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!

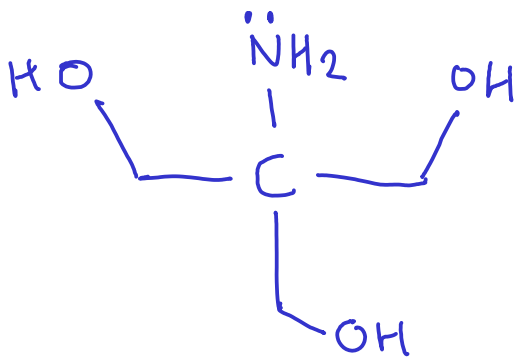
$$pH = pK_{a,\,acidic} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

Henderson-Hasselbalch Equation

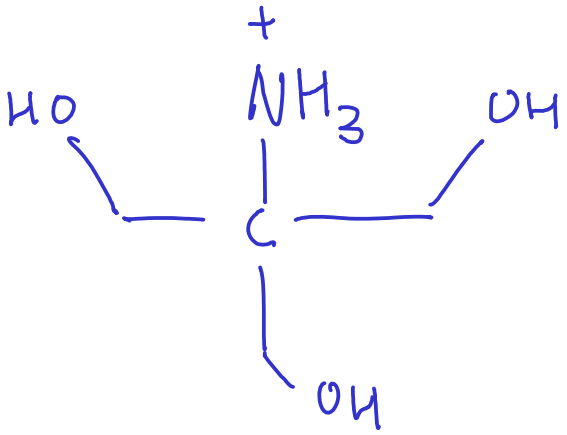
Ratio determines pH; the actual concentrations don't!

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

Buffer calculation: Tris buffer - Tris(hydroxymethyl)-aminomethane



tris base



tris-HCl (conjugate acid of tris base)

Cl^-

pKa = 8.06

Calculate the pH of a buffer made from 50 mL of 0.10M tris and 50 mL of 0.15M tris-HCl. Assume volumes add.

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

[tris]: $M_1V_1 = M_2V_2$ $(0.10\,M)(50.0\,mL) = M_2(100.0\,mL)$

$0.050\,M = M_2$

[tris-HCl]: $M_1V_1 = M_2V_2$ $(0.15\,M)(50.0\,mL) = M_2(100.0\,mL)$

$0.075\,M = M_2$

$$pH = 8.06 + \log\left(\frac{0.050}{0.075}\right) = \boxed{7.88}$$

Take 100. mL of the previous buffer (0.05 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 reacts with the basic component of the buffer, changing it to its conjugate acid (tris-HCl).

$$\text{tris} + H_3O^+ \longrightarrow \text{tris-H}^+ + H_2O$$

$$(\text{tris} + HCl \longrightarrow \text{tris-HCl})$$

We need to find out the NEW concentrations of the species in the buffer system

Species	Initial mmol	Δ in rxn	Final mmol	[Concentration]
tris	100 mL x 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-HCl	100 mL x 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 x 0.10 M = 0.5 mmol	−0.5 mmol	0 mmol	0

* The volume of the system is now 105 mL due to the added 5.0 mL of HCl!

Now, find pH using Henderson-Hasselbalch equation:

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

The pH of the original buffer was 7.88, so the pH has decreased 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.

$M_1V_1 = M_2V_2$

$(0.10\ M)(5.0\ mL) = M_2(105\ mL)$

$0.00476\ M\ HCl = [H_3O^+]$

So, $pH = 2.32$

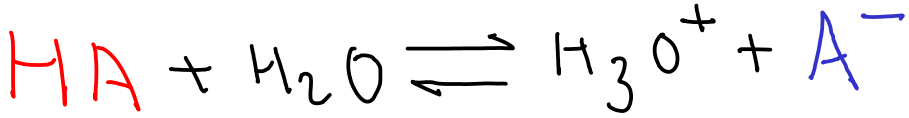
... which is a change of 4.68 pH units from water's original pH of 7.00!

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!

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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!

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

When does the color of the indicator change?

IF the pH is << pKa, then the log term above must be both large AND negative!

- What color is the solution?

$[HA] >> [A^-]$ ... so the SOLUTION IS RED!

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

- What color is the solution?

$[A^-] >> [HA]$ ... so the SOLUTION IS BLUE!

- 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.

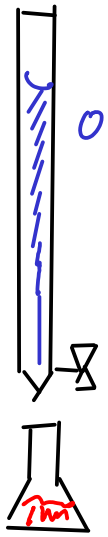
Titration

- 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?



0.35 M $NaOH$

20 mL

0.88 M $HC_2H_3O_2$

Reaction:

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

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 0.88M HC_2H_3O w/ 0.35 M NaOH

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

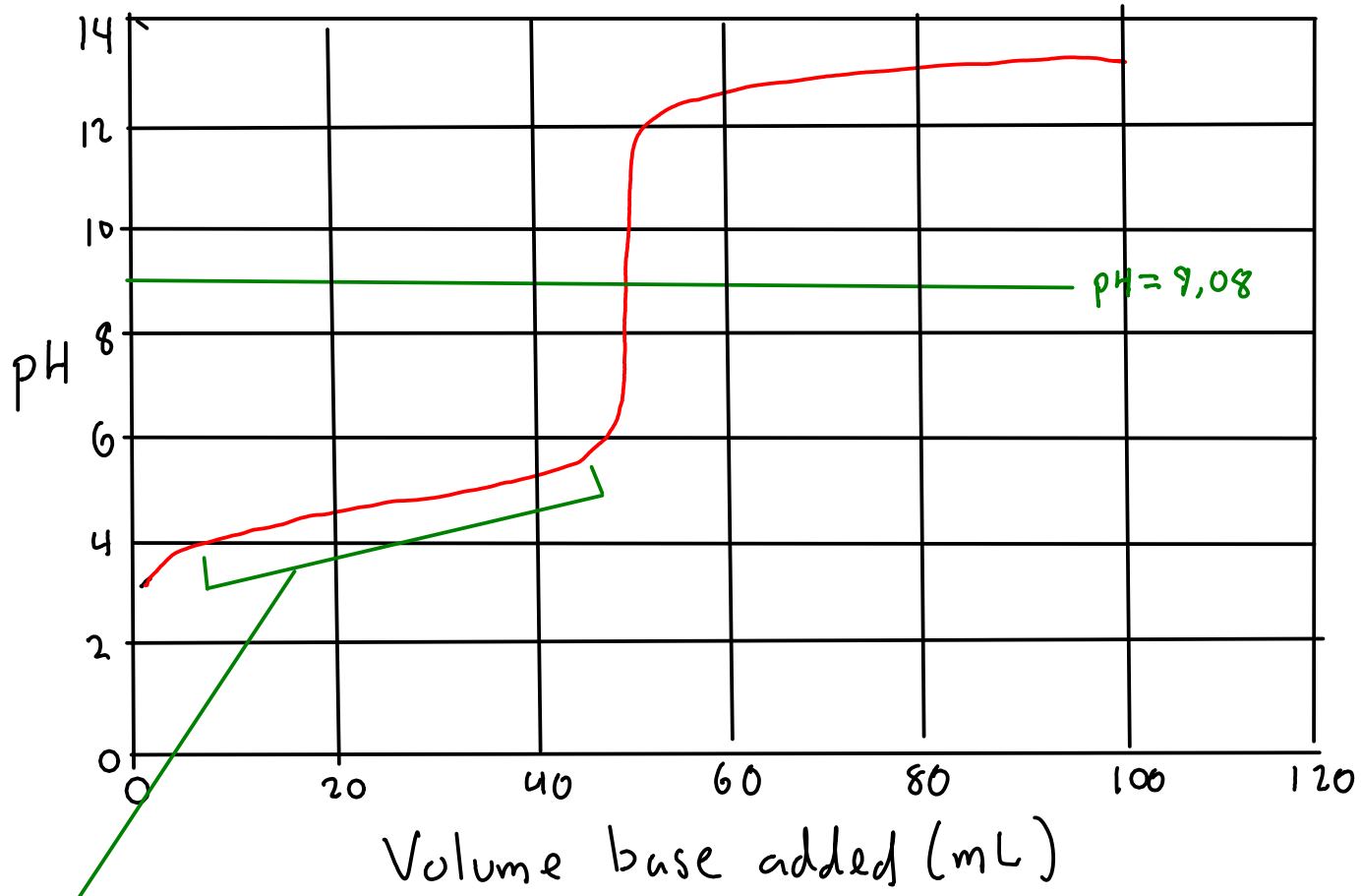
$$17.6\text{ mmol } HC_2H_3O_2 \times \frac{\text{mol NaOH}}{\text{mol } HC_2H_3O_2} \times \frac{\text{L}}{0.35\text{ mol NaOH}} = \boxed{50.3\text{ mL of 0.35M NaOH}}$$

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



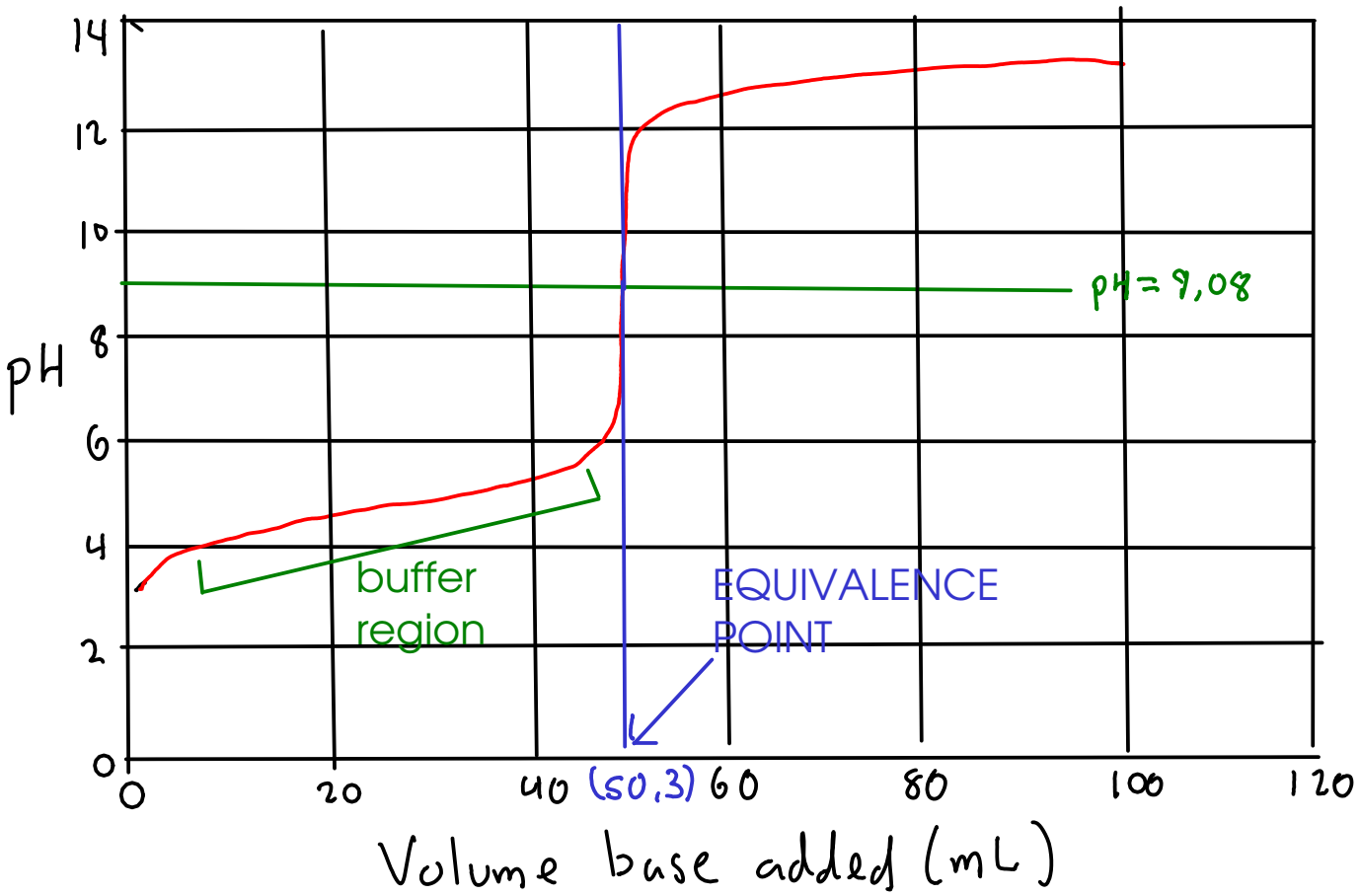
buffer region: With a moderate amount of NaOH added, we have a solution that contains significant amounts of both acetic acid and its conjugate base (acetate ion). We have a buffer.

$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$

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

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

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

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

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

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

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

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

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

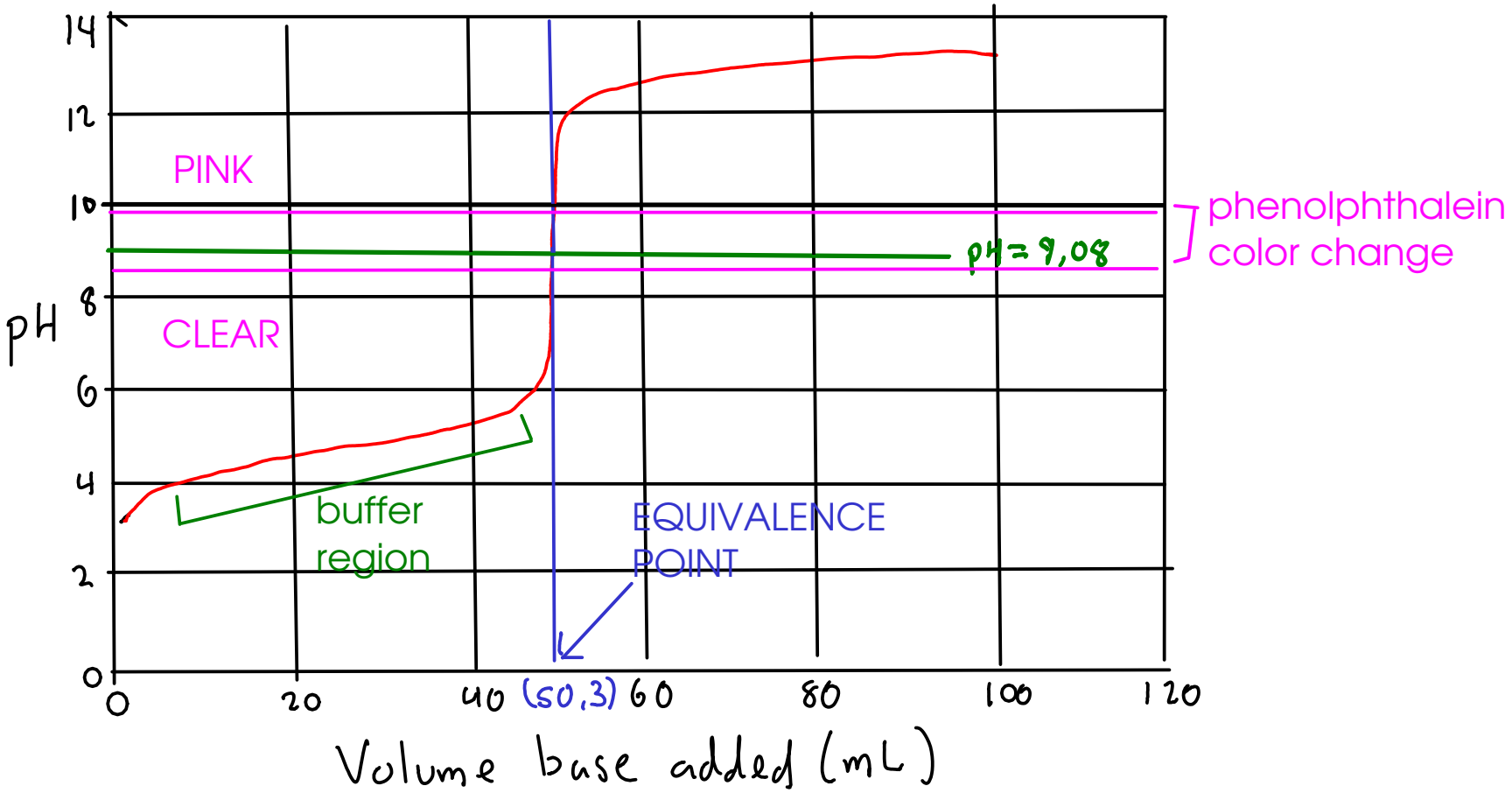
$x = 1.21\times10^{-5}$, pOH = 4.92, **pH = 9.08**

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

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

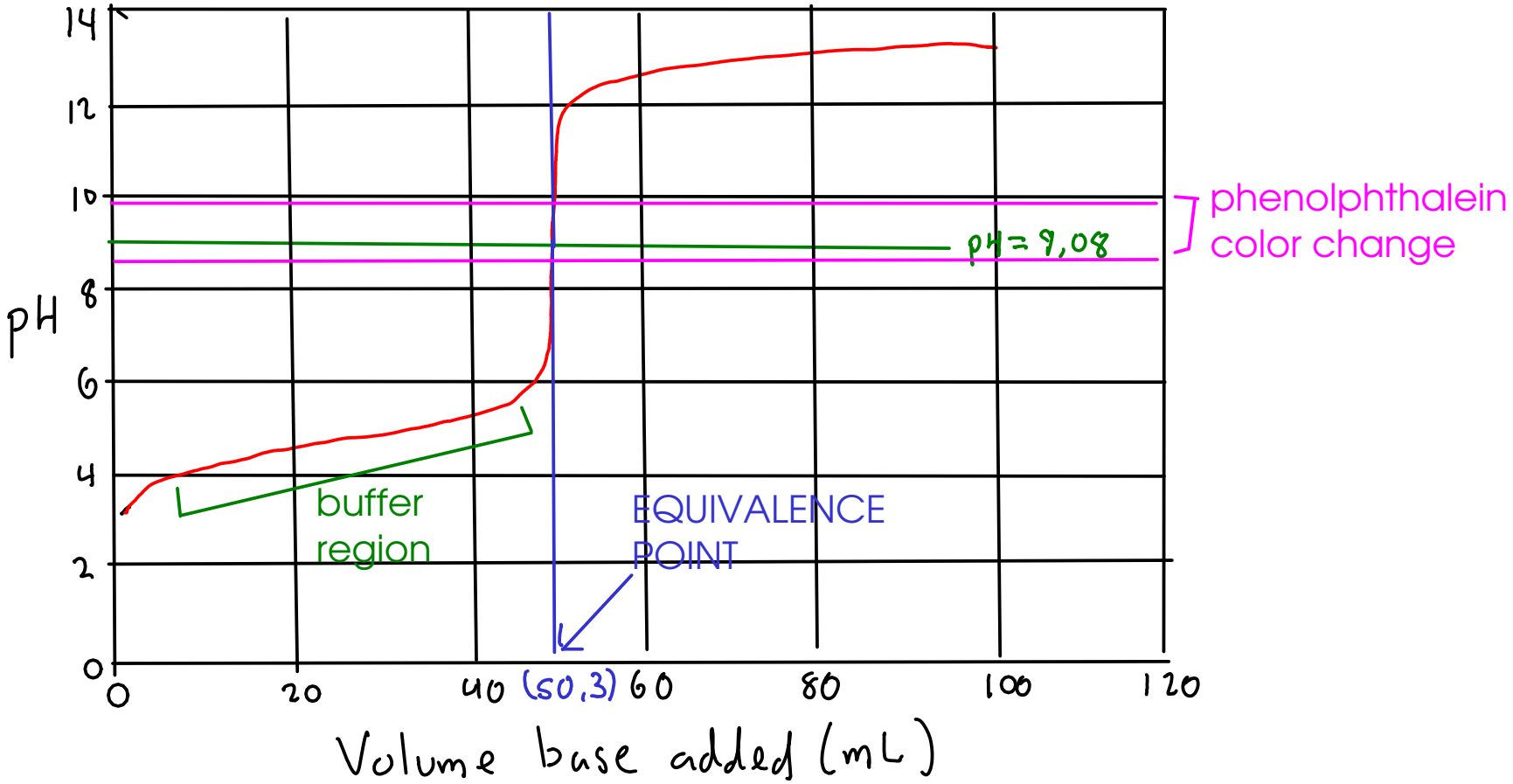
Once you figure out the concentration of acetate ion, this is simply the calculation of the pH of a salt solution!

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

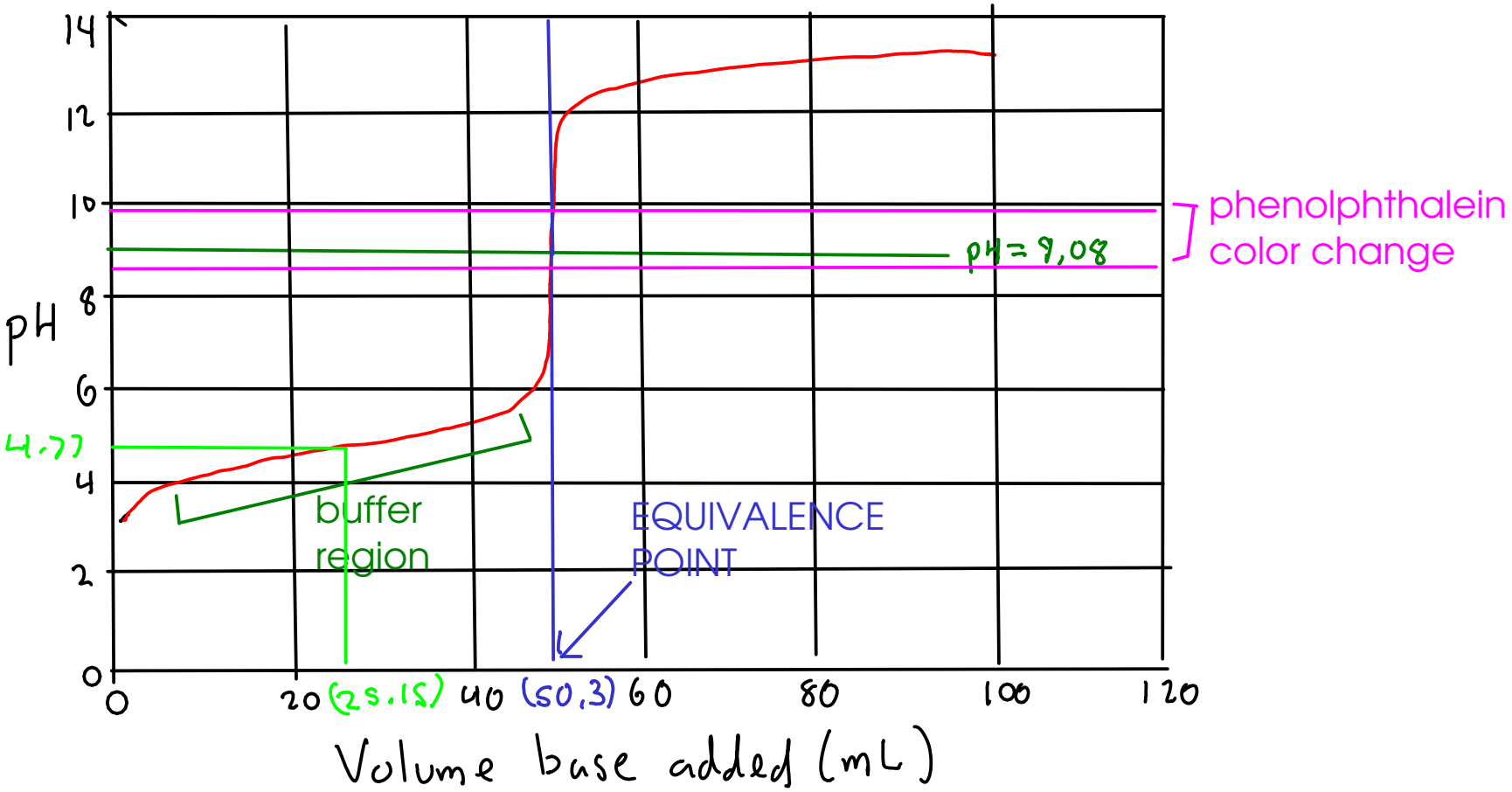
$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$

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 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.

$$pH = pK_{a,HC_2H_3O_2} + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

$= 0$, since the ratio $= 1$

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

Useful for finding acid ionization constants!