Algebra for Modelling Titration Curves
Or: Where the @#$^! Does ϕ come from?

Interested in how we get from charge balance to phi (fraction of titration, ϕ) for the titration of a diprotic weak acid with a strong base? Remember, phi tells us where we are relative to the n^{th} equivalence point in a titration. For example, ϕ = 1 means we are at the 1^{st} equivalence point, ϕ = 1.5 means we have passed the 1^{st} equivalence point and are midway to the second equivalence point, if there is one.

For a long time, I just accepted that the phi function was reasonable, but now I want to know how it is derived. The Harris textbook starts the derivation, but then skips a lot of algebra and jump to the result, something I've become uncomfortable with! Since the algebra to determine phi may not be obvious, here it is! I show the derivation for the titration of a weak diprotic acid with a strong base, NaOH. The derivation for other acid/base combinations is similar. Note that terms highlighted in yellow will be cancelled in the subsequent step.

In this system we have the following reactions and equilibria to consider:

$$H_2A + 2\,NaOH \rightarrow Na_2A + 2H_2O$$
$$H_2A \rightleftharpoons HA^- + H^+$$
$$HA^- \rightleftharpoons A^{2-} + H^+$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Begin with charge balance

$$[H^+] + [Na^+] = [HA^-] + 2[A^{2-}] + [OH^-]$$

At any time in the titration, the total acid concentration, F_A and the sodium concentration $[Na^+]$ are:

$$F_A = \frac{C_a V_a}{V_a + V_b} \text{ and } [Na^+] = \frac{C_b V_b}{V_a + V_b}$$

Where C_a and C_b are the intital concentration of the weak acid and NaOH, V_a is the volume of acid solution used and V_b is the volume of titrant solution added. Inserting into the charge balance:

$$[H^+] + [Na^+] = \alpha_{HA^-} F_A + 2\alpha_{A^{2-}} F_A + [OH^-]$$

and

$$[H^+] + \frac{C_b V_b}{V_a + V_b} = \alpha_{HA^-}\left(\frac{C_a V_a}{V_a + V_b}\right) + 2\alpha_{A^{2-}}\left(\frac{C_a V_a}{V_a + V_b}\right) + [OH^-]$$

Multiplying both sides by (V_a+V_b) and simplifying:

$$(V_a + V_b)\left([H^+] + \frac{C_b V_b}{V_a + V_b}\right) = (V_a + V_b)\left(\alpha_{HA^-}\left(\frac{C_a V_a}{V_a + V_b}\right) + 2\alpha_{A^{2-}}\left(\frac{C_a V_a}{V_a + V_b}\right) + [OH^-]\right)$$

$$(V_a + V_b)[H^+] + (V_a + V_b)\left(\frac{C_b V_b}{V_a + V_b}\right) = (V_a + V_b)\left(\alpha_{HA^-}\left(\frac{C_a V_a}{V_a + V_b}\right)\right) + (V_a + V_b)\left(2\alpha_{A^{2-}}\left(\frac{C_a V_a}{V_a + V_b}\right)\right) + (V_a + V_b)[OH^-]$$

$$[H^+]V_a + [H^+]V_b + C_b V_b = \alpha_{HA^-}(C_a V_a) + 2\alpha_{A^{2-}}(C_a V_a) + [OH^-]V_a + [OH^-]V_b$$

Collecting "a" terms on one side and "b" terms on the other:

$$C_bV_b + [H^+]V_b - [OH^-]V_b = \alpha_{HA^-}(C_aV_a) + 2\alpha_{A^{2-}}(C_aV_a) + [OH^-]V_a - [H^+]V_a$$

Dividing both sides by C_aV_a:

$$\frac{C_bV_b}{C_aV_a} + \frac{[H^+]V_b}{C_aV_a} - \frac{[OH^-]V_b}{C_aV_a} = \frac{\alpha_{HA^-}(C_aV_a)}{C_aV_a} + \frac{2\alpha_{A^{2-}}(C_aV_a)}{C_aV_a} + \frac{[OH^-]V_a}{C_aV_a} - \frac{[H^+]V_a}{C_aV_a}$$

Simplifying:

$$\frac{C_bV_b}{C_aV_a} + \frac{[H^+]V_b}{C_aV_a} - \frac{[OH^-]V_b}{C_aV_a} = \alpha_{HA^-} + 2\alpha_{A^{2-}} + \frac{[OH^-]}{C_a} - \frac{[H^+]}{C_a}$$

Now we have something that has (C_bV_b/C_aV_a) in it, but we still have V_b appearing in other terms and we need to somehow get rid of it in all terms except for (C_bV_b/C_aV_a).

I struggled with this for a while, but it turns out that we need to factor (C_bV_b/C_aV_a) out of the left side (This part isn't very obvious, but we need to get to the correct form for phi). Factoring the left side and simplifying:

$$\frac{C_bV_b}{C_aV_a}\left(1 + \frac{[H^+]V_b}{C_bV_b} - \frac{[OH^-]V_b}{C_bV_b}\right) = \alpha_{HA^-} + 2\alpha_{A^{2-}} + \frac{[OH^-]}{C_a} - \frac{[H^+]}{C_a}$$

$$\frac{C_bV_b}{C_aV_a}\left(1 + \frac{[H^+]}{C_b} - \frac{[OH^-]}{C_b}\right) = \alpha_{HA^-} + 2\alpha_{A^{2-}} + \frac{[OH^-]}{C_a} - \frac{[H^+]}{C_a}$$

Rearranging:

$$\frac{C_bV_b}{C_aV_a} = \phi = \frac{\alpha_{HA^-} + 2\alpha_{A^{2-}} + \frac{[OH^-]}{C_a} - \frac{[H^+]}{C_a}}{\left(1 + \frac{[H^+]}{C_b} - \frac{[OH^-]}{C_b}\right)}$$

Which can be rewritten to match the format in the text:

$$\frac{C_bV_b}{C_aV_a} = \phi = \frac{\alpha_{HA^-} + 2\alpha_{A^{2-}} - \frac{[H^+] + [OH^-]}{C_a}}{\left(1 + \frac{[H^+] - [OH^-]}{C_b}\right)}$$