

pH versus Concentration

John Denker

* Contents

[1 Overview](#)

[2 Handy Estimates](#)

[3 Numerical Evaluation](#)

[4 Derivation](#)

[4.1 Cubic](#)

[4.2 Cubic, with Buffer](#)

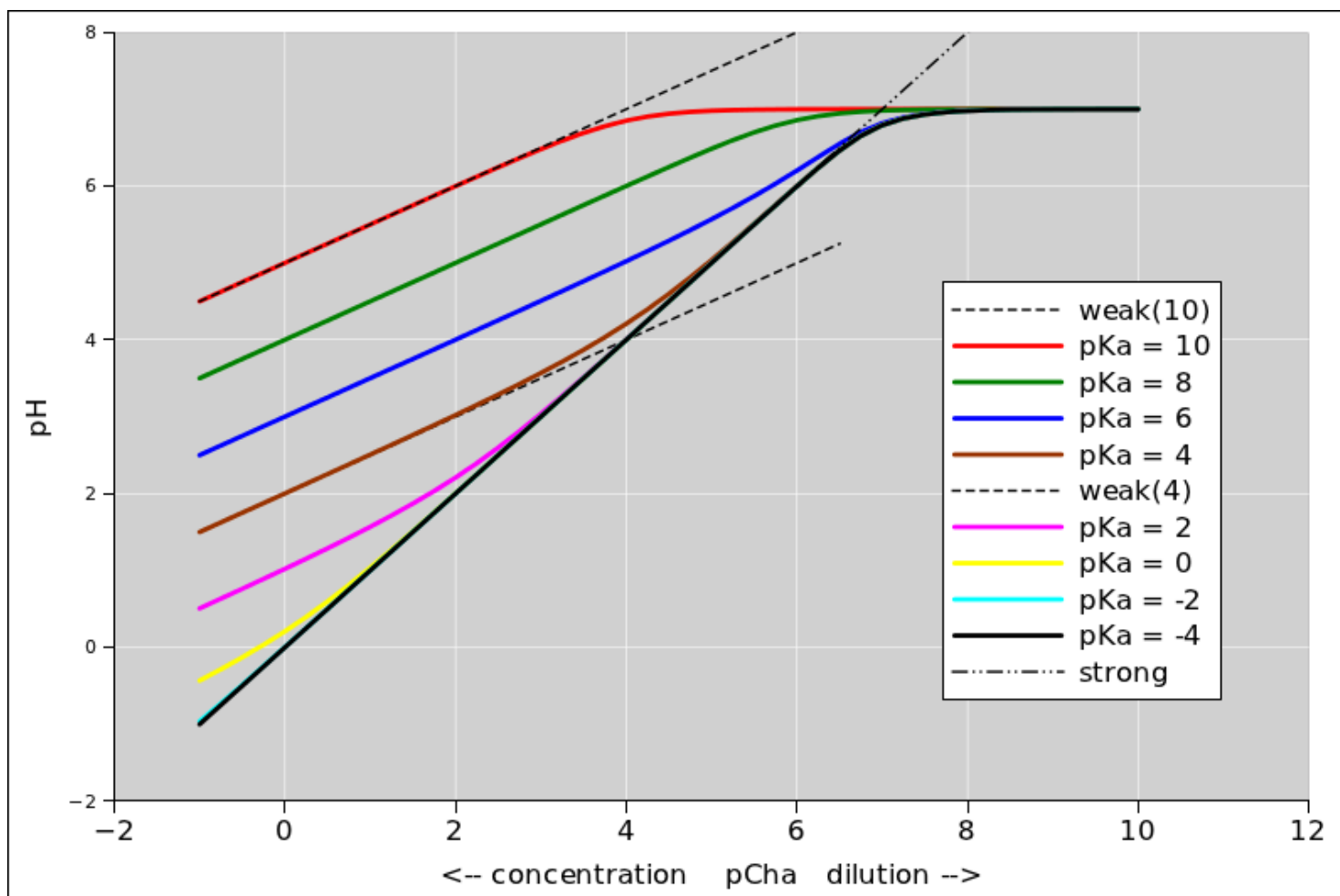
[4.3 Quadratic](#)

[5 References](#)

1 Overview

[Figure 1](#) shows pH as a function of concentration, for various pK_a values, including weak acids and strong acids, as well as intermediate-strength acids, which are particularly interesting.

The pK_a values for some common acids and bases are tabulated in [reference 1](#). In this document, we consider only monoprotic acids.



[Figure 1](#): pH versus Concentration for Various pK_a Values

These curves have a number of interesting properties:

1. For a very weak acid (such as the one represented by the red curve), there is a large range of concentrations (many decades) where the pH closely follows the weak-acid rule of thumb, namely the following straight-line approximation:

$$pH = \frac{pK_a + pC_{HA}}{2} \quad (1)$$

For an explanation of the notation used here, see [reference 2](#) or [reference 3](#).

If we express same relationship in terms of concentration (rather than log concentration) we get:

$$[H^+] = \sqrt{K_a C_{HA}} \quad (2)$$

2. For an acid that is not very weak but also not what we would call a “strong” acid (such as the one represented by the brown curve), the pH follows the weak-acid rule of thumb for a while, but then bends up to follow the strong-acid rule, namely the following straight-line approximation:

$$pH = pC_{HA} \quad (3)$$

To say the same thing in other words: It is interesting that over the whole range from $pK_a = 0$ to $pK_a = 5$ or 6 , the acid follows the weak-acid rule at high concentration, but then follows the strong-acid rule at moderately low concentration.

The meaning of [equation 3](#) is clear: it just says that all the acid molecules are ionized (and that auto-ionization of the

water molecules is negligible). This is what we expect for a reasonably concentrated strong acid ... and it also makes sense for a moderately-dilute moderately-weak acid. Simple entropy considerations suggest that greater dilution favors greater ionization.

3. Eventually all the curves bend over to join the ultra-dilute asymptote (virtually pure water), namely the following horizontal straight-line approximation:

$$\text{pH} = \frac{\text{p}K_w}{2} \quad (4)$$

2 Handy Estimates

1. You can get a good estimate by reading the curves in [figure 1](#) and interpolating.
2. If you want to calculate an estimate, the three straight-line approximations mentioned in [section 1](#) can be combined via a two-step process, namely:
 - o First compute the weak-acid approximation and the strong-acid approximation. If the weak-acid rule claims your acid is stronger than a strong acid, it's obviously wrong. Use the strong acid rule instead. More specifically, use whichever predicts the higher pH (either the strong-acid rule or the weak-acid rule).
 - o Secondly, compute the pure-water approximation. If the result of the previous step predicts a higher pH than pure water, it's obviously wrong; use the water pH instead. More specifically, use whichever predicts the lower pH (either the result from the previous step or the water pH).
3. If you are anywhere near a computer, it is easy to compute the exact answer, as discussed in [section 3](#).

3 Numerical Evaluation

The curves in [figure 1](#) were computed by solving the following equation. It is a cubic polynomial, with one positive root and two negative roots. The positive root is the only one that makes sense as a concentration.

$$[\text{H}^+]^3 + K_a [\text{H}^+]^2 - (K_w + K_a C_{\text{HA}}) [\text{H}^+] - K_a K_w = 0 \quad (5)$$

Compare [equation 25](#).

It is easy to solve [equation 5](#) with an iterative root-finding algorithm. I've had good luck with the Brent algorithm ([reference 4](#)).

In contrast, beware that standard “algebraic” formulas for solving the cubic can give wrong answers in some cases. Depending on details of the implementation, the formulas can be numerically unstable. That is to say, the result gets trashed by roundoff errors. Specifically: I tried using the standard library routine `gsl_poly_complex_solve_cubic()` and it failed spectacularly for certain values of $\text{p}K_a$ and $\text{p}C_{\text{HA}}$. Some of the alleged results were off by multiple orders of magnitude. Some of the alleged results were complex numbers, even though the right answers were real numbers. It might be possible to rewrite the code to make it behave better, but that's not a job I'm eager to do.

Lesson #1: Something that looks like an “exact” closed-form solution might not be at all suitable for real-world numerical calculation ... whereas an approximate, iterative solution might be highly accurate in practice.

Lesson #2: The failure of the algebraic method serves as a reminder of the difference between uncertainty and significance. The inputs to the method might or might not be uncertain; it doesn't actually matter. The output (i.e. the root as plotted in [figure 1](#)) has a tolerance of a few percent. The internal calculations use IEEE double-precision floating point, which is good to about 16 decimal digits ... which is not enough for the task at hand. Even though the tolerance allows uncertainty in the second digit, there is significance in the 16th digit and beyond. So, if you see a number of the form:

$$X = \left(1.497925297894696 \dots \right) \quad (6)$$

$$(\pm 0.01)$$

you should not assume it is safe to round things off. In this case, such a number already has too few digits. For more on this, see [reference 5](#).

The C++ code to calculate the pH as a function of concentration can be found in [reference 6](#).

4 Derivation

4.1 Cubic

For an explanation of the notation used here, see [reference 2](#) or [reference 3](#).

[Equation 5](#) can be derived from the definition of the acid dissociation constant:

$$K_a := \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (7)$$

and the water dissociation constant:

$$K_w := [\text{H}^+][\text{OH}^-] \quad (8)$$

and the conservation laws, namely conservation of A-groups:

$$[\text{A}^-] + [\text{HA}] = C_{\text{HA}} \quad (9)$$

as well as conservation of charge:

$$[\text{H}^+] - [\text{A}^-] - [\text{OH}^-] = 0 \quad (10)$$

That gives us four equations in four unknowns. Turning the crank on the algebra gives us

$$[\text{H}^+]^3 + K_a [\text{H}^+]^2 - (K_w + K_a C_{\text{HA}}) [\text{H}^+] - K_a K_w = 0 \quad (11)$$

which is the same as [equation 5](#). The details of the derivation are given in [section 4.2](#), leading to a fancier version of this equation, namely [equation 25](#).

4.2 Cubic, with Buffer

Let's consider a system that is the same as in [section 4.1](#), except that we also add a certain amount of very strong base. This gives us a buffer solution.

As in [equation 7](#) the acid dissociation constant is:

$$K_a := \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (12)$$

As in [equation 8](#) the water dissociation constant is:

$$K_w := [\text{H}^+][\text{OH}^-] \quad (13)$$

And as in [equation 9](#), A-groups are conserved:

$$[A^-] + [HA] = C_{HA} \quad (14)$$

At this point, we add a new equation, stating that the B-groups are conserved:

$$[B^+] + [BOH] = C_{BOH} \quad (15)$$

and since we are assuming the base is very strong, we can immediately simplify this to

$$[B^+] = C_{BOH} \quad (16)$$

and as in [equation 10](#), the charge is conserved, except that now we have to include the base:

$$[H^+] + [B^+] - [A^-] - [OH^-] = 0 \quad (17)$$

Now we turn the crank. We start by plugging into [equation 12](#), using [equation 14](#) to eliminate the unknown $[HA]$ from the system of equations.

That gives us

$$K_a = \frac{[H^+] [A^-]}{C_{HA} - [A^-]} \quad (18)$$

hence:

$$K_a C_{HA} - K_a [A^-] = [H^+] [A^-] \quad (19)$$

hence:

$$[A^-] = \frac{K_a C_{HA}}{[H^+] + K_a} \quad (20)$$

We now plug into the charge-conservation expression, [equation 17](#), using [equation 16](#), [equation 20](#), and [equation 13](#) to get rid of all the unknowns. That gives us

$$[H^+] + C_{BOH} - \frac{K_a C_{HA}}{[H^+] + K_a} - \frac{K_w}{[H^+]} = 0 \quad (21)$$

Multiplying through by $[H^+]$ gives us

$$[H^+]^2 + [H^+] C_{BOH} - [H^+] \frac{K_a C_{HA}}{[H^+] + K_a} - K_w = 0 \quad (22)$$

Multiplying through by the remaining denominator gives us

$$[\text{H}^+]^3 + [\text{H}^+]^2 K_a + [\text{H}^+]^2 C_{\text{BOH}} + [\text{H}^+] K_a C_{\text{BOH}} - [\text{H}^+] K_a C_{\text{HA}} - [\text{H}^+] K_w - K_a K_w = 0 \quad (23)$$

which can be rearranged to give the “usual” result:

$$[\text{H}^+]^3 + (C_{\text{BOH}} + K_a) [\text{H}^+]^2 + (K_a C_{\text{BOH}} - K_w - K_a C_{\text{HA}}) [\text{H}^+] - K_a K_w = 0 \quad (24)$$

By setting C_{BOH} to zero we obtain [equation 5](#), so you can see why we didn’t bother showing the derivation until now.

Now suppose we throw in some strong acid HA' in addition to (or instead of) the strong base. You can easily show that the only thing that matters is Q , namely the *difference* between the amount of strong base and the amount of strong acid. This gives us a more general equation:

$$[\text{H}^+]^3 + (Q + K_a) [\text{H}^+]^2 + (K_a Q - K_w - K_a C_{\text{HA}}) [\text{H}^+] - K_a K_w = 0 \quad (25)$$

where $Q := C_{\text{BOH}} - C_{\text{HA}}$,

4.3 Quadratic

It is sometimes convenient to restrict attention to the parts of [figure 1](#) that are not too near the top. That is, we focus attention on solutions that are definitely acidic, with a pH well below the pH of water. In this case, [equation 5](#) simplifies to:

$$[\text{H}^+]^2 + K_a [\text{H}^+] - K_a C_{\text{HA}} = 0 \quad (26)$$

as you can see by starting with [equation 5](#) and setting K_w to zero. [Equation 26](#) can also be easily derived directly from [equation 7](#), [equation 9](#), and the simplified charge-conservation law:

$$[\text{H}^+] - [\text{A}^-] = 0 \quad (27)$$

[Equation 26](#) is a quadratic polynomial. It has one positive root and one negative root.

5 References

1. Oliver Seely,
“Dissociation Constants for Common Acids and Bases”
<http://www.csudh.edu/oliver/chemdata/data-ka.htm>
2. Stephen K. Lower,
“Acid-base Equilibria and Calculations”
<http://www.chem1.com/acad/pdf/clxacid2.pdf>
3. David Laude,
“Complex Equilibria– What to do when assumptions aren’t okay”
<http://laude.cm.utexas.edu/courses/ch302/lecture/ln15s09.pdf>
4. Richard Brent,
“Algorithms for Minimization Without Derivatives”
http://people.sc.fsu.edu/~jburkardt/cpp_src/brent/brent.html
5. John Denker,
“Measurements and Uncertainties”
<http://www.av8n.com/physics/uncertainty.htm>
6. John Denker,
“plot pH as a function of concentration, for various pKa values”

Search