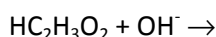


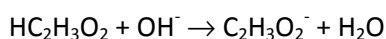
Strong acids: HCl, HBr, HI, HNO₃, HClO₄, H₂SO₄

Strong bases: group I and II hydroxides

When an acid and base are combined, (whether in a titration or a buffer), the extent of the reaction is important. If at least one reactant is a strong acid or a strong base, the reaction will go to completion (until the limiting reactant is consumed).



Since OH⁻ is a strong base, the reaction will proceed completely to the right (with a forward arrow). The base accepts a proton, so the products are C₂H₃O₂⁻ + H₂O.



So, to determine what is present after an acid-base neutralization, write the reactants and products and construct a table of moles that shows what was present initially (**Start**), what was **A**dded to it, and what is present after the **N**eutralization reaction is complete. (If you were given volumes and molarities, they must be converted to moles). This is what happens when 0.2 mol OH⁻ are added to 0.5 mol HC₂H₃O₂.

	$\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- \rightarrow \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O}$			
St	0.5 mol			
A		0.2 mol		
N	0.3 mol	0 mol	0.2 mol	

In the example above, 0.2 mol OH⁻ is added to 0.5 mol HC₂H₃O₂. OH⁻ is the limiting reactant, so it will be consumed when the reaction is neutralized. This causes 0.2 moles of the weak acid to react (leaving 0.3 unreacted), and causing 0.2 mol of the conjugate base to be formed.

Whenever there are similar amounts of a weak acid and its conjugate base present in a solution, use the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

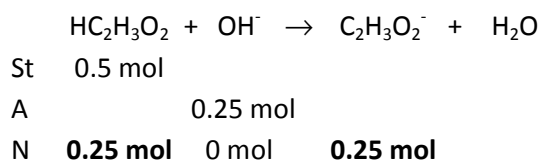
This equation is valid only if the ratio of base to acid (can be moles or concentrations) is between 0.1 and 10. The system shown above is valid since the amounts of HA and A⁻ are similar. The pK_a is that of the conjugate acid (HC₂H₃O₂ in this case). If only the K_b of the conjugate base is available, it must be converted into the K_a of the acid by using this relationship:

$$K_a K_b = K_w = 1.0 \times 10^{-14}$$

$$K_a = \frac{1.0 \times 10^{-14}}{K_b}$$

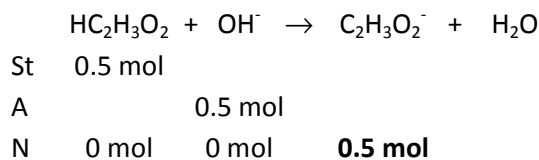
The StAN table and resulting calculations should be the first thing you do once you know the number of moles initially and the number of moles that were added. This qualifies for any solution to which an acid or base is added – whether it's just a buffer calculation or an acid-base titration.

An acid-base titration has a few extra considerations. First, if you are told the pH at the **half-equivalence point** (*a.k.a.* midpoint or halfway point), this is equal to the pK_a of the weak acid being titrated. This is because at half of the volume to the equivalence point, half of the original weak acid has been converted into its conjugate base:



In this case, when starting with 0.5 mol of weak acid, it will take 0.25 mol of OH^- to reach the half-equivalence point. It can be shown using the H-H equation that when amounts of HA and A^- are equal, $\text{pH} = pK_a$.

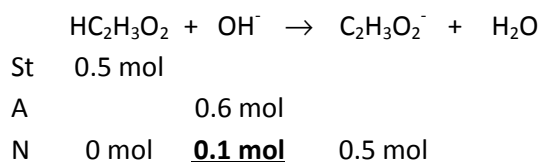
To reach the **equivalence point**, identical moles of the two reactants must be added. In other words, exactly enough base is added to neutralize the acid that was there originally.



Notice that the 0.5 mol HA has been *totally and exactly reacted* at the equivalence point. What remains is 0.5 mol of $\text{C}_2\text{H}_3\text{O}_2^-$, its conjugate base produced as a result.

To calculate the pH at the equivalence point, first calculate the molarity of the conjugate base solution. Remember to divide moles by the new solution volume (original volume + volume of base added). Then, calculate the pH of the weak base solution (being sure to use K_b , not K_a).

If the weak acid is the limiting reactant, you will have excess OH^- present in the solution – this occurs **after the equivalence point**. Simply calculate the OH^- molarity (using the new total volume) and use it to calculate pOH and pH (ignoring the A^- present in the solution).

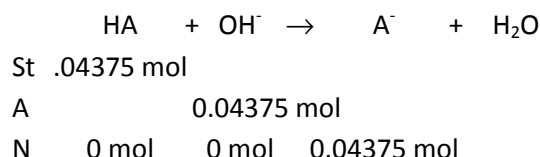


Example:

125 mL of 0.350 M HA is titrated with 0.200 M OH⁻. What is the volume and pH at the equivalence point if pH is 3.85 at the half-equivalence point? What is the volume after 175 mL OH⁻ is added?

$$.125 \text{ L} \times \frac{0.350 \text{ mol}}{1 \text{ L}} = 0.04375 \text{ mol HA} = 0.04375 \text{ mol OH}^- \times \frac{1 \text{ L}}{0.200 \text{ mol}} = \underline{\underline{0.219 \text{ L OH}^- \text{ added}}}$$

Use StAN to determine what is present at the equivalence point:



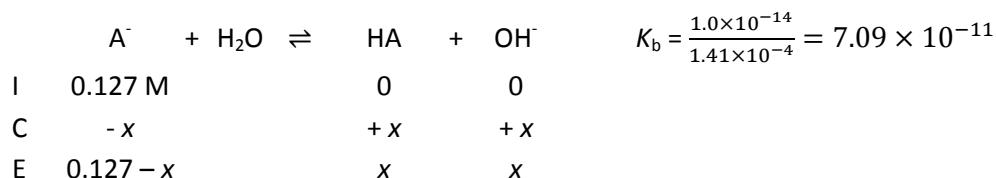
Calculate the concentration using the new total volume:

$$[A^-] = \frac{0.04375 \text{ mol}}{.125 \text{ L} + .219 \text{ L}} = 0.127 \text{ M A}^-$$

pH = 3.85 at the half-equivalence point, so pK_a of HA = 3.85.

$$K_a = 10^{-3.85} = 1.41 \times 10^{-4}$$

Convert the K_a above into the K_b of A⁻, then use it to calculate the pH of a 0.127 M A⁻ solution.



$$K_b = 7.09 \times 10^{-11} = \frac{x^2}{0.127 - x} \cong \frac{x^2}{0.127}$$

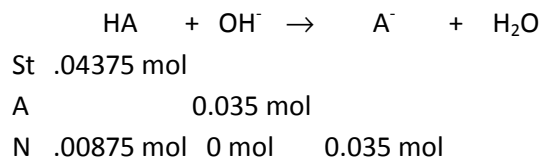
$$x = \sqrt{(0.127)(7.09 \times 10^{-11})} = 3.00 \times 10^{-6} = [\text{OH}^-]_{\text{eq}}$$

$$\text{pOH} = -\log(3.00 \times 10^{-6}) = 5.52$$

$$\text{pH} = 14 - 5.52 = \underline{\underline{8.47}}$$

Now, calculate pH after 175 mL OH⁻ were added. Start by calculating moles added and make a new StAN table.

$$.175 \text{ L} \times \frac{.200 \text{ mol}}{1 \text{ L}} = 0.035 \text{ mol OH}^- \text{ added}$$



Since HA and A⁻ are within 10x of each other, we can use the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.85 + \log\frac{0.035}{0.00875} = \underline{\underline{4.45}}$$

Practice:

1. 250 mL of a weak acid are titrated with 0.175 M NaOH. The equivalence point occurs after adding 136 mL NaOH. The pH at the half-equivalence point is 5.25.
 - a. What was the initial concentration of the weak acid?
 - b. What is the pH at the equivalence point?
 - c. What is the pH after adding 50, 75, and 150 mL NaOH?
2. 300 mL of 0.155 M acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, are titrated with 0.225 M NaOH.
 - a. What volume of NaOH is required to reach the equivalence point?
 - b. What is the pH at the half-equivalence point and equivalence point?
 - c. What is the pH after adding 80, 120, and 300 mL NaOH?
3. 100 mL of 0.755 M HCl is titrated with 0.525 M NaOH.
 - a. What volume of NaOH is required to reach the equivalence point?
 - b. What is the pH at the half-equivalence point (hint, you cannot use the H-H equation) and equivalence point?
 - c. What is the pH after adding 25, 50, 100, and 200 mL of NaOH?
4. 225 mL of 0.435 M $\text{NH}_3(aq)$ are titrated with 0.150 M HCl.
 - a. What volume of HCl is required to reach the equivalence point?
 - b. What is the pH at the half-equivalence point and equivalence point?
 - c. What is the pH after adding 300, 400, and 700 mL HCl?