [H_3O]^{n-k+1-j} \prod_{m=0}^{j-1} K_{a(m+k)}}.$$

Hence, for a n -protic acid, the relation between pH and x is given by

$$\begin{aligned} 10^{-pH} &= c_A(x) \sum_{i=1}^n \prod_{k=1}^i \frac{K_{ak}}{K_{ak} + 10^{-pH}(1 - Q_k)} - \frac{K_b c_B(x)}{K_b + K_w 10^{pH}} + K_w 10^{pH} \\ &= c_A(x) \sum_{i=1}^n \prod_{k=1}^i \frac{\sum_{j=1}^{n-k+1} 10^{-pH(n-k+1-j)} \prod_{m=0}^{j-1} K_{a(m+k)}}{10^{-pH(n-k+1)} + \sum_{j=1}^{n-k+1} 10^{-pH(n-k+1-j)} \prod_{m=0}^{j-1} K_{a(m+k)}} \\ &\quad - \frac{K_b c_B(x)}{K_b + K_w 10^{pH}} + K_w 10^{pH}. \end{aligned}$$

In Figure 7, I show a titration of a 4-protic weak acid as the analyte (concentration 1 mol L^{-1} , initial volume as 50 mL , $K_{a1} = 10^{-1}$, $K_{a2} = 10^{-2}$, $K_{a3} = 10^{-4}$ and $K_{a4} = 10^{-9}$) against a strong base with concentration 1 mol L^{-1} .

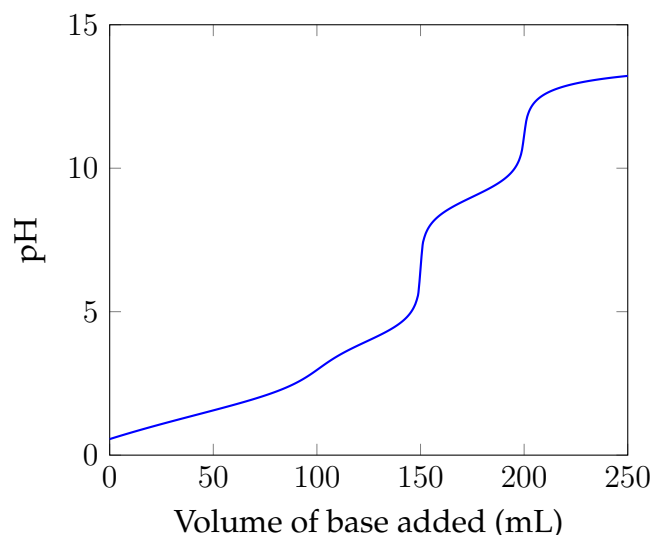


Figure 7: Weak 4-protic acid-strong base titration

6 Conclusion

An explicit formula (15) was found for an n -protic acid strong acid and m -protic strong base titration. Further, implicit formulae were found for weak-weak and weak-strong combinations of n -protic acids and m -protic bases. All this was accomplished using considerations of equilibrium.

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