Debra asked the following on the blog:

> How do I attack this problem? I want to compare the effect of adding 1mmol of HCL to 100 ml of 0.2M acetate buffer at two different starting pH's. (pKa of acetate buffer =4.7
> Initial pH = 4.7
> Initial pH = 5.7
> Thank you

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**Short answer:**

The effect of adding the acid, on pH, is largest the closer you are to the equivalence point which is pH 4.7 for that buffer made up of acetate.

**Long answer:**

I've changed the question to adding 10 mmol of HCl to 1 L 0.2 Molar acetate buffer.

First of all you need to set up a charge balance that is zero in its initial condition. This is done by introducing the ion $Z^-$ or $Z^+$ (either a cation or anion) so that the charge balance is zero.

Notice: I haven't written brackets [] around the compounds and ions to show I'm dealing with concentration – it's implicit

1. Set up the charge balance

$$Na^+ - \frac{HAc + Ac^-}{1 + \frac{H^+}{10^{-4.7}}} + H^+ - Z^- = 0$$

You know for sure that $Na^+$ is 0.2 and HAc + $Ac^-$ is 0.2 M and $H^+$ is $10^{-4.7}$ M. The reason why I'm using sodium is that the acetate usually comes with Na as sodiumacetate.

Then Z- is 0.100019953 M at pH=4.7 and the charge balance is zero in the initial condition (table 1). Please recall that at pH = pKa half the compound is in the dissociated form and that we know that HAc + $Ac^-$ is 0.2 mol/L.

| | |
|---|---|
| $Na^+$ | 0.2 |
| $Ac^-$ | 0.1 |
| $H^+$ | $10^{-4.7}$ |
| $Z^-$ | 0.100019953 |

**Table 1.** The charge balance in its initial condition

There is an excel spreadsheet showing this (acetatebuffer.xls). This initial condition is shown in row 3.

Now we add 10 mmol of HCl to the 1 L of 0.2 M Acetate buffer adjusted to pH 4.7 – as above.

To do this we care about the $Cl^-$ from the dissociation of HCl and let the $H^+$ distribute across the equation or the equilibrium. $Cl^-$ can be said to go into the pool of $Z^-$ or can be added into a separate parameter – it makes no difference. In this case I just add the 10 mmol or 0.01 M to the Z- so that it is 0.110019953 mol/L.

The new condition is that we only know what is seen in table 2.

| | |
|---|---|
| $Na^+$ | 0.2 |
| $Ac^-$ | |
| $H^+$ | |
| $Z^-$ | 0.110019953 |

**Table 2.** The new situation with a new charge balance

We need to find $Ac^-$ and $H^+$ so that the charge balance still is zero after the addition of 10 mmol of HCl to the 0.2 Molar buffer of acetate.

When the $H^+$ is $10^{-4.613}$ the charge balance is fulfilled. This can be seen in row 5 of the excel spreadsheet.

So adding 10mmol of HCl to 1 L of 0.2 M acetate buffer makes the pH decrease from 4.7 to 4.61

In the case pH is 5.7, the pH hardly changes after 10 mmol of HCl has been put into the solution. This is shown in row 7 of the same spreadsheet.

In the section about pKa and Ka you can see how the concentration of acetate ($Ac^-$) can be calculated from total acetate and acetic acid ($Ac^-$ and HAc).