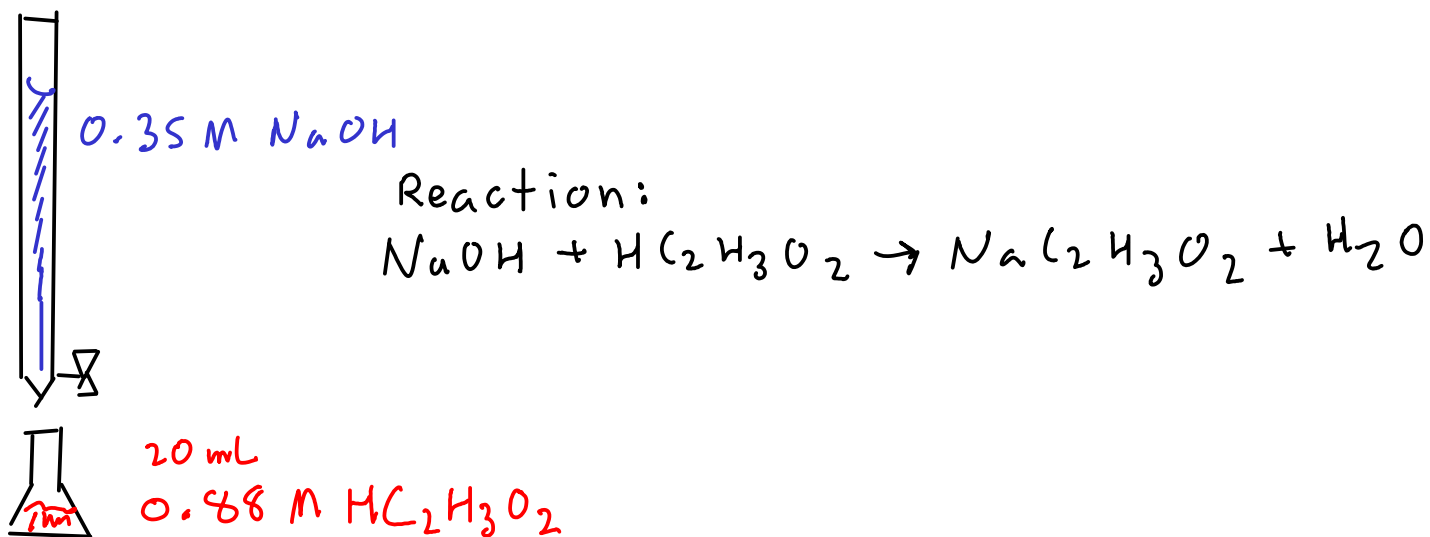


186 Titration

- 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 NaOH

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

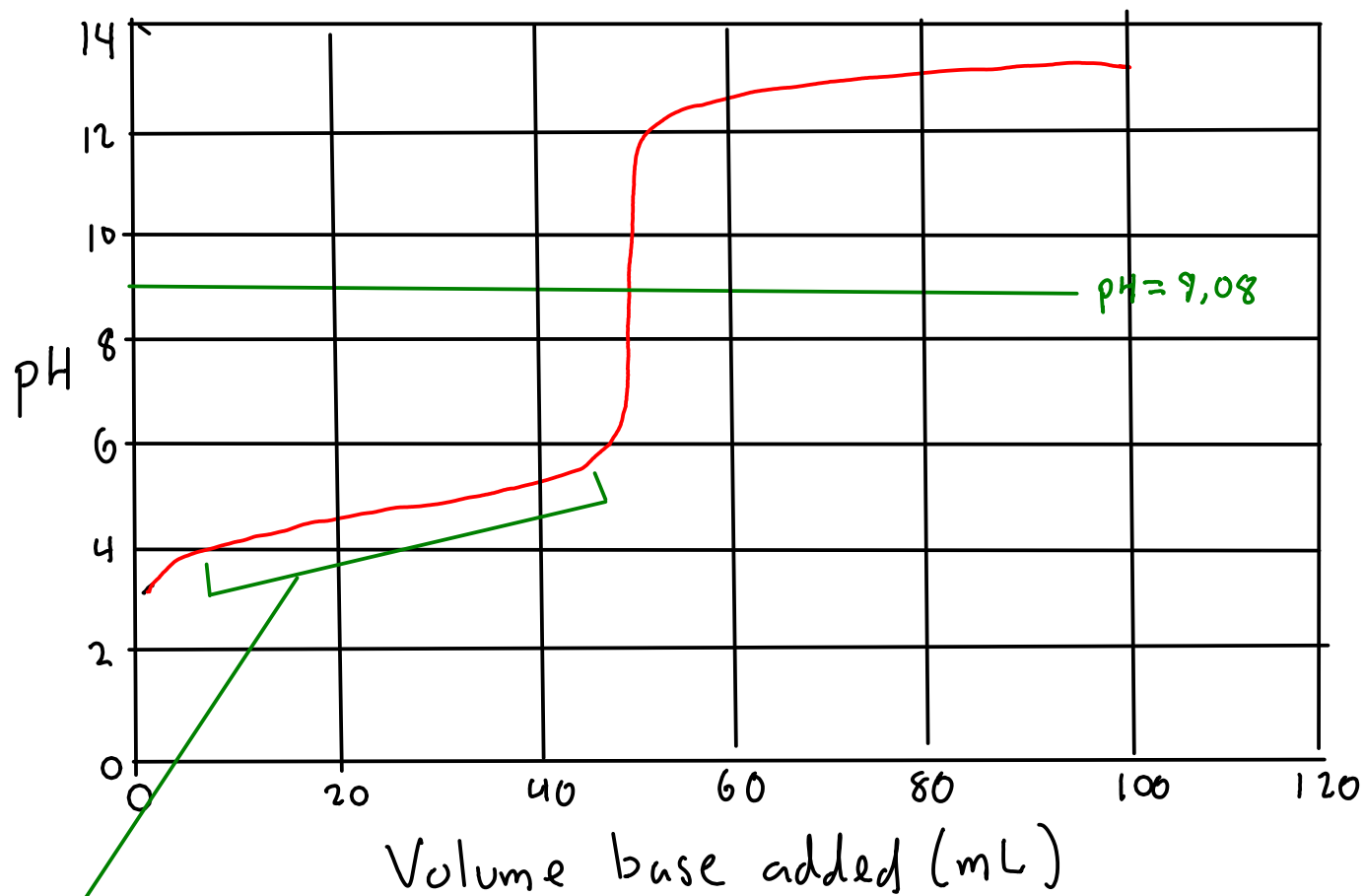
$$17.6 \text{ mmol } \text{HC}_2\text{H}_3\text{O}_2 \times \frac{\text{mol NaOH}}{\text{mmol } \text{HC}_2\text{H}_3\text{O}_2} \times \frac{\text{L}}{0.35 \text{ mol NaOH}} = 50.3 \text{ mL of } 0.350 \text{ M NaOH}$$

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

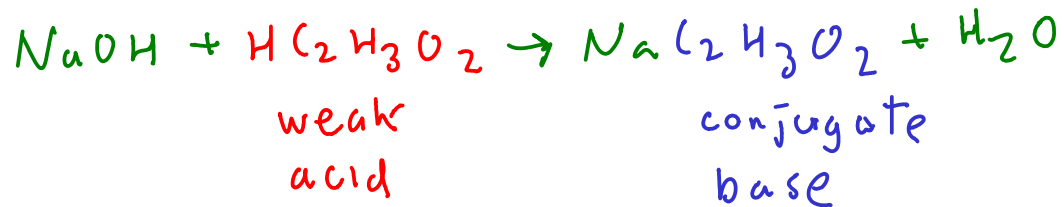
In the lab, we have used phenolphthalein indicator for vinegar titrations. Phenolphthalein changes from colorless to pink over the range of about pH 9 to pH 10. How does this indicator show where the endpoint is?

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

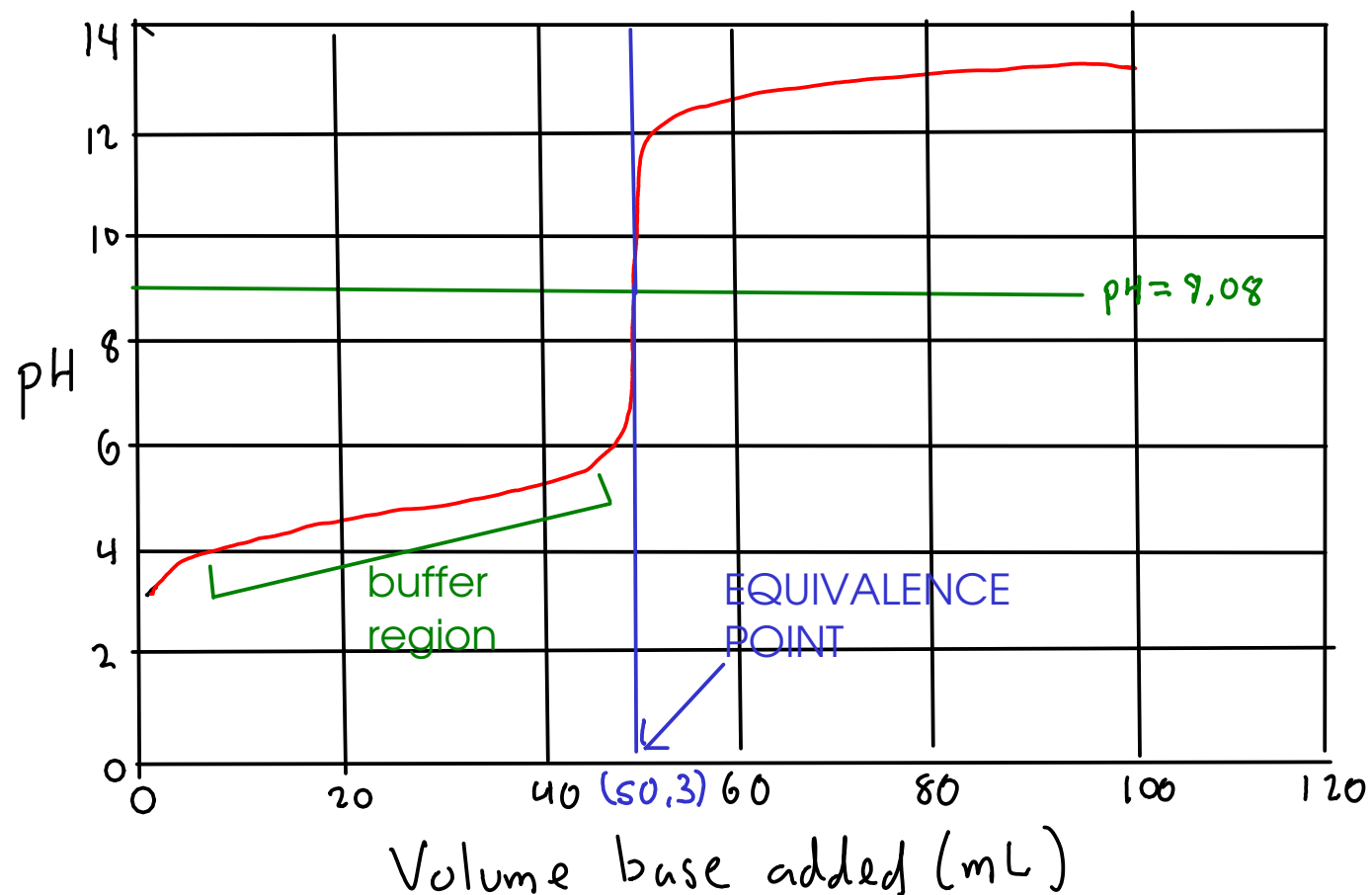
Titration curve for the titration of 20 mL of 0.88 M acetic acid with 0.35 M sodium hydroxide



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.

190 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 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	Δ	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

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

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

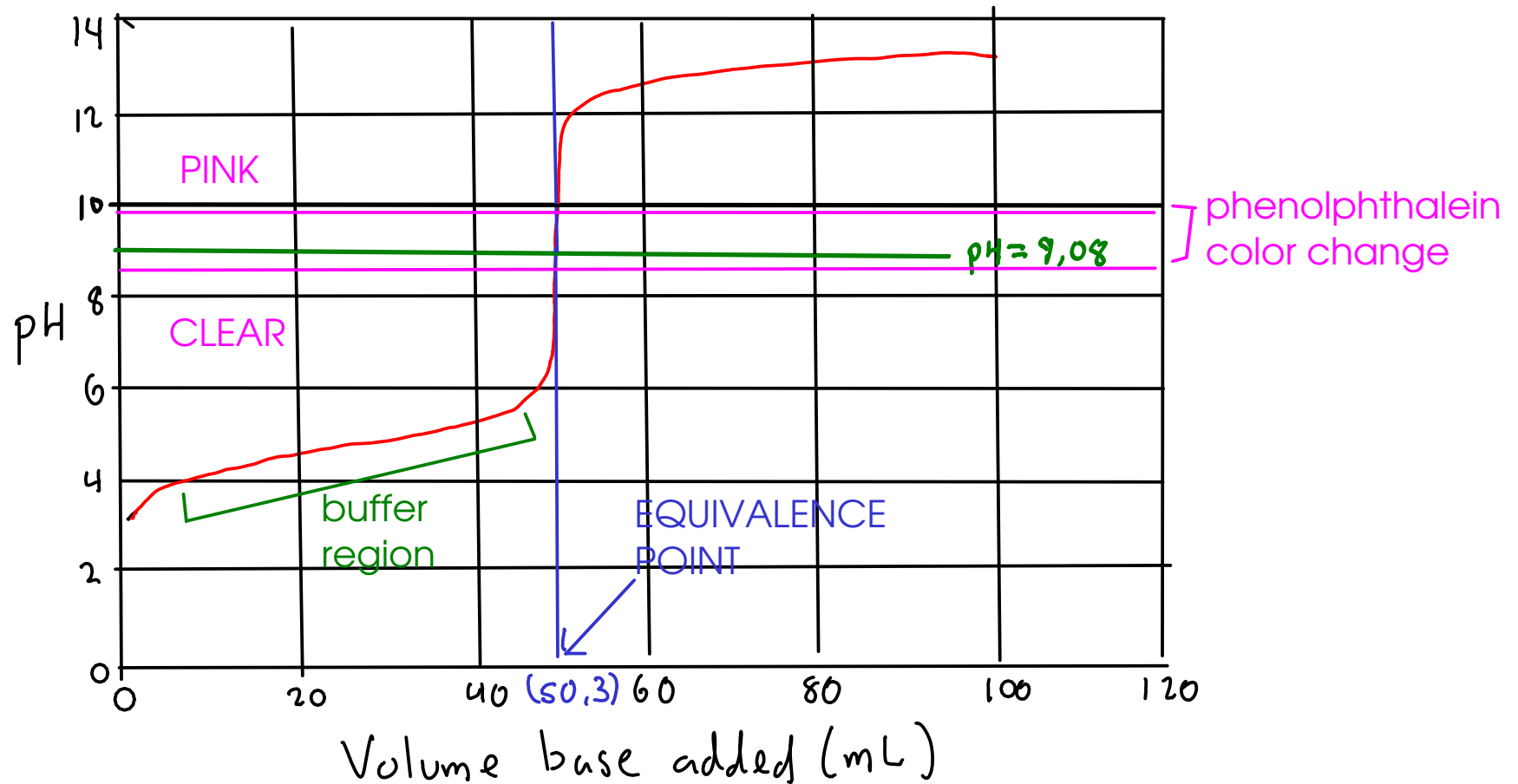
$$K_a, \text{HC}_2\text{H}_3\text{O}_2 = 1.7 \times 10^{-5}$$

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

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

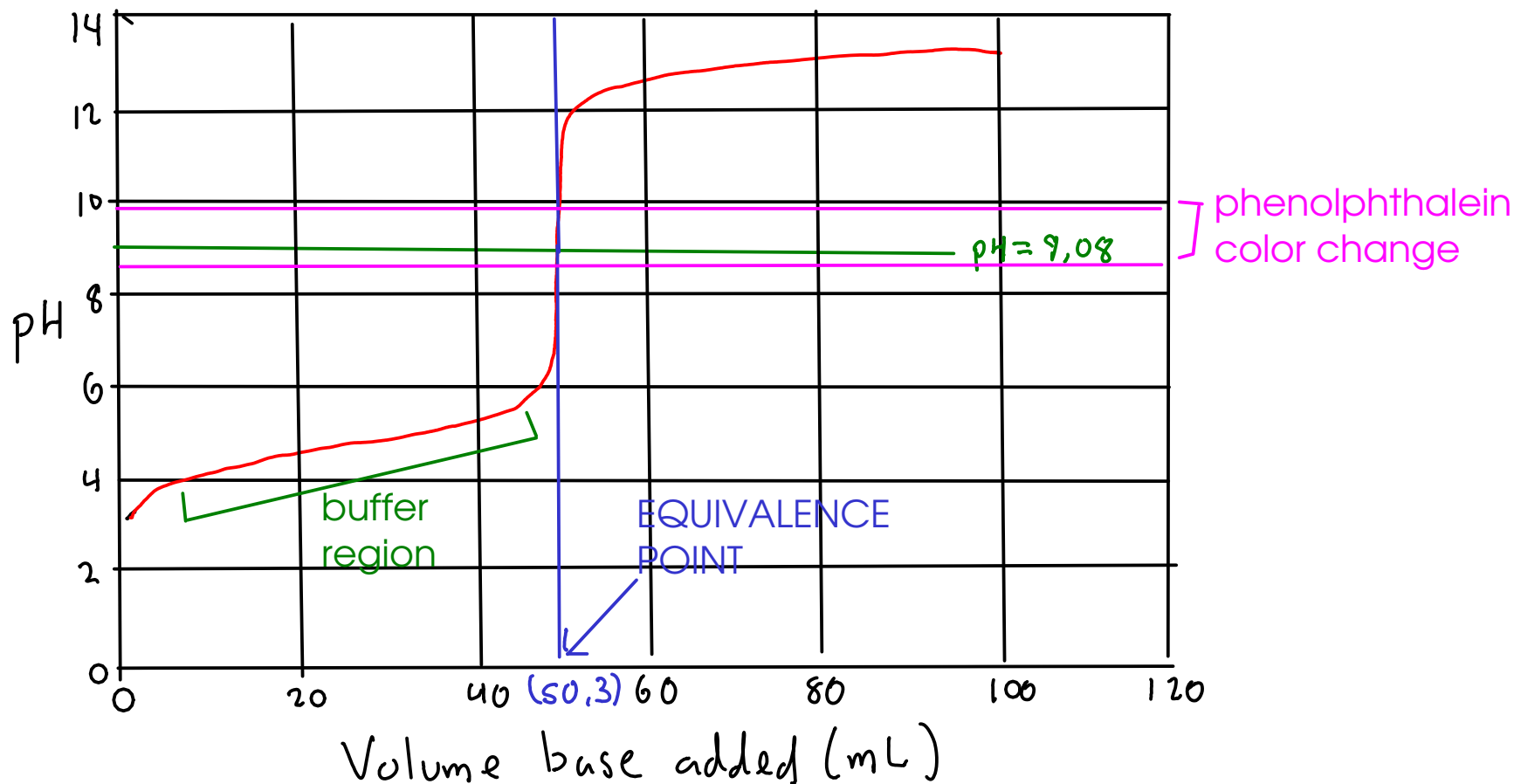
Once you figure out the concentration of acetate ion, this is simply the calculation of the pH of a salt solution!

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.

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

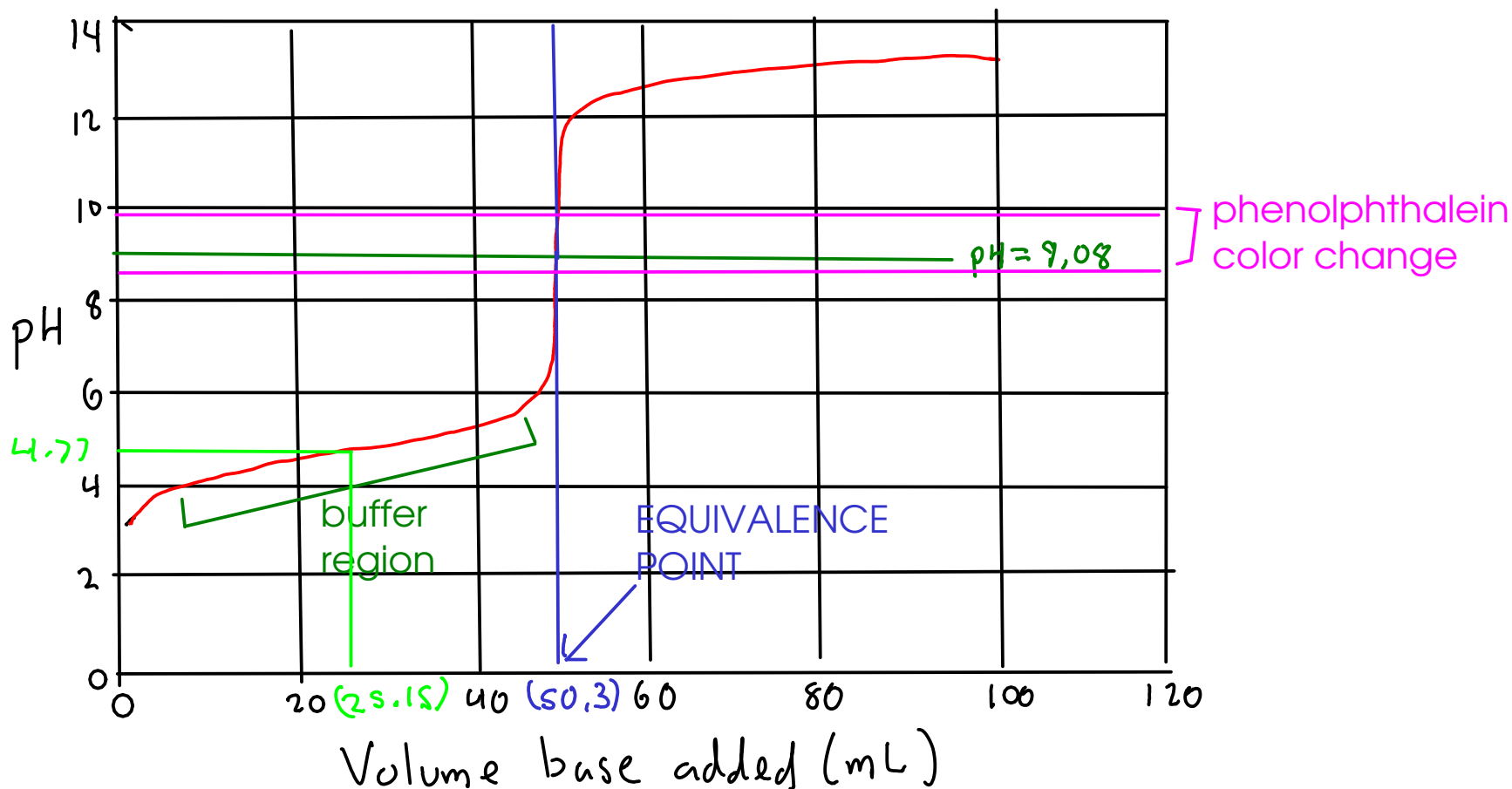


17,6 mmol $\text{HC}_2\text{H}_3\text{O}_2$
initially

Add 25.15 mL base

$$25,15 \text{ mL} \times \frac{.350 \text{ mol}}{\text{L}} = 8,8025 \text{ mmol NaOH}$$

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



The total volume is 25.15 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.

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

$\underbrace{\hspace{10em}}_{= 0, \text{ since the ratio} = 1}$

At the halfway point, the $\text{pH} = \text{pK}_{\text{a}}$ of the acid!

Useful for finding acid ionization constants!