

# Titrations Buffers

Wednesday, February 01, 2017 1:56 PM

## Titration and Buffers Activity

**Goal:** Our goal in this activity is to introduce a straight forward strategy to predict and understand titration curves. We will be focusing on a few critical points that allow us to quickly assess most of the information that can be communicated/learned in a titration.

**Definitions you should be familiar with:**

$$pH = -\log[H_3O^+] \quad pOH = -\log[OH^-] \quad pH + pOH = 14 \quad [H_3O^+][OH^-] = 10^{-14}$$

$$pK_a = -\log K_a \quad pK_b = -\log K_b \quad pK_a + pK_b = 14 \quad pK_a * pK_b = 10^{-14}$$

Let's start simple – something that you have done before:

1. Calculate the pH of a 10 mM solution of acetic acid ( $pK_a$  4.75). We will be abbreviating acetic acid as HAc and acetate  $Ac^-$ . Recall that you want to start this by setting up an ICE table:

	HAc	+	H <sub>2</sub> O (l)	⇌	Ac <sup>-</sup>	+	H <sub>3</sub> O <sup>+</sup>
I	0.01		X		0		0
C	-x		X		+x		+x
E	0.01 - x		X		x		x

$$10^{-4.75} = \frac{x^2}{0.01 - x}$$

$$0 = x^2 + 10^{-4.75}x - 10^{-6.75}$$

$$0 = x^2 + 1.78 \times 10^{-5}x - 1.78 \times 10^{-7}$$

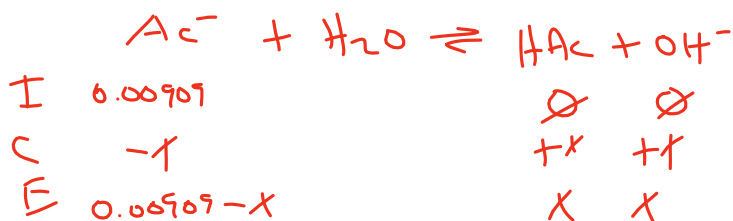
$$[H_3O^+] = 4.13 \times 10^{-4} \text{ M}$$

$$pH = 3.38$$

$$a=1 \quad b=1.78 \times 10^{-5} \quad c=-1.78 \times 10^{-7}$$

$$x = 4.13 \times 10^{-4}$$

2. Now do the same for a 9.09 mM solution of acetate ( $Ac^-$ ). Remember to use the base dissociation reaction and the  $K_b$ .



$$pK_b = 14 - 4.75 = 9.25$$

$$K_b = 10^{-9.25}$$

$$10^{-9.25} = \frac{x^2}{0.00909 - x} = \frac{x^2}{0.00909}$$

$$[OH^-] = 2.26 \times 10^{-6} \text{ M}$$

$$pOH = 5.64$$

$$pH = 8.35$$

$$\frac{9.09 \times 10^{-3}}{1000} > 10^{-9.25}$$

Shortcut is OK

Small  $K_b$ , so test for shortcut

$$x^2 = 5.11 \times 10^{-12}$$

$$x = 2.26 \times 10^{-6}$$

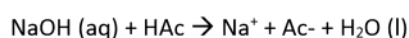
Ok, so how does this apply to titrations? Well, let's first establish what titrations are. **Acid-Base Titration: The repeated addition of known amounts of a strong base into a solution containing an acid. It could also be reversed – the addition of a strong acid into a solution containing a base.**

It's important to recognize the role of the STRONG acid or base here. When a strong base is added to an acid, the reaction always goes to completion – so there is not an equilibrium. Consequently, if we know how much acid and base we have, we can use the limiting reactant principle to guide us to determine the amount of reactants and products in solution.

For example:

3. If 5 mL of 100 mM NaOH is added to a 100 mL solution of 10 mM acetic acid (HAc), determine the concentration of acetate (Ac<sup>-</sup>) that is produced and the concentration of acetic acid that is left over.

Start this by writing out a reaction – note that this is a solid reaction arrow and NOT an equilibrium arrow:



Conveniently, everything reacts with a stoichiometric coefficient of 1, so the limiting reactant is easy to find (the reactant with the smallest number of moles). Go ahead and determine the:

- a. moles of NaOH:  $\frac{0.005 \text{ L} \times 0.1 \text{ mol NaOH}}{\text{L}} = 0.0005 \text{ mol NaOH}$
- b. moles of HAc:  $\frac{0.1 \text{ L} \times 0.01 \text{ mol}}{\text{L}} = 0.001 \text{ mol HAc}$
- c. moles of products and reactants that exist after the reaction. I like to do this step as an ICE table using moles (moles because you don't need to worry about the dilution that is occurring – the change will be the initial value from the limiting reactant).

	HAc	+	NaOH	→	Ac <sup>-</sup>	+	H <sub>2</sub> O
I	0.001 mol		0.0005 mol		0		
C	-0.0005		-0.0005		+0.0005		
E	0.0005		0		0.0005		

L.R. (pointing to NaOH)

Now that you know the moles, go ahead and determine the concentration of each. Make sure to account for the extra volume that you added.

$$V = 100 \text{ mL} + 5 \text{ mL} = 105 \text{ mL} = 0.105 \text{ L}$$

$$[\text{Ac}^-] = \frac{0.0005 \text{ mol}}{0.105 \text{ L}} = 0.00476 \text{ M}$$

$$[\text{HAc}] = \frac{0.0005 \text{ mol}}{0.105 \text{ L}} = 0.00476 \text{ M}$$

Cool, now we know the concentration of HAc and Ac-. The big question is, how did this change the pH? In problem 1, you figured out that 10 mM HAc has a pH of 3.38.

Do you expect the pH to be more acidic or basic?

Why?

NaOH is added, so it should get more basic

Can you calculate this value? Yes, of course. You can take the concentrations you determined in problem 3, plug them into the ICE table in problem 1, do some algebra and come up with the pH. However, there is an easier way if we apply a new concept:

**Buffer:** A solution containing a weak acid and its conjugate base. These solutions resist change to pH when strong acids or bases are added.

You'll note that the solution that we are working with contains some weak acid (HAc) and its conjugate base (Ac-), so it is a buffer. When we are working with a buffer, we can make a safe assumptions about the chemical equilibrium (that  $x \ll$  initial concentrations of HAc or Ac-) and greatly simplify this calculation. Here is the math starting with the equilibrium constant  $K_a$ :

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

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

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

$$pH = pK_a + \log \frac{[A]}{[HA]}$$

This new equation is the **Henderson-Hasselbalch** equation. It can be used ONLY if the  $pH = pK_a \pm 1$ .

- Using this new equation, calculate the pH of the solution we produced in problem 3. Note that you know three of these terms.

$$pH = 4.75 + \log \frac{0.00476}{0.00476}$$

$$pH = 4.75 + 0$$

$$pH = 4.75$$

What do you notice about the pH and pKa?

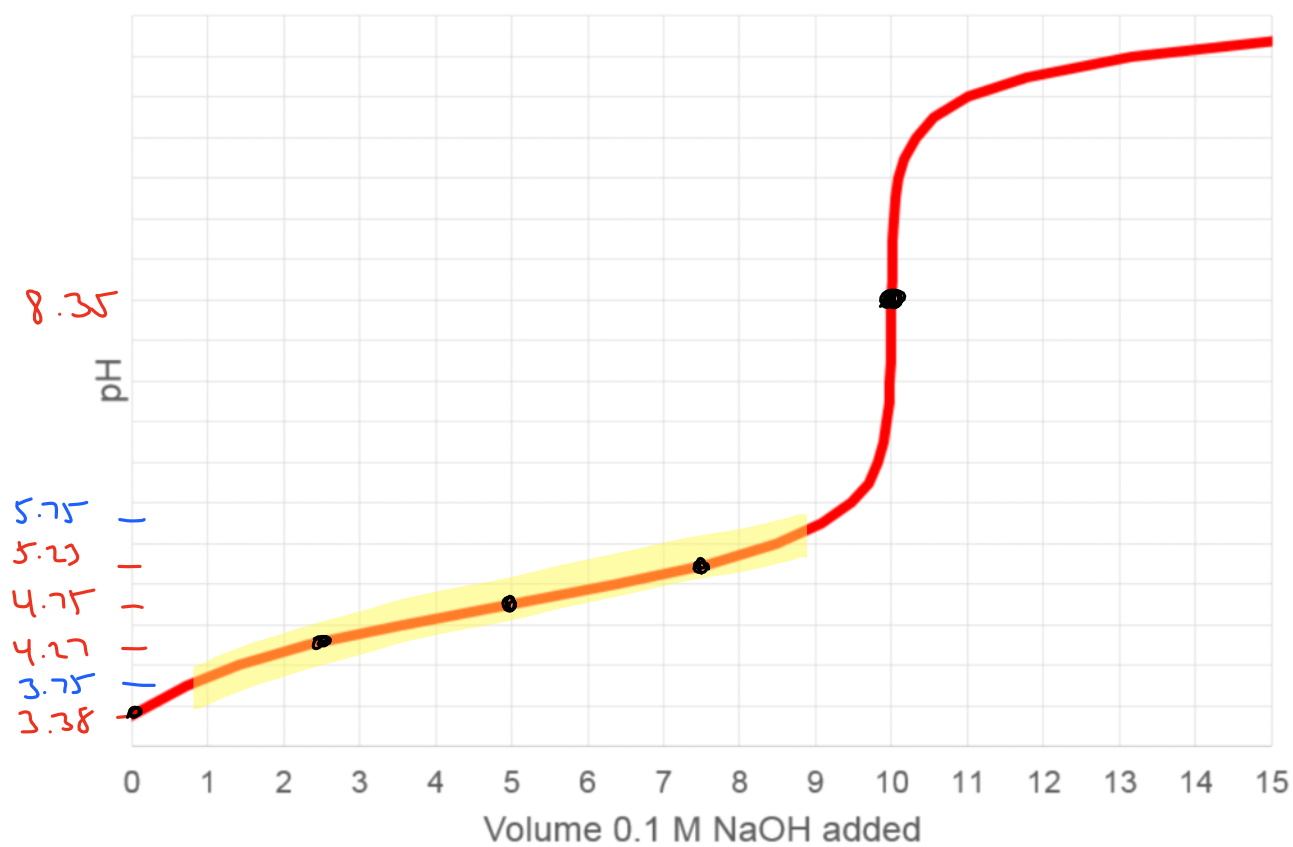
they are equal

This is a special situation in titrations known as the **half-equivalence point**: when enough NaOH is added to convert exactly 50% of the weak acid to the conjugate base. In this case, the  $[HA] = [A^-]$  and  $pH = pK_a$ . As we'll see, this is a very useful resource when trying to understand titrations.



Perhaps you noticed – the  $[Ac^-]$  at this point is exactly the concentration of acetate from problem 2 – so you have already calculated the pH of this point! Let's summarize what we've calculated and label these values on the graph below. The points that are boldfaced are the 3 that you MUST know to draw a titration curve.

- initial pH (calculated in problem 1) 3.38
- pH after 2.5 mL NaOH is added (problem 5a) 4.27
- pH after 5 mL NaOH is added (problem 4) 4.75
- pH after 7.5 mL NaOH is added (problem 5a) 5.23
- pH of equivalence point (problem 2 and 6) 8.35



Clearly label the buffer range (remember this is  $\pm 1$  pH unit from the pKa).

on graph  
3.75  $\rightarrow$  5.75

Let's take some time to think about this more carefully in the context of the chemical makeup of the buffer. We know that the buffer is composed of HAc and Ac and we've also seen that the pH changes as this ratio changes.

7. Consider each of the following situations. Determine which chemical specie is in the highest concentration:

- $\text{pH} < \text{pKa}$  HAc (more acidic)
- $\text{pH} = \text{pKa}$   $\text{HAc} = \text{Ac}^-$
- $\text{pH} > \text{pKa}$   $\text{Ac}^-$  (more basic)

8. Ok, let's put some numbers to this.

- Determine the ratio of  $\text{Ac}^-$ :HAc when the  $\text{pH} = 3.94$ . We know that  $[\text{HAc}] > [\text{Ac}^-]$  (see previous problem), so this ratio should be less than one. Use the H-H equation and solve for the ratio.

$$3.94 = 4.75 + \log \frac{\text{Ac}^-}{\text{HAc}}$$

$$-0.81 = \log \frac{\text{Ac}^-}{\text{HAc}}$$

$$\frac{[\text{Ac}^-]}{[\text{HAc}]} = 0.155$$

$$[\text{Ac}^-] = 0.155 [\text{HAc}]$$

so  $[\text{Ac}^-]$  is  $\sim 15\%$   $[\text{HAc}]$

- If the total buffer concentration is 10 mM, calculate  $[\text{HAc}]$ .

$$10 \text{ mM} = [\text{HAc}] + [\text{Ac}^-]$$

$$[\text{Ac}^-] = 10 - [\text{HAc}]$$

$$[\text{Ac}^-] = 0.155 [\text{HAc}]$$

$$10 - [\text{HAc}] = 0.155 [\text{HAc}]$$

$$10 = 1.155 [\text{HAc}]$$

$$[\text{HAc}] = 8.66 \text{ mM}$$

- If the total buffer concentration is 10 mM, what is the minimum  $[\text{HAc}]$  for the solution to still be considered a buffer?

$$\text{minimum} = 4.75 - 1 = 3.75$$

$$3.75 = 4.75 + \log \frac{\text{Ac}^-}{\text{HA}}$$

$$\log \frac{\text{Ac}^-}{\text{HA}} = 1$$

$$\frac{\text{Ac}^-}{\text{HA}} = 10$$

$$\text{Ac}^- = 10 \text{ HA}$$

from total ( )

$$10 - [\text{HA}] = 10 [\text{HA}]$$

$$10 = 11 [\text{HA}]$$

$$[\text{HA}] = 0.909 \text{ M}$$