

General Solution of a Weak Acid Problem - Harris, 9-3

Let's consider the general case of a weak acid HA, with formal concentration F_{HA} and acid dissociation constant K_a . Applying the systematic treatment to such a problem, we get:

Charge Balance: $[H^+] = [A^-] + [OH^-]$

"Atomic" balance on A: $F_{\text{HA}} = [HA] + [A^-]$ (A is not assembled or torn apart)

(Can't write true atomic balances on O or H until we know if they are present in A)

Equilibrium expression for HA: $\frac{[H^+][A^-]}{[HA]} = K_a$

Equilibrium expression for autoionization of water: $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$

Let's apply this to determining the pH of common vinegar, which is 0.84₁ M acetic acid (CH₃COOH) in water. We'll use HA as a shorthand for acetic acid, and A⁻ as short for its conjugate base, the acetate ion (CH₃COO⁻). Appendix G indicates that the pK_a of acetic acid is 4.756. That means that (to demo pK_a):

$$pK_a = -\log_{10} K_a = 4.756 \Rightarrow K_a = 10^{-pK_a} = 10^{-4.756} = 1.75_4 \times 10^{-5}$$

With this variable replaced with a number, the system of four equations above entails four variables: $[H^+]$, $[OH^-]$, $[HA]$, and $[A^-]$; thus it is soluble if F_{HA} is known (and not a variable). While that could be done with brute force, "chemical intuition" can make things much easier on us. We know acetic acid is an acid, with a not-ultra-puny K_a ($\gg K_w$) and at a respectable concentration. Thus we can reasonably hope that the solution will be acidic, which will mean $[OH^-]$ will be quite small, probably negligible relative to $[A^-]$ in the charge balance sum. We can assume anything we want, with little risk, provided we check our assumptions. Think of it this way: if I'm writing a novel on my computer, and I have an idea for a plot twist, I can write it all out. Then I read it, and see if it sucks. If it does, I'm out only the time and energy it took me to write it. If it may makes the novel move along much more surely and quickly than anything else I had in mind, it's a risk worth taking.

Here, the assumption $[OH^-] \ll [A^-]$ allows us to simplify the charge balance to just $[H^+] = [A^-]$. Then, with the atomic balance and HA expression (we don't need the water equilibrium unless we want to solve for the additional variable $[OH^-]$), we can solve for $[H^+]$:

$$F_{\text{HA}} = [HA] + [A^-] = [HA] + [H^+] \Rightarrow [HA] = F_{\text{HA}} - [H^+]$$

$$\frac{[H^+][A^-]}{[HA]} = K_a = \frac{[H^+][H^+]}{F_{\text{HA}} - [H^+]} \Rightarrow K_a(F_{\text{HA}} - [H^+]) = [H^+]^2 \Rightarrow 0 = [H^+]^2 + K_a[H^+] - K_aF_{\text{HA}}$$

Solving the quadratic: $[H^+] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-K_a \pm \sqrt{K_a^2 + 4K_aF_{\text{HA}}}}{2}$

$$= \frac{-1.75 \times 10^{-5} \pm \sqrt{5.90 \times 10^{-5}}}{2} = -8.77 \times 10^{-5} \pm 3.84 \times 10^{-3} = 3.8_3 \times 10^{-3} \text{ or a negative value}$$

Checking validity of assumption: $[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = 2.6_1 \times 10^{-12}$ Much smaller than $[A^-] = [H^+]$

\therefore the assumption is valid and the solution obtained by making it is correct, within significant figures.

The pH of vinegar is therefore $\text{pH} \approx -\log_{10}[H^+] = -\log_{10}(3.8_3 \times 10^{-3}) = 2.41_7$ (moderately acidic)

Important: When looking for approximations one might make, inspect the *sums* involved in a problem. A very small quantity can be ignored in a sum, but not in a product.

In retrospect, we see we could have actually gotten away with an even more drastic simplifying assumption in working this problem. Acetic acid is weak enough that (in the absence of other species) the bulk of it remains associated in water. Thus $[HA] \gg [A^-]$, and we could have approximated $[HA]$ as just F_{HA} , simplifying the rest of the math as well: (Yes, this is confusing: $[A^-]$ is tiny, but still $\gg [OH^-]$!)

$$[H^+] = [A^-] + [OH^-] \approx [A^-]$$

$$F_{HA} = [HA] + [A^-] \approx [HA]$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \approx \frac{[H^+][H^+]}{F_{HA}} \Rightarrow [H^+]^2 = K_a F_{HA} \Rightarrow [H^+] = \sqrt{K_a F_{HA}}$$

So, in this case, $[H^+] = \sqrt{(1.75 \times 10^{-5})(0.84_1)} = 3.8_{36} \times 10^{-3} \text{ M} = [A^-]$

Since the putative $[A^-]$ is indeed negligibly small relative to F_{HA} (0.0038 M vs 0.84 M), within the significant figures of the given information, this assumption is also valid, and the results calculated on the basis of it correct. An assumption along this line is dicier to make, but worth a shot when the K_a value of the acid is appreciably different from its formal concentration. (Either $K_a \gg F_{HA}$, and we assume that most of the acid is dissociated, or $K_a \ll F_{HA}$, and we assume most of it remains as HA.)

General Solution of a Weak Base Problem - Harris 9-4

Solving a general weak base problem follows in the footsteps of doing so for a weak acid, as outlined in Harris 9-4. Here we assume that we have a basic solution, and thus $[H^+]$ is negligible, however. We can also try getting away with assuming the base is so weak that most of it remains as B, or strong enough that the vast majority of it will be present as BH^+ .

Fraction of [Dissociation of an Acid/Association of a Base] (α) - Harris 9-3 and 9-4

A simple but very useful quantity in working on acid/base problems is the fraction of dissociation or association, more commonly referred to as the "alpha fraction" of a given species:

$$\alpha_{\text{specific form}} \equiv \frac{\text{Concentration of species present in specified form}}{\text{Total concentration of species}}$$

$$\alpha_{A^-} = \frac{[A^-]}{[HA] + [A^-]} \quad (\text{Harris: "Fraction of dissociation of HA"})$$

$$\alpha_{BH^+} = \frac{[BH^+]}{[BH^+] + [B]} \quad (\text{Harris: "Fraction of association of B"})$$

Generalized equations for α in terms of pH can be derived, and so it's pretty easy to make an $\alpha(\text{pH})$ plot.

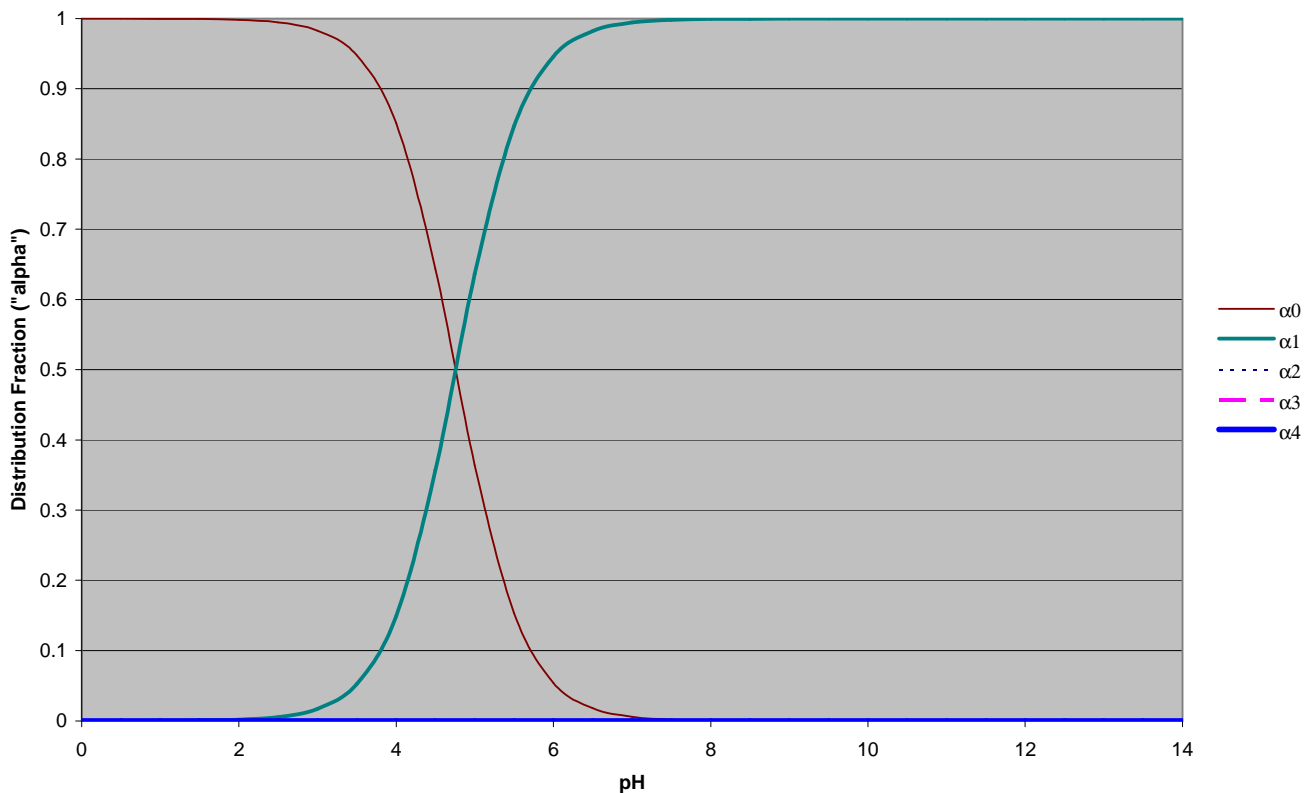
Example: What's the alpha fraction of acetate ion in common vinegar, α_{A^-} ? Using our work above,

$$\alpha_{\text{CH}_3\text{COO}^-} = \alpha_{A^-} = \frac{[A^-]}{[HA] + [A^-]} = \frac{[H^+]}{F_{HA}} = \frac{3.8_3 \times 10^{-3} \text{ M}}{0.84_1 \text{ M}} = 0.0045_{54}$$

This underscores the fact that the vast majority of the acetic acid is undissociated, present as HA. The fraction of dissociation of acetic acid in this solution is very small, as per our valid assumption above!

[Spreadsheet demo: \$\alpha\$ fraction vs. pH for acetic acid](#)

Acid/Base Distribution Diagram



Buffers – Harris 9-5

Buffer: a solution containing both a weak (acid or base) and its conjugate, in similar quantities

Buffers have the important property that they resist changes in pH due to dilution or the addition of acid or base. They manage this by having both acid and base poised to react at even a slight change in pH: their pH must be in the region of the $\alpha(\text{pH})$ plot where α quickly transitions from 0 to 1, which is within one unit of their pK_a (e.g., between 3.75 and 5.75 for acetic acid/acetate ion, its pK_a being 4.756).

« Show α plot for acetic acid / acetate system again, emphasizing that α change means reaction »

To actually prepare a buffer in the lab, you would start with a solution of a weak acid or base, then add strong base or acid to it, monitoring the pH with a pH meter. This would cause, at first, a rapid change in pH. Then, as the amount of conjugate increased to near parity, the pH would become harder to change, and you would have a buffer. You would continue adding the strong base or acid until the pH was equal to the buffer pH you wanted. You couldn't just pick any acid or base you wanted to make a buffer of a specific pH, though: you would need the slowdown to occur near that pH, and that would require the pK_a for the acid in the conjugate pair to be within about one unit of the buffer pH. If that's not the case, you could still move the pH to that value, but the amounts of HA and A^- (or of B and BH^+) would be very lopsided, and you wouldn't have a buffer. So in real life, the key to making a good buffer is picking a conjugate pair with the right pK_a value.

« Demo? Add NaOH to acetic acid / vinegar? Use autotitrator? »

Another way to make the same buffer, if more labor-intensive, would be to mix appropriate amounts of the two conjugates together directly. That's rarely actually done, but often the subject of calculations.

A key insight to dealing with problems such as these is that in many situations, the conjugates just "sit there" once added to solution: they dissolve, but do not (to an appreciable extent), react. For example, if we combine 0.1 mol of acetic acid and 0.1 mol of sodium acetate in water, at equilibrium we will have, very nearly, 0.1 mol of acetic acid and 0.1 mol of acetate ion floating around in solution.

Mathematically, $[A^-] \approx F_{NaA}$ and $[HA] \approx F_{HA}$. This is because HA is a weak enough acid that it doesn't dissociate much, and A^- is a weak enough base that it doesn't associate much. Moreover, their conjugates being present in solution only serves to further suppress their acting as acids and bases.

This approximation greatly simplifies calculations of this sort, and is essential to providing the Henderson-Hasselbalch equation with much of its utility. The approximation breaks down when:

- the concentrations are very lopsided (F_{HA} and F_{NaA} differ by a factor of more than 100)
- the solution is very dilute or highly concentrated (F_{HA} and F_{NaA} are outside the mM range)
- the conjugates are not both quite weak (pK_a isn't somewhere between 4 and 10) ($pK_a > 10 \Rightarrow pK_b < 4$)

If more than one of these limitations are close to being exceeded, they can conspire to undermine the validity of the assumption; so with anything that matters, you want to confirm its validity at the end.

The Henderson-Hasselbalch Equation – Harris 9-5

For quick and dirty buffer work, nothing beats the HH. It is merely a rewriting of the equilibrium

expression for a weak acid:
$$K_a = \frac{[H^+][A^-]}{[HA]}$$
 Taking the $-\log_{10}$ of both sides,

$$-\log_{10} K_a = -\log_{10} [H^+] + -\log_{10}[A^-] - -\log_{10}[HA] \Rightarrow pK_a = pH - \log_{10}[A^-] + \log_{10}[HA]$$

$$pH = pK_a + \log_{10}[A^-] - \log_{10}[HA] = pK_a + \log \left(\frac{[A^-]}{[HA]} \right) \text{ -or- } \left(\frac{[B]}{[BH^+]} \right)$$

The pK_a in this expression is always that of the acid in the denominator; and you can confirm that you have the sign and arrangement of the last term right by asking yourself what should happen to the pH if you increase the amount of acid (HA or BH^+) present in the solution: the pH should go down.

Note that this derivation of the Henderson-Hasselbalch equation didn't involve any assumptions: it is always valid! What is often assumed, and often valid, is that $[A^-] \approx F_{NaA}$ and $[HA] \approx F_{HA}$, such that

$$pH = pK_a + \log \left(\frac{[A^-]}{[HA]} \right) \approx pK_a + \log \left(\frac{F_{NaA}}{F_{HA}} \right)$$

The HH tells us that when $pH = pK_a$, the concentration of A^- and HA in solution are equal. This is called the "buffer point," and is the optimal pH for a buffer made from A^- and HA .