A Closer Look at Titrations

Our analysis of titrations in CH 223 skimmed over two topics that might prove troublesome to the observant student. They are:

- the effect on pH in a strong acid - strong base (or strong base - strong acid) titration when the moles of strong acid and strong base are almost (but not quite) identical; and
- The effect on pH from a weak acid if 100 * K_a is about equal to C_a, or if approximation methods fail

We will reflect on both of these situations in more detail. A brief discussion of the corresponding pH effect in a strong base - strong acid titration when n_{sa} and n_{sb} are about equal will be discussed. In addition, a brief discussion of a weak base pH calculation when approximations fail will be summarized below.

This handout uses notation from the "Titration Calculations" lab used in CH 223.

Case #1: The Effect on pH in a strong acid - strong base titration when the moles of strong acid (n_{sa}) and strong base (n_{sb}) are almost (*but not quite*) equal

The problem: Consider this question:

> What is the pH when 24.99999 mL of 0.10 M NaOH have been added to 50.0 mL of 0.050 M HCl?

In this problem we have a *slight* excess of strong acid (n_{sa}) relative to the strong base (n_{sb}), and we are in the "pre-equivalence region" despite the minimal excess. Using the system outlined in the "Titration Calculations" lab for a strong acid - strong base titration, we can calculate pH:

$$\mathbf{pH = -\log\left(\frac{n_{sa} - n_{sb}}{V_{sa} + V_{sb}}\right)}$$

$$\mathbf{pH = -\log\left(\frac{0.0500\ L\ *\ 0.050\ M\ -\ 0.02499999\ L\ *\ 0.10\ M}{0.050\ L\ +\ 0.024999\ L}\right)}$$

$$\mathbf{pH = 7.88}$$

But does this answer make sense? If you have more acid than base, the pH ought to have a value *less than* 7. How can an excess of acid create a basic pH? Remember that in a strong acid - strong base titration, the pH at the equivalence point equals 7. Having a basic pH prior to equivalence would create a titration graph not observed in the laboratory.

The problem with the pH calculation rests in the equation used. At extreme dilutions, we have to take the autoionization of water into account to get a valid value of pH.

A more thorough analysis for dilute acid concentrations follows. **Let us calculate the pH of a $1.33*10^{-8}$ M HCl solution.**

Conventional acid-base theory would predict a pH using

$$pH = -\log\,[H_3O^+] = -\log\,(1.33*10^{-8}) = 7.87$$

which is too basic considering a strong acid is present.

To calculate the pH correctly, we need the following:

1. A **charge balance equation** that sets all of the negative charges equal to the positive charges. Here, the only cation is $\mathbf{H_3O^+}$, and the anions are $\mathbf{Cl^{-1}}$ and $\mathbf{OH^{-1}}$**.** The hydroxide comes from the autoionization of water. Hence, due to all solutions being electrically neutral, we can say:

   $$[H_3O^+] = [Cl^{-1}] + [OH^{-1}]$$

2. We also need the equation for the autoionization of water; namely,

   $$[H_3O^+] * [OH^{-1}] = K_w$$

   where the **autoionization of water equilibrium constant,** $\mathbf{K_w = 1.00*10^{-14}}$ at 25 °C

Also realize that $\mathbf{[Cl^{-1}] = 1.33*10^{-8}}$ **M** in our HCl solution.

We can rearrange the autoionization of water equation and substitute in the value of $[OH^{-1}]$ from the charge balance equation as follows:

$$[H_3O^+] = \frac{K_w}{\left[OH^{-1}\right]} = \frac{K_w}{\left[H_3O^+\right] - \left[Cl^{-1}\right]}$$

Rearranging, one gets:

$$[H_3O^+]([H_3O^+] - [Cl^{-1}]) = K_w$$

and upon further rearrangement of the equation into a quadratic formula

$$[H_3O^+]^2 - [Cl^{-1}][H_3O^+] - K_w = 0$$

where a = 1, b = $[Cl^{-1}]$, and c = K_w. Using the quadratic formula, the following expression is found:

$$[H_3O^+] = \frac{\left[Cl^{-1}\right] \pm \sqrt{\left[Cl^{-1}\right]^2 + 4K_w}}{2}$$

This is a more thorough method to calculate $[H_3O^+]$ between a strong acid and strong base, but its implementation can be more challenging.

In our example, $\mathbf{[Cl^{-1}] = 1.33*10^{-8}}$ **M** and $\mathbf{K_w = 1.00*10^{-14}}$. Using the quadratic formula for $[H_3O^+]$, above, we find that

$$[H_3O^+] = 1.07*10^{-7}\ M$$

and

$$pH = 6.97$$

which is a sensible answer due to the slight abundance of strong acid (HCl) over neutral water.

In the original example used at the beginning of Case #1, NaOH *and* HCl were used. This leads to a different version of the total charge equation:

$$[H_3O^+] + [Na^+] = [Cl^{-1}] + [OH^{-1}]$$

All cations must equal all anions in a charge equation; hence, the addition of the spectator ion Na^+ to the charge equation from the NaOH.

Because $[Na^+]$ and $[Cl^{-1}]$ are constants - i.e. they do not interfere with the pH - the resulting quadratic equation is only slightly different:

$$[H_3O^+] = \frac{\left(\left[Cl^{-1}\right] - \left[Na^+\right]\right) \pm \sqrt{\left(\left[Cl^{-1}\right] - \left[Na^+\right]\right)^2 + 4K_W}}{2}$$

In the original problem, 24.99999 mL of 0.10 M NaOH were added to 50.0 mL of 0.050 M HCl. Calculating the diluted concentrations of the spectator ions leads to:

$$[Na^+] = \frac{0.02499999\ L\ *\ 0.10\ M}{0.02499999\ L + 0.0500\ L} = 0.0333333244\ M$$

$$[Cl^-] = \frac{0.050\ L\ *\ 0.050\ M}{0.02499999\ L + 0.0500\ L} = 0.0333333378\ M$$

Additional significant figures are required to prevent $([Cl^{-1}] - [Na^+])$ from going to zero. With the additional significant figures,

$$([Cl^{-1}] - [Na^+]) = 1.34*10^{-8}\ M$$

and upon substituting into the expanded quadratic formula above, one calculates

$$[H_3O^+] = 1.07*10^{-7}\ M$$

and

$$pH = 6.97$$

Note that the above procedure could be developed for a strong base - strong acid titration equation just as readily using a focus on the $[OH^{-1}]$ generated instead of the $[H_3O^+]$.

Case #2: The effect on pH from a weak acid if 100 * K_a is about equal to C_a, or if approximation methods fail

The problem: Consider this question:

What is the pH of 0.0010 M formic acid? $K_a = 1.8*10^{-4}$

In most situations, the pH of a weak acid can be calculated thusly:

$$\mathbf{pH = -\log \sqrt{K_a * C_a}}$$

$$\mathbf{pH = -\log \sqrt{1.8 \times 10^{-4} * 0.0010}}$$

pH = 3.37 *...but this answer is wrong!*

The approximation method used in this approach does not apply because **100 * K_a is not less than C_a.** The approximation method works well for acids with a small K_a values and acid concentrations which are relatively high. But alas! The world does not always fit in these categories, so we need a more comprehensive method to calculate $[H_3O^+]$ and pH for these systems.

Recall that

$$K_a = \frac{[H_3O^+][A^{-1}]}{[HA]}$$

where **K_a = acid dissociation constant**, **A^{-1} = conjugate base of the weak acid**, and **HA = equilibrium concentration of the weak acid**. Also recall that **C_a = initial concentration of weak acid**.

At equilibrium,

$$[H_3O^+] = [A^{-1}]$$

and also at equilibrium

$$[HA] = C_a - [A^{-1}]$$

Substitution of these expressions into the K_a expression above leads to

$$K_a = \frac{[H_3O^+][A^{-1}]}{[HA]} = \frac{[H_3O^+]^2}{C_a - [H_3O^+]}$$

Rearrangement leads to the following quadratic formula:

$$[H_3O^+]^2 + K_a[H_3O^+] - K_aC_a = 0$$

Placing the terms in the quadratic formula provides the following expression for $[H_3O^+]$:

$$[H_3O^+] = \frac{-K_a \pm \sqrt{K_a^2 + 4K_aC_a}}{2}$$ *exact method to calculate $[H_3O^+]$ for a weak acid*

Solving when $K_a = 1.8*10^{-4}$ and $C_a = 0.0010$ M leads to:

$$[H_3O^+] = 3.4*10^{-4} \text{ M}$$

and

$$pH = 3.47$$

which is the correct answer as determined experimentally.

The quadratic expression for $[H_3O^+]$ works well on *all* weak acid pH calculations, although its implementation is much more cumbersome and for results which vary little if at all from the approximation method.

Example: What is the pH of a 0.030 M acetic acid solution? $K_a = 1.75*10^{-5}$

Approximation solution:

$$pH = -\log \sqrt{K_a * C_a} = -\log (1.75*10^{-5} * 0.030)^{0.5} = 3.14$$

Exact solution:

$$[H_3O^+] = \frac{-K_a \pm \sqrt{K_a^2 + 4K_aC_a}}{2} = 7.16*10^{-4}, \text{ and } pH = 3.15$$

Not much difference for a significantly greater amount of calculation, but certain experimental conditions warrant the extra effort.

Note that a corresponding equation can be deduced for a weak base of initial concentration C_b with a dissociation constant of K_b and $[OH^{-1}]$:

$$[OH^{-1}] = \frac{-K_b \pm \sqrt{K_b^2 + 4K_bC_b}}{2}$$

and at times its use may be warranted over the approximation pH equation:

$$pH = 14 + \log \sqrt{K_b * C_b}$$

especially if 100 * K_b approaches the value of C_b.