

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

① Take log of both sides

② Multiply by -1

③ Rearrange, solving for pH

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

$[A^-]$  ... from the salt

$[HA]$  ... from the weak acid

- We ASSUME that the initial concentrations of both the acid and its conjugate are equal to the equilibrium concentrations. Valid IF there are significant amounts of both species initially.

$$\text{pH} = \text{p}K_{a, \text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

ex: acidic buffer



$$\text{pH} = \text{p}K_{a, \text{HC}_2\text{H}_3\text{O}_2} + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

ex: basic buffer



$$\text{pH} = \text{p}K_{a, \text{NH}_4^+} + \log \left( \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right)$$

$$\text{p}K_a + \text{p}K_b = 14,00 \quad \dots \text{ is the } -\log \text{ of } K_a \times K_b = K_w$$

Calculate the pH of a buffer made from 30.2 grams of ammonium chloride (FW = 53.492 g/mol) and 29 mL of 18.1 M ammonia diluted to 150. mL with water.

$$\text{pH} = \text{p}K_{a,\text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$



To use the H-H equation, we merely need to know: (1) The nominal concentration of both ammonia and ammonium ion, (2) The pKa of ammonium ion.

$$[\text{NH}_3] = ? \quad M_1 V_1 = M_2 V_2 \dots \text{since ammonia is DILUTED to make the buffer}$$

$$(18.1 \text{ M})(29 \text{ mL}) = M_2 (150. \text{ mL}); M_2 = 3.499333333 \text{ M NH}_3$$

$$[\text{NH}_4^+] = ?$$

$$30.2 \text{ g NH}_4\text{Cl} \times \frac{\text{mol NH}_4\text{Cl}}{53.492 \text{ g NH}_4\text{Cl}} = 0.5645704031 \text{ mol NH}_4^+$$

$$[\text{NH}_4^+] = \frac{0.5645704031 \text{ mol NH}_4^+}{0.150 \text{ L}} = 3.763802687 \text{ M NH}_4^+$$

$$K_b = 1.8 \times 10^{-5}; \text{ p}K_b = 4.74, \text{ so } \text{p}K_a = 14.00 - 4.74 = 9.26$$

(pKa + pKb = 14.00)

$$\text{pH} = 9.26 + \log \left( \frac{3.499333333}{3.763802687} \right) = \boxed{9.22}$$

## <sup>171</sup> BUFFER SELECTION

- Buffer pH is controlled by the pKa of the acidic species in the buffer.

$$\text{pH} = \text{p}K_{a, \text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right)$$

- Choose a buffer system so that the desired pH is within +/- 1 pH unit of the pKa
- You also need to ensure that the components of the buffer do not interact with your chemistry!

## BUFFER PREPARATION

- many buffers are prepared by mixing specific amounts of both components of the Buffer system (acid / conjugate base or base / conjugate acid)

Some buffer "recipes" call for making the conjugate ion FROM the weak acid or base ... by adding a STRONG acid or base!



The reaction of the strong acid with the weak base goes essentially to completion!

If you have more ammonia than nitric acid, you will end up with a solution containing a significant amount of both ammonia and ammonium ion ... a buffer!

## BUFFER CAPACITY

- A buffer is good only as long as there is a significant concentration of both the acidic and basic species
- buffer capacity: how much acid or base can a buffer resist before losing its ability to buffer
- Buffer pH depends on the RATIO of acid to base!

$$\text{pH} = \text{p}K_{a,\text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right)$$

Henderson-Hasselbalch Equation

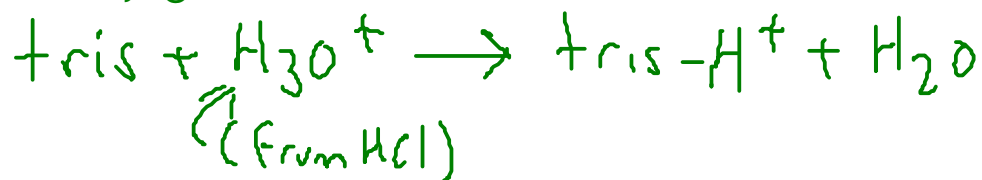
Ratio determines pH; the actual concentrations don't!

- So, if you make a buffer with 1.0M HA and 1.0M A<sup>-</sup>, it will have the same pH as a buffer with 2.0M HA and 2.0M A<sup>-</sup> .... but the 2M buffer will have a higher BUFFER CAPACITY - it will resist more additions of acid or base.



174 Take 100. mL of the previous buffer (0.050 M tris / 0.075 M tris-HCl), and add 5.0 mL of 0.10 M HCl. What is the pH of the mixture?

The HCl should react with basic component of the buffer (tris), and change it to its conjugate acid



... so we need to find out the NEW concentrations of each species in the system.

Species	Initial mmol	$\Delta$ in rxn	Final mmol	[conc.]
tris	100 mL $\times$ 0.050 M = 5.0 mmol	-0.5 mmol	4.5 mmol	$\frac{4.5 \text{ mmol}}{105 \text{ mL}} = 0.0428571 \text{ M}$
tris-H <sup>+</sup>	100 mL $\times$ 0.075 M = 7.5 mmol	+0.5 mmol	8.0 mmol	$\frac{8.0 \text{ mmol}}{105 \text{ mL}} = 0.0761905 \text{ M}$
HCl	5 mL $\times$ 0.10 M = 0.5 mmol	-0.5 mmol	0 mmol	0

\* Solution volume is now 105 mL (100 mL of buffer plus 5 mL of HCl)

$$\text{pH} = 8.06 + \log \left( \frac{0.0428571 \text{ M}}{0.0761905 \text{ M}} \right) = \boxed{7.81}$$

The original pH was 7.88, so the pH dropped by 0.07 pH units.

Compare this 0.07 unit pH change with adding 5.0 mL of 0.10 M HCl to 100. mL of pure water.

$$M_1 V_1 = M_2 V_2$$

$$(0.10 \text{ M})(5.0 \text{ mL}) = M_2 (105 \text{ mL})$$

$$0.0047619 \text{ M HCl} = M_2$$

This is a strong acid, so hydronium concentration equals acid concentration!

$$[\text{H}_3\text{O}^+] = 0.0047619 \text{ M}$$

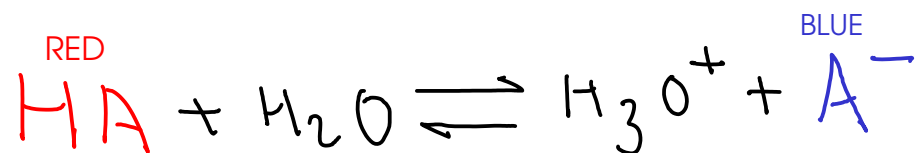
$$\text{pH} = 2.32$$

... which is a change of 4.68 pH units from water's original pH of 7.00!

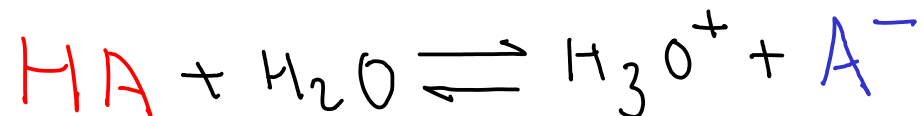


## INDICATORS

- Instead of using a pH meter to monitor acidity, we may choose to use an acid-base INDICATOR.
- Acid-base indicators are weak acids or weak bases which are highly colored.
- The color of the undissociated indicator MUST BE DIFFERENT than the color of the dissociated form!



The indicator must be present in very low concentrations - so that the indicator's equilibrium DOES NOT CONTROL the pH of the solution!



Look at the Henderson-Hasselbalch equation - we want to know how much of the red form and how much of the blue form are present!

$$\text{pH} = \text{pK}_{a,\text{ind}} + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right)$$

When does the color of the indicator change?

If the pH is  $\ll$  pKa, then the log term above must be both large AND negative!

- What color is the solution?



If the pH is  $\gg$  pKa, then the log term above must be both large AND positive!

- What color is the solution?



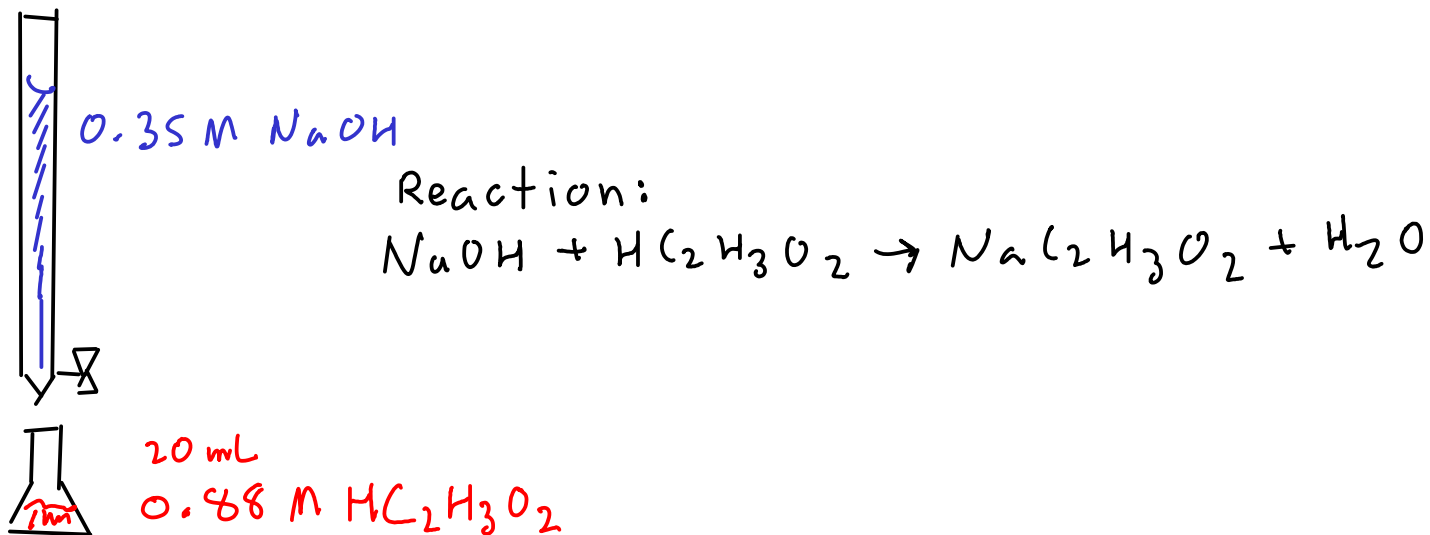
- So, the color changes when the pH of the solution is near the pKa of the indicator, BUT we can only DETECT the change when enough of the other form is present.

## 178 Titration

- also called volumetric analysis. See the end of Ebbing chapter 4 for more details.
- frequently used to determine concentration of unknown acids or bases.
- typically react a basic sample with a STRONG ACID, or an acidic sample with a STRONG BASE

### Example:

Titrate 20 mL of vinegar (acetic acid) with 0.35 M NaOH. Let's study this titration. What happens to the pH of the solution during the titration? How does an indicator work?



Vinegar is typically about 0.88M acetic acid. What would the EQUIVALENCE POINT (the point where we react away all of the acetic acid) be?



20.0 mL of 0.88M  $\text{HC}_2\text{H}_3\text{O}_2$  w/ 0.35 M  $\text{NaOH}$

$$20.0 \text{ mL} \times \frac{0.88 \text{ mol}}{\text{L}} = 17.6 \text{ mmol } \text{HC}_2\text{H}_3\text{O}_2$$

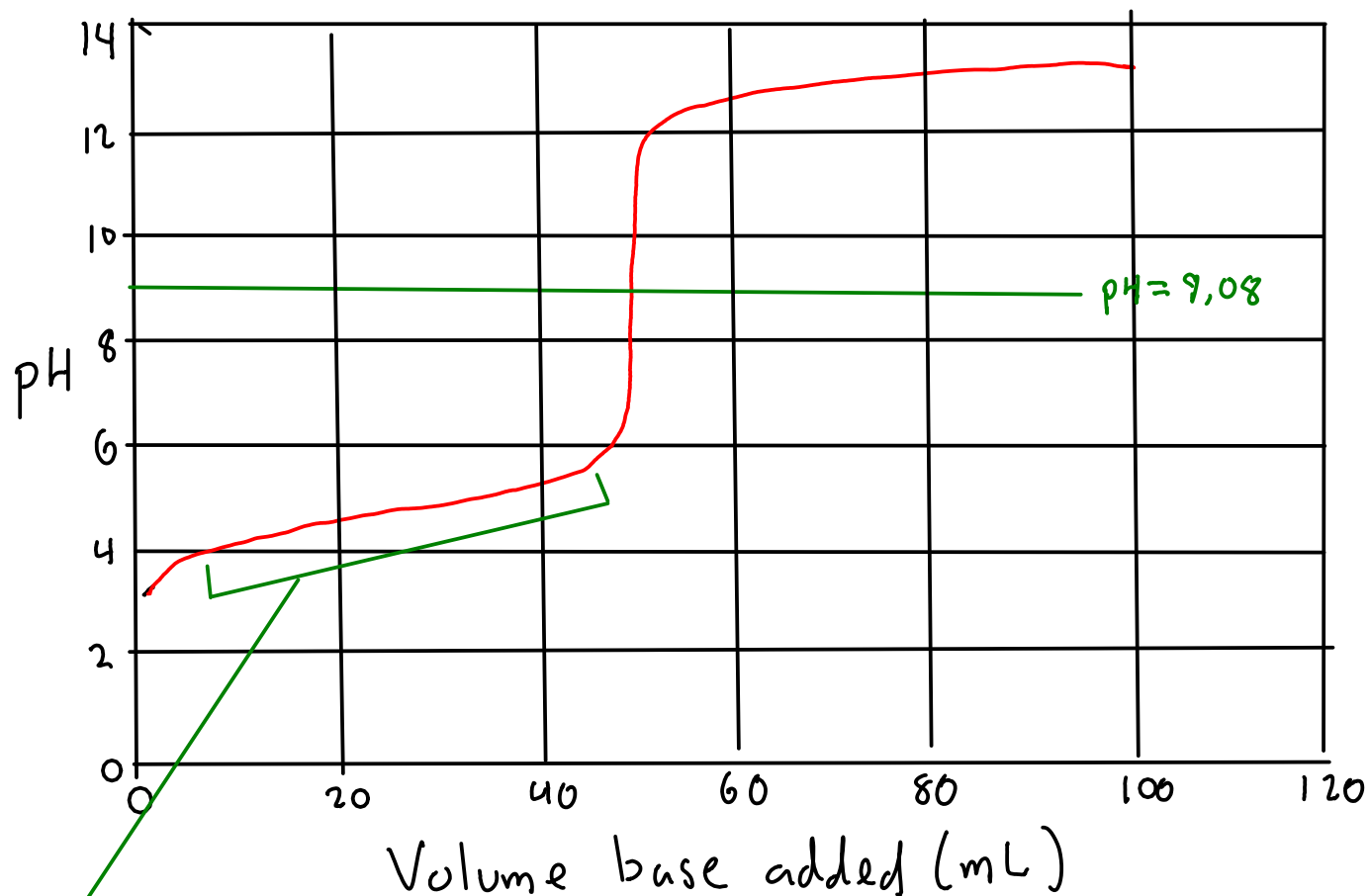
$$17.6 \text{ mmol } \text{HC}_2\text{H}_3\text{O}_2 \times \frac{\text{mol NaOH}}{\text{mmol } \text{HC}_2\text{H}_3\text{O}_2} \times \frac{\text{L}}{0.35 \text{ mol NaOH}} = 50.3 \text{ mL of } 0.350 \text{ M NaOH}$$

But how do we tell the titration is over if we don't already know the concentration of the acid?

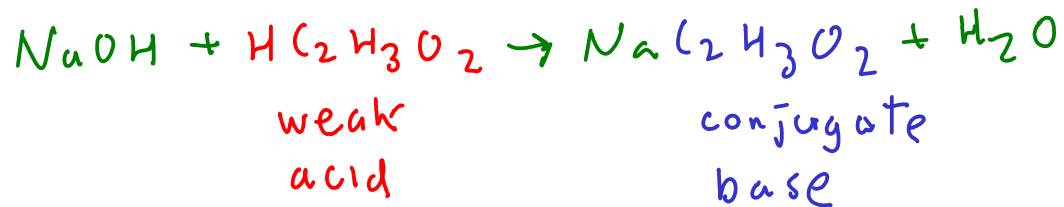
In the lab, we have used phenolphthalein indicator for vinegar titrations. Phenolphthalein changes from colorless to pink over the range of about pH 9 to pH 10. How does this indicator show where the endpoint is?

Let's look at the pH of the solution during the titration- that may show us what's going on!

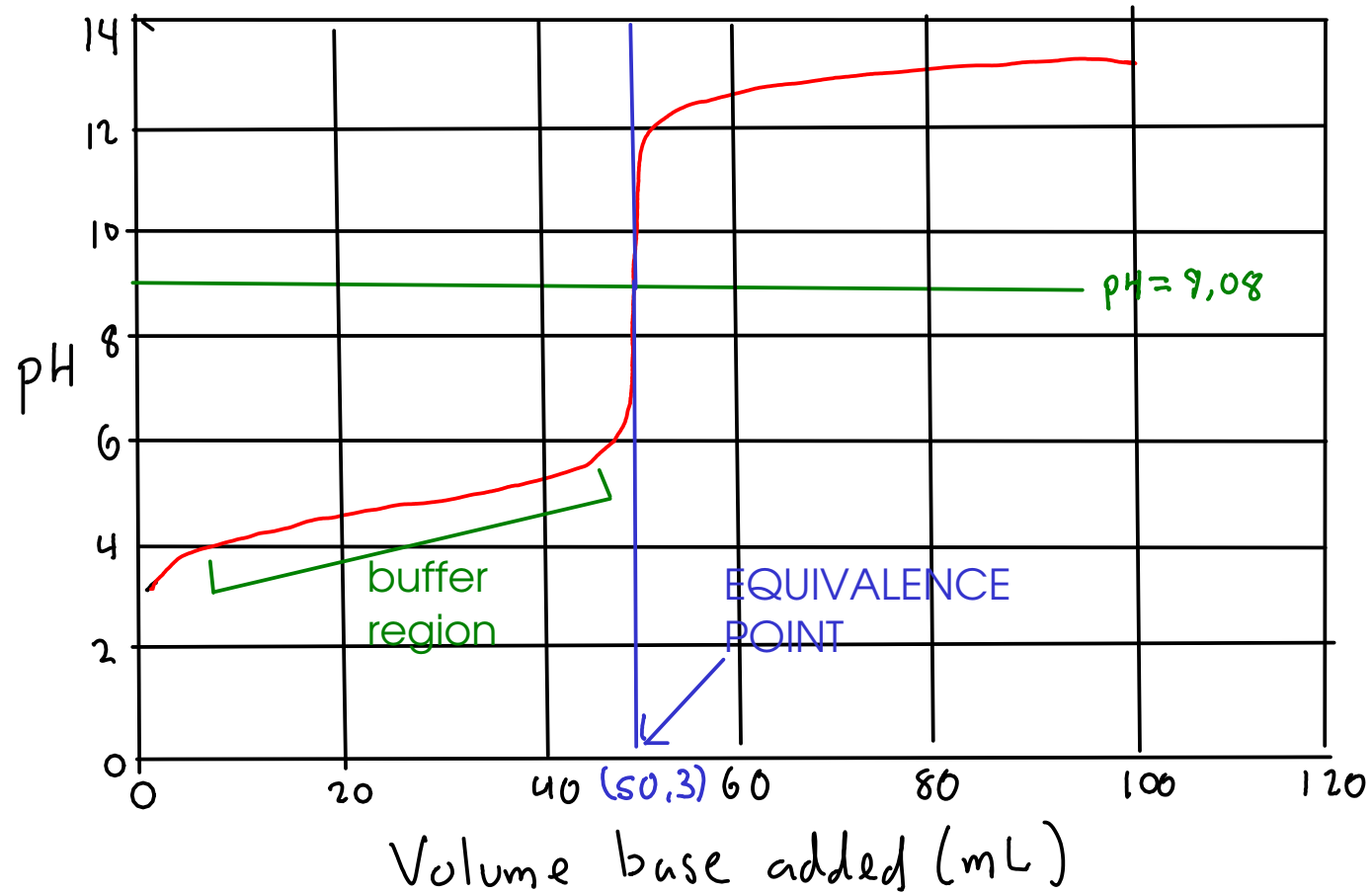
Titration curve for the titration of 20 mL of 0.88 M acetic acid with 0.35 M sodium hydroxide



buffer region: With a moderate amount of NaOH added, we have a solution that contains significant amounts of both acetic acid and its conjugate base (acetate ion). We have a buffer.



The equivalence point:



Equivalence point: We're reacting away more and more of the original acetic acid and converting it to acetate ion. At the equivalence point, all of the acetic acid has been converted, and we have only a solution of acetate ion.

Let's calculate the pH at the equivalence point.



20.0 mL of 0.88 M  $\text{HC}_2\text{H}_3\text{O}_2$  w/ 0.35 M  $\text{NaOH}$

$$20.0 \text{ mL} \times \frac{0.88 \text{ mol}}{\text{L}} = 17.6 \text{ mmol } \text{HC}_2\text{H}_3\text{O}_2$$

$$17.6 \text{ mmol } \text{HC}_2\text{H}_3\text{O}_2 \times \frac{\text{mol } \text{NaOH}}{\text{mol } \text{HC}_2\text{H}_3\text{O}_2} \times \frac{\text{L}}{0.35 \text{ mol NaOH}} = 50.3 \text{ mL of } 0.35 \text{ M NaOH}$$

At the equivalence point, we have 17.6 mmol of ACETATE ION in 70.3 (20+50.3) mL of solution.

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{17.6 \text{ mmol}}{70.3 \text{ mL}} = 0.250 \text{ M } \text{C}_2\text{H}_3\text{O}_2^-$$



	init	$\Delta$	equiv
$[\text{C}_2\text{H}_3\text{O}_2^-]$	0.250	-x	0.250-x
$[\text{OH}^-]$	0	+x	x
$[\text{HC}_2\text{H}_3\text{O}_2]$	0	+x	x

$$\frac{x^2}{0.250-x} = K_b$$

$$\frac{x^2}{0.250} = 5.88 \times 10^{-10}$$

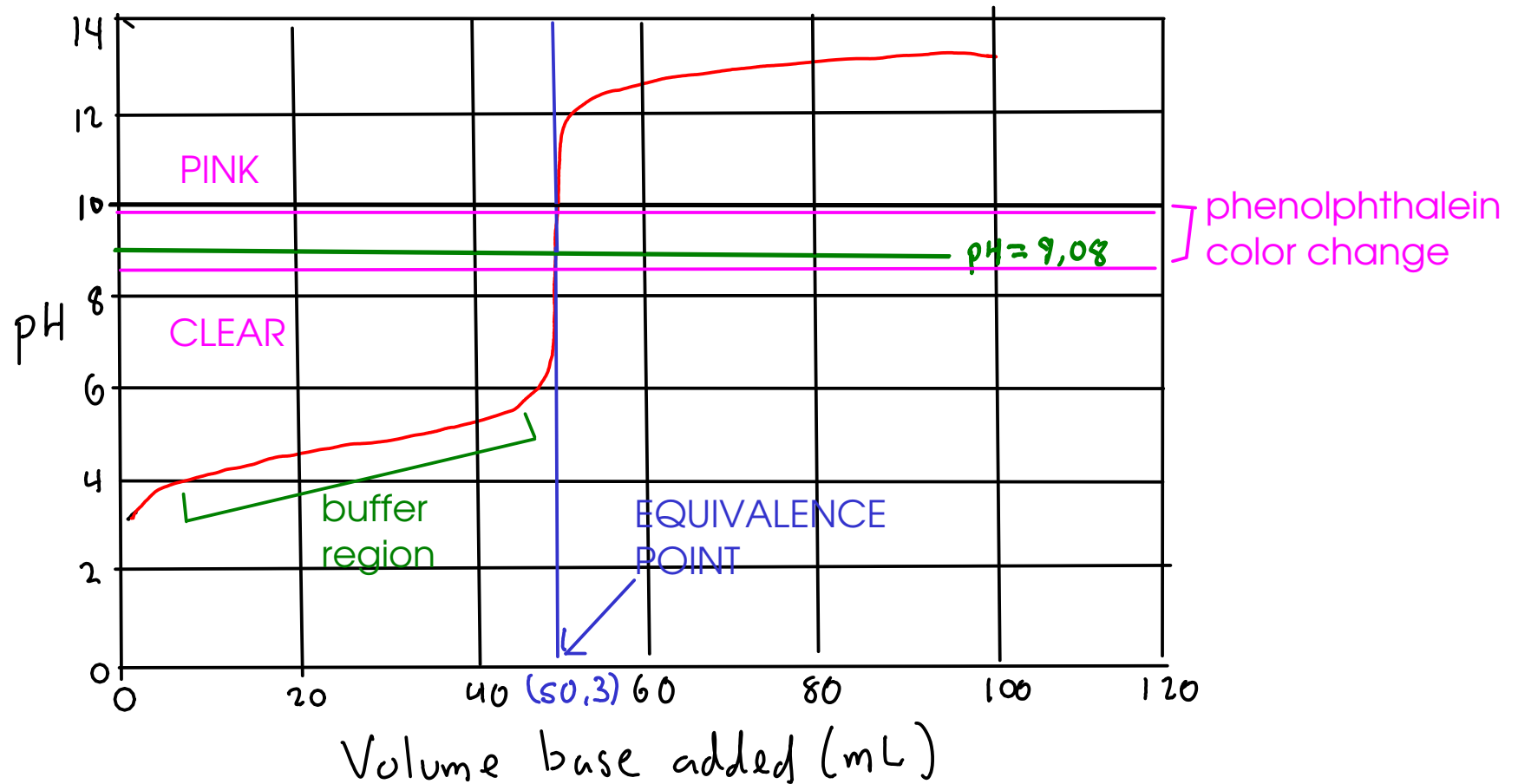
$$K_a, \text{HC}_2\text{H}_3\text{O}_2 = 1.7 \times 10^{-5}$$

$$K_b, \text{C}_2\text{H}_3\text{O}_2^- = 5.88 \times 10^{-10} \quad (K_a \times K_b = K_w)$$

$$x = 1.21 \times 10^{-5}, \quad \text{pOH} = 4.92, \quad \text{pH} = 9.08$$

Once you figure out the concentration of acetate ion, this is simply the calculation of the pH of a salt solution!

What about that phenolphthalein indicator?



Near the equivalence point, a very small volume of base added (a drop!) will change the pH from slightly over 6 to near 12. Since phenolphthalein changes colors at about pH 9-10, we can stop the titration within a drop of the equivalence point.