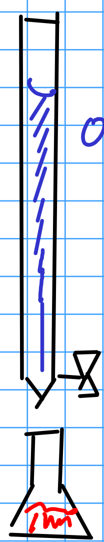
Titration

- 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 base sample with a STRONG ACID, or an acid 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?



0.35 M NaOH

Reaction:

$$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$$

20 mL
0.88 M $HC_2H_3O_2$

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?

$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$

20.0 mL of 0.88 M HC_2H_3O w/ 0.35 M NaOH

$20.0\ mL \times \frac{0.88\ mol}{L} = 17.6\ mmol\ HC_2H_3O_2$

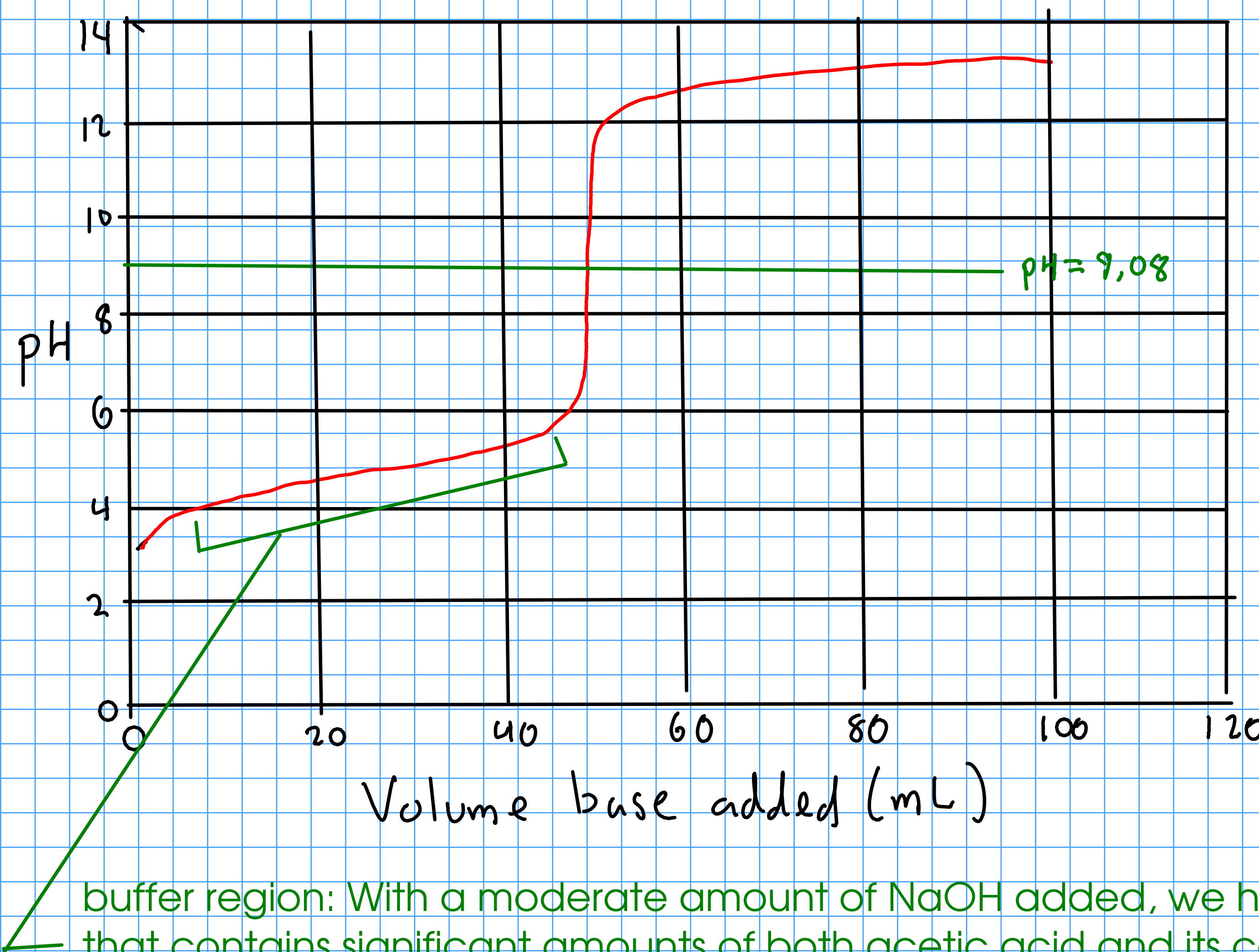
$17.6\ mmol\ HC_2H_3O_2 \times \frac{mol\ NaOH}{mol\ HC_2H_3O_2} \times \frac{L}{0.35\ mol\ NaOH} = \boxed{50.3\ mL\ \text{of}\ 0.35\ M\ NaOH}$

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



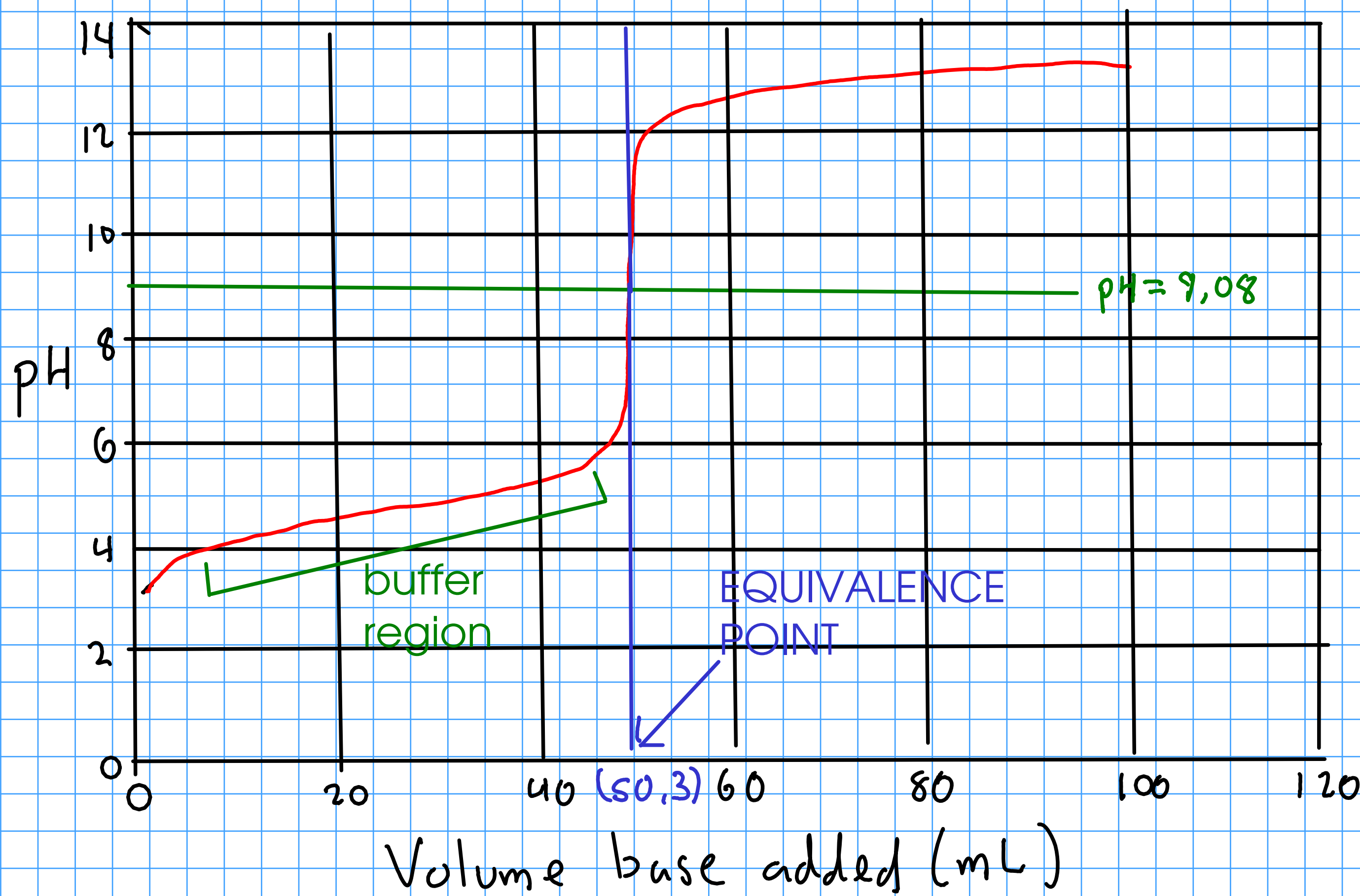
buffer region: With a moderate amount of NaOH added, we have a solution that contains significant amounts of both acetic acid and its conjugate base (acetate ion). We have a buffer.

$$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$$

weak acid

conjugate base

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.

$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$

20.0 mL of 0.88 M HC_2H_3O w/ 0.35 M NaOH

$20.0\ mL \times \frac{0.88\ mol}{L} = 17.6\ mmol\ HC_2H_3O_2$

$17.6\ mmol\ HC_2H_3O_2 \times \frac{mol\ NaOH}{mol\ HC_2H_3O_2} \times \frac{L}{0.35\ mol\ NaOH} = \boxed{50.3\ mL \text{ of } 0.35M\ NaOH}$

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

$[C_2H_3O_2^-] = \frac{17.6}{70.3} = 0.250\ M\ C_2H_3O_2^-$

$C_2H_3O_2^- + H_2O \rightleftarrows OH^- + HC_2H_3O_2$

	init	Δ	equil
$[C_2H_3O_2^-]$	0.250	$-x$	$0.250-x$
$[OH^-]$	0	$+x$	x
$[HC_2H_3O_2]$	0	$+x$	x

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

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

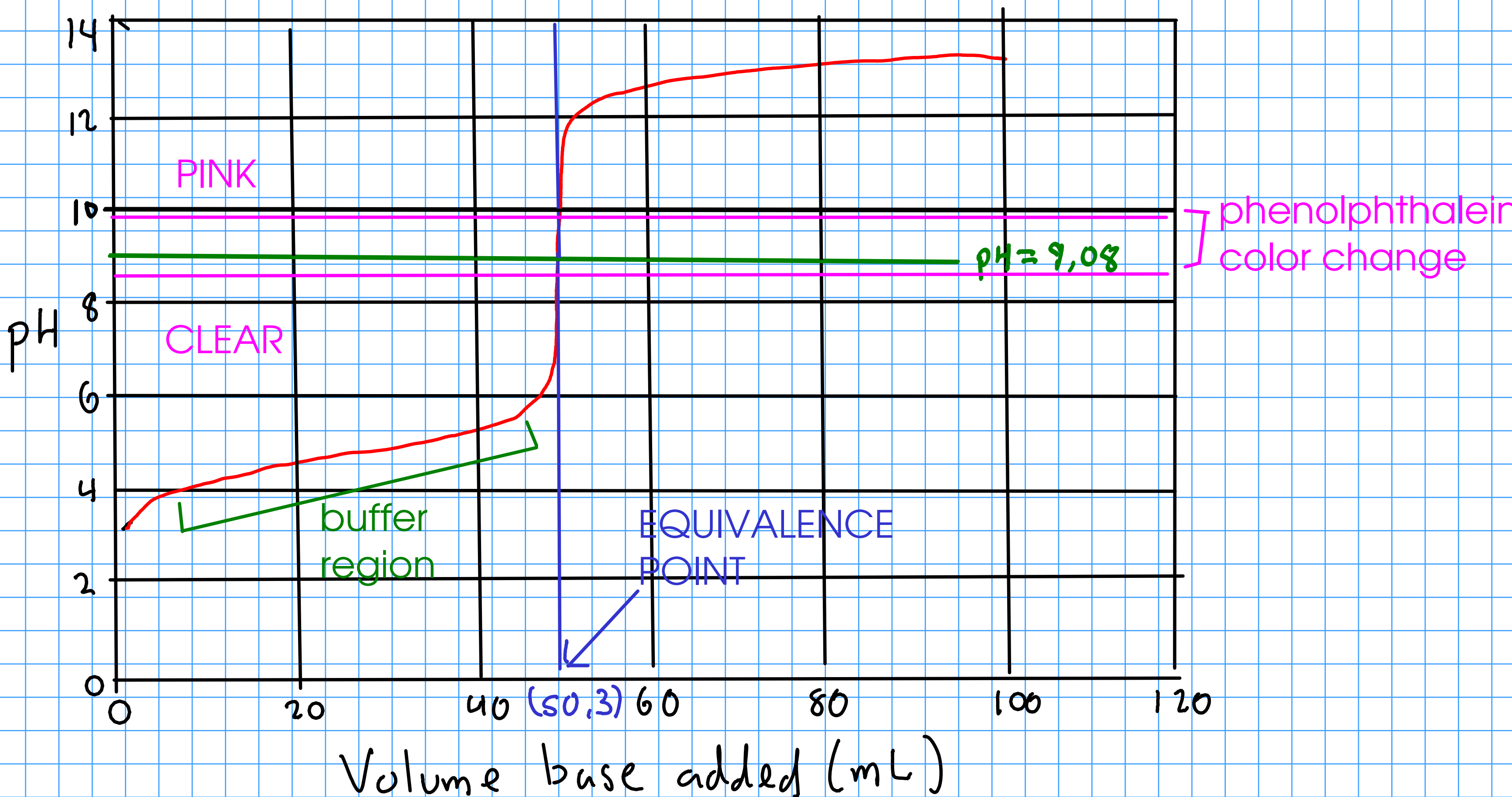
$K_{a,HC_2H_3O_2} = 1.7\times10^{-5}$

$K_{b,C_2H_3O_2^-} = 5.88\times10^{-10}$ $(K_a \times K_b = K_w)$

$\frac{x^2}{0.250} = 5.88\times10^{-10}$

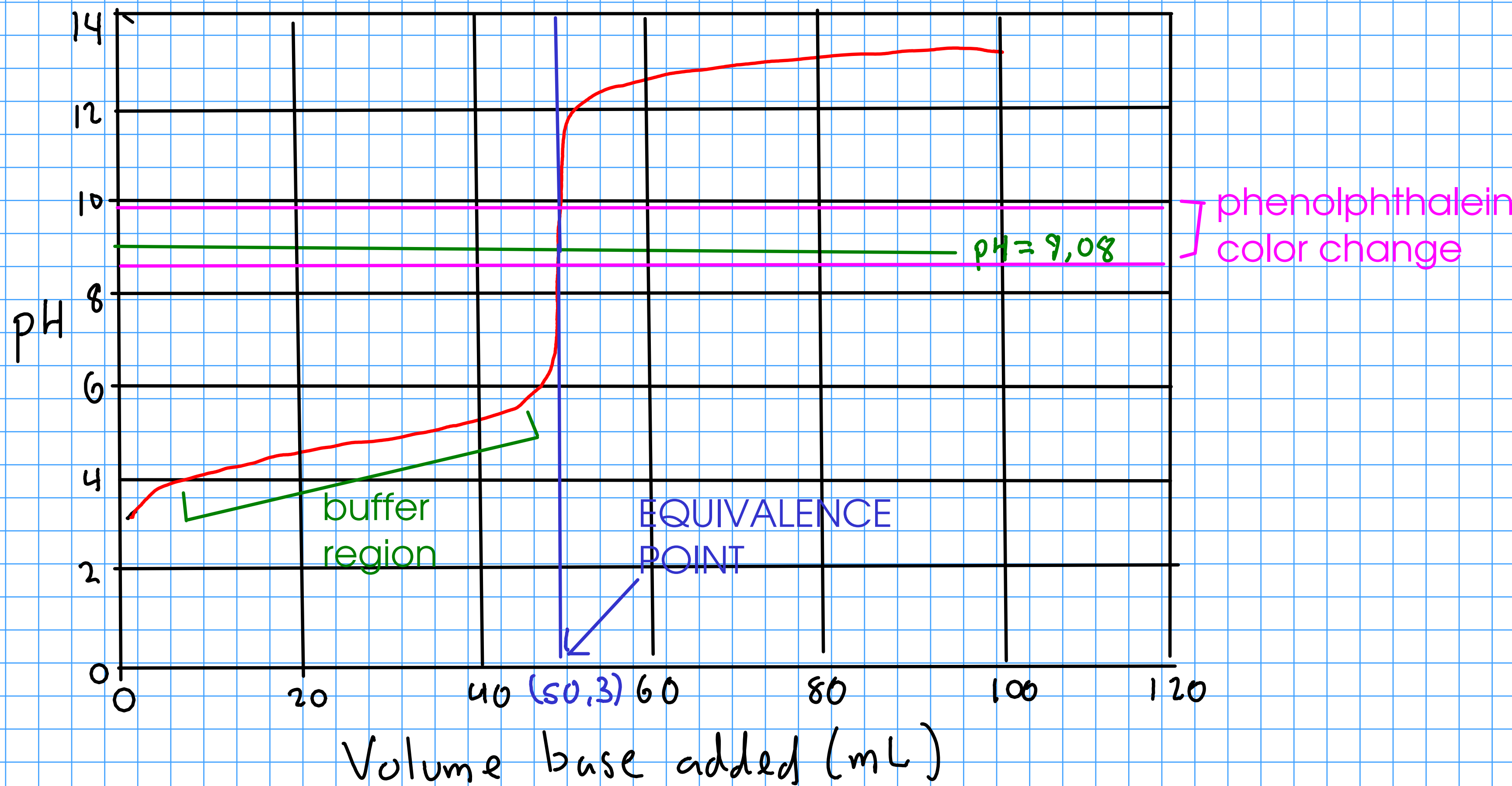
$x = 1.21\times10^{-5}$, $pOH = 4.92$, $\boxed{pH = 9.08}$

What about that phenolpthalein 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.

Another interesting point: The halfway point



What's special about it? It's the point where we have added half the required acid to reach the equivalence point

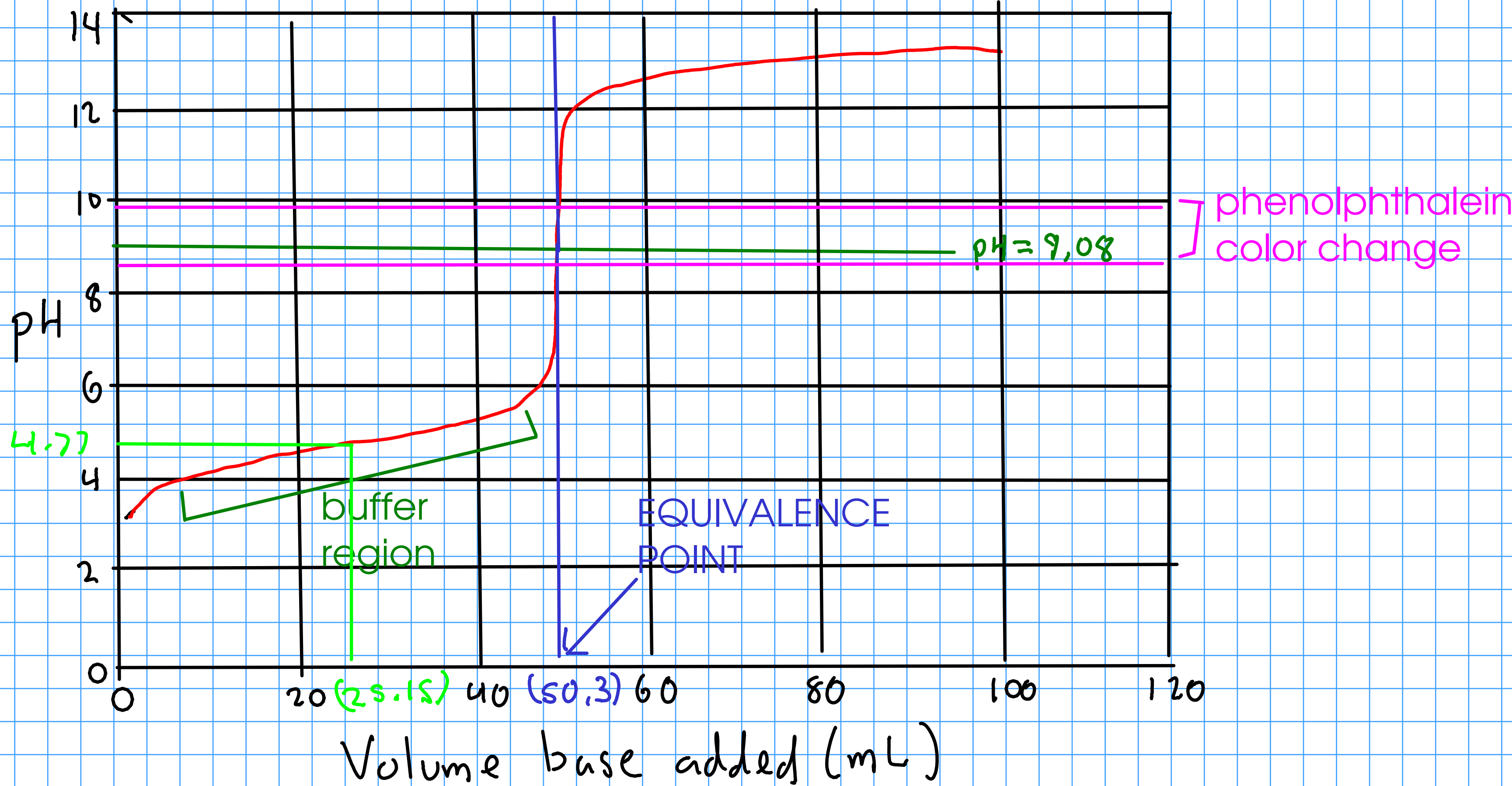
$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$

17,6 mmol $HC_2H_3O_2$ initially

Add 25.15 mL base

$25.15\ mL \times \frac{.350\ mol}{L} = 8.8025\ mmol\ NaOH$

8.8 millimoles is also the amount of acid left, and the added base gets converted to acetate ion!



The total volume is 45.15 mL, and both the acid and base are present at the same concentration. We have a BUFFER.

Find the pH of this buffer using the Henderson-Hasselbalch equation.

$$pH = pK_{a,HC_2H_3O_2} + \underbrace{\log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)}_{=0\text{, since the ratio} = 1}$$

At the halfway point, the pH = pKa of the acid!

Useful for finding acid ionization constants!