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

Henderson-Hasselbalch Equation

ex: acidic buffer

$HC_2H_3O_2 / NaC_2H_3O_2$

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

---

ex: basic buffer

NH_3 / NH_4NO_3

$$pH = pK_{a,NH_4^+} + \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

$pK_a + pK_b = 14{,}00$ ... is the -log of $K_a \times K_b = K_w$

178 Calculate the pH of a buffer made from 30.2 grams of ammonium chloride and 29 mL of 18.1 M ammonia diluted to 150. mL with water.

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

base: NH_3 acid: NH_4^+ ; $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

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

$[NH_3] = ?$ $\quad M_1V_1 = M_2V_2$

$(18.1\ M)(29\ mL) = M_2(150.\ mL)$

$M_2 = 3.499333333\ M$

$[NH_4^+] = ?$ $\quad NH_4Cl: 53.492\ g/mol$

$$30.2\ g\ NH_4Cl \times \frac{mol\ NH_4Cl}{53.492\ g\ NH_4Cl} = 0.564570403\ mol\ NH_4Cl$$

$$[NH_4^+] = \frac{0.564570403\ mol\ NH_4Cl}{0.150\ L} = 3.763802687\ M$$

$K_{b,NH_3} = 1.8 \times 10^{-5}$; $pK_b = 4.74$, so $pK_a = 9.26$

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

BUFFER SELECTION

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

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

- 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 / conuugate acid)

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

$$NH_3 + HNO_3 \longrightarrow NH_4^+ + NO_3^-$$

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!

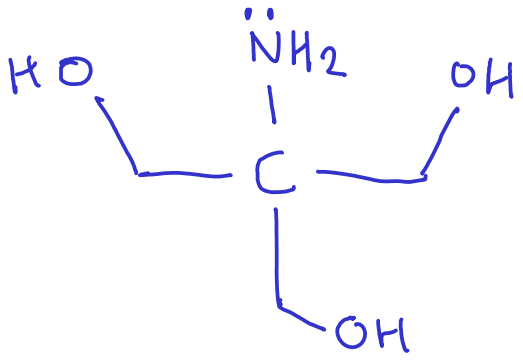
$$pH = pK_{a,\,acidic} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

Henderson-Hasselbalch Equation

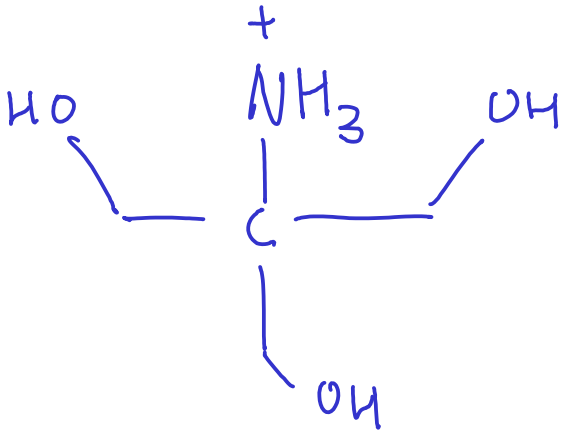
Ratio determines pH; the actual concentrations don't!

- 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]: $M_1V_1 = M_2V_2$ $\quad (0.10\,M)(50\,mL) = M_2(100\,mL)$

$0.050\,M = M_2$

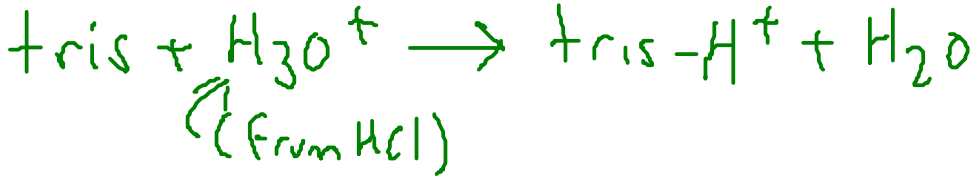
[tris-H^+]: $(0.15\,M)(50\,mL) = M_2(100\,mL)$

$0.075\,M = M_2$

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

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	Δ in rxn	Final mmol	[Conc.]
tris	100 mL × 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+	100 mL × 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 × 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)

Find pH with H-H equation

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

The original pH was 7.88, so we saw a decrease of 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.

$$M_1V_1 = M_2V_2$$

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

$$0.00476\,M\ HCl = M_2$$

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

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

$$\boxed{pH = 2.32}$$

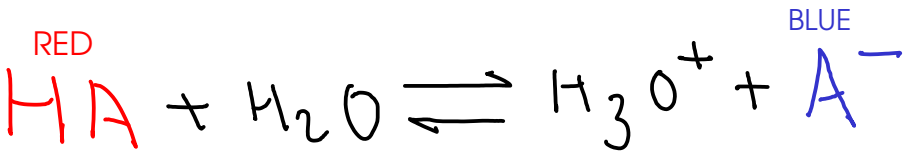
... which is a change of 4.68 pH units from water's original pH of 7.00!

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?

$[HA] >> [A^-]$ ... and 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?

$[A^-] >> [HA]$ ... and 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.

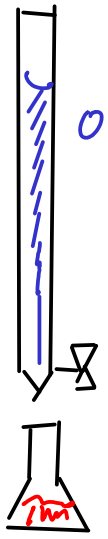
Titration

- 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

0.48 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

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

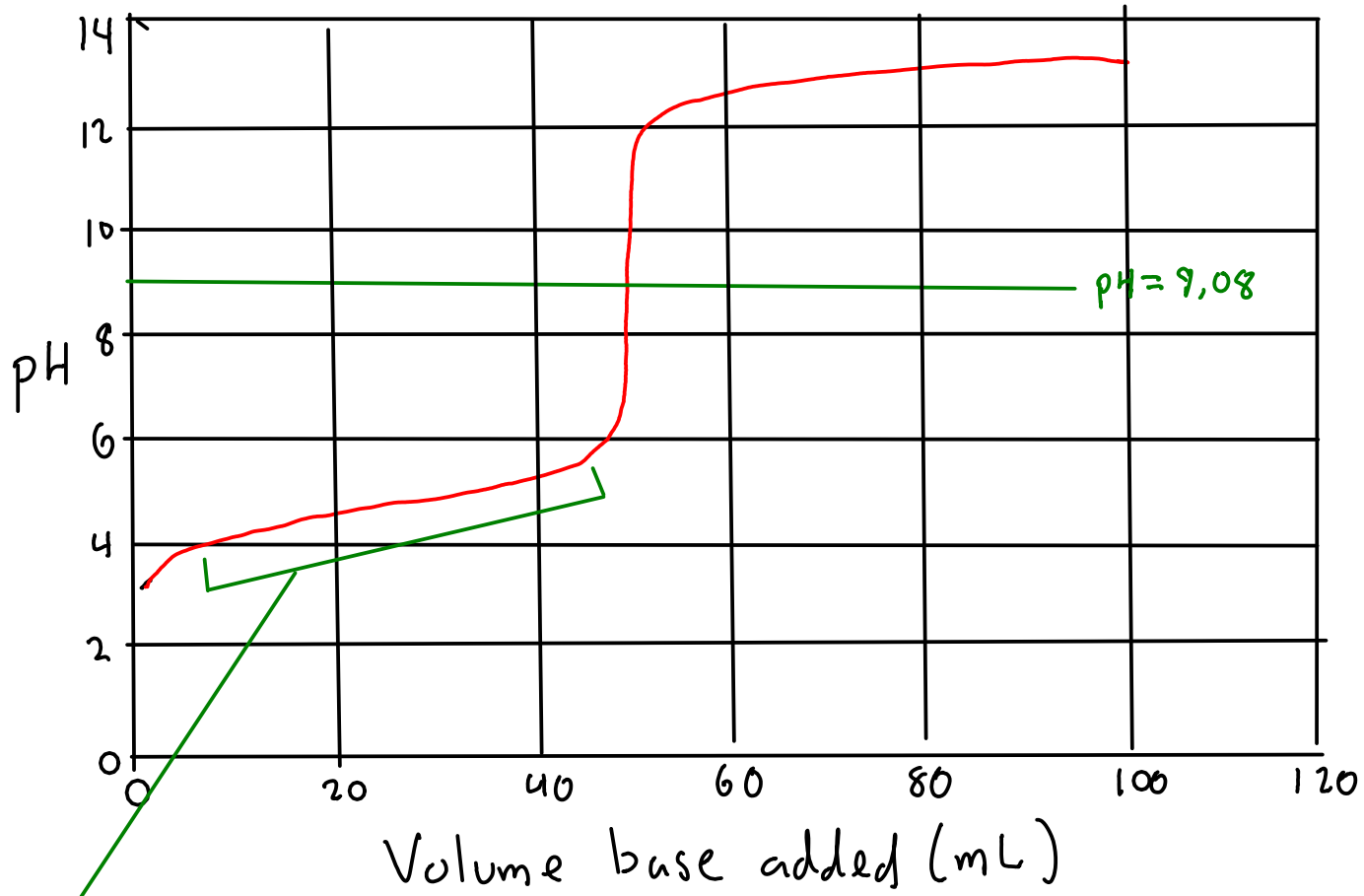
$$17.6\,mmol\ HC_2H_3O_2 \times \frac{mol\ NaOH}{mm\ HC_2H_3O_2} \times \frac{L}{0.35\,mol\ NaOH} = 50.3\,mL\ of\ 0.350\,M\ NaOH$$

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



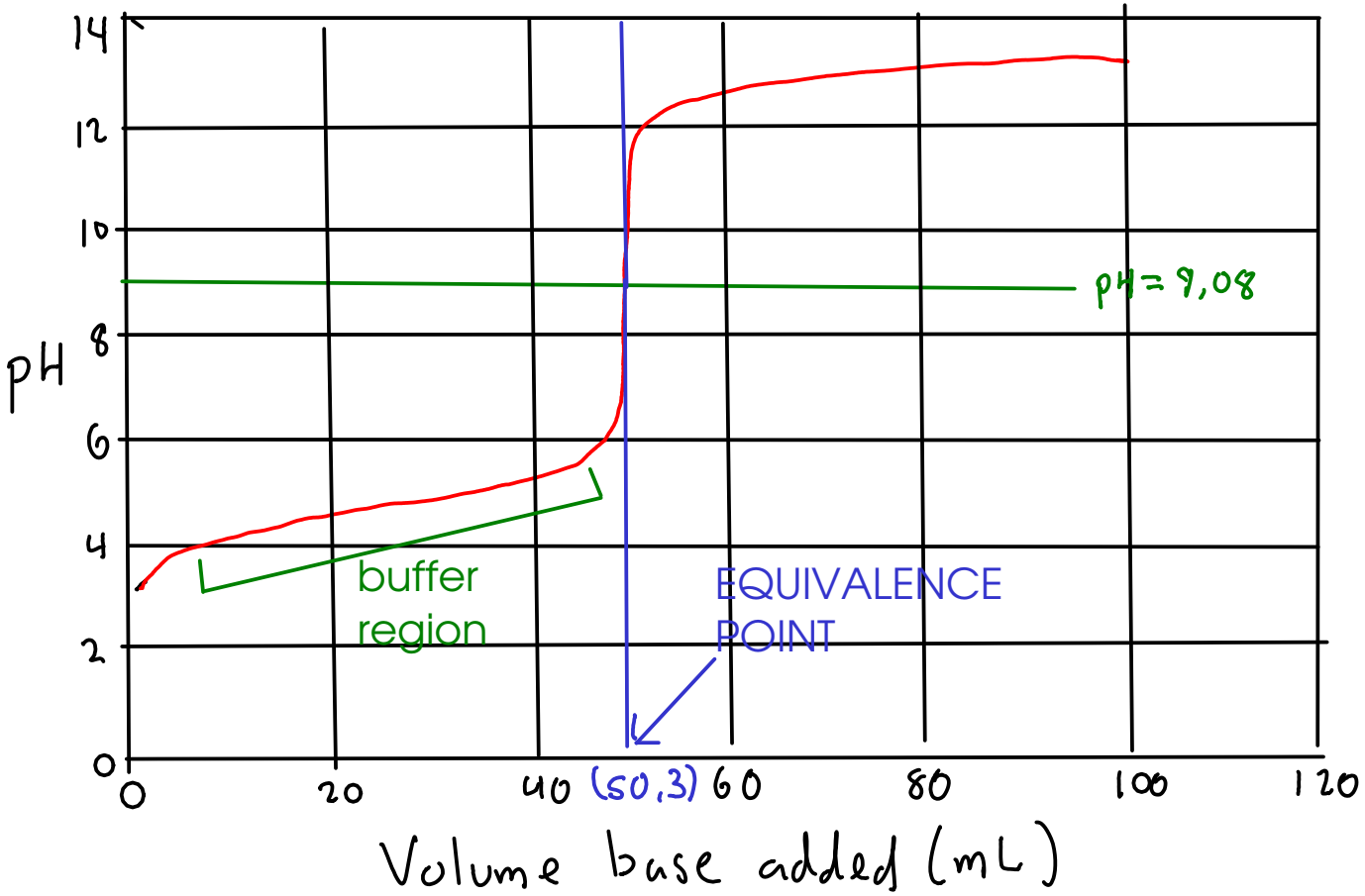
buffer region: With a moderate amount of NaOH added, we have a solution that contains significant amounts of both acetic acid and its conjugate base (acetate ion). We have a buffer.

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

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

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

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

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

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

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

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

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

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

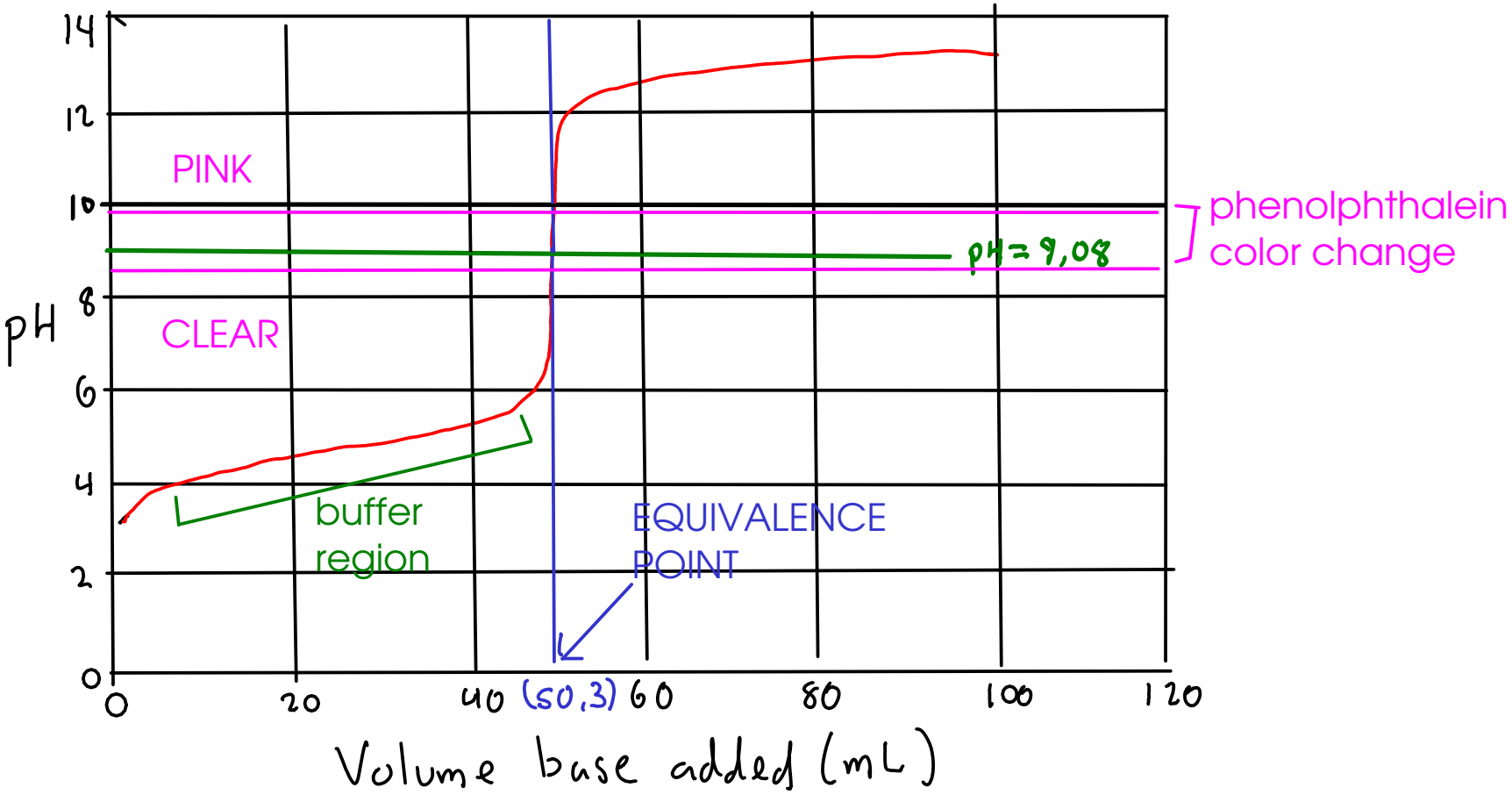
$x = 1.21\times10^{-5}$, pOH = 4.92, $\boxed{\text{pH} = 9.08}$

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

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

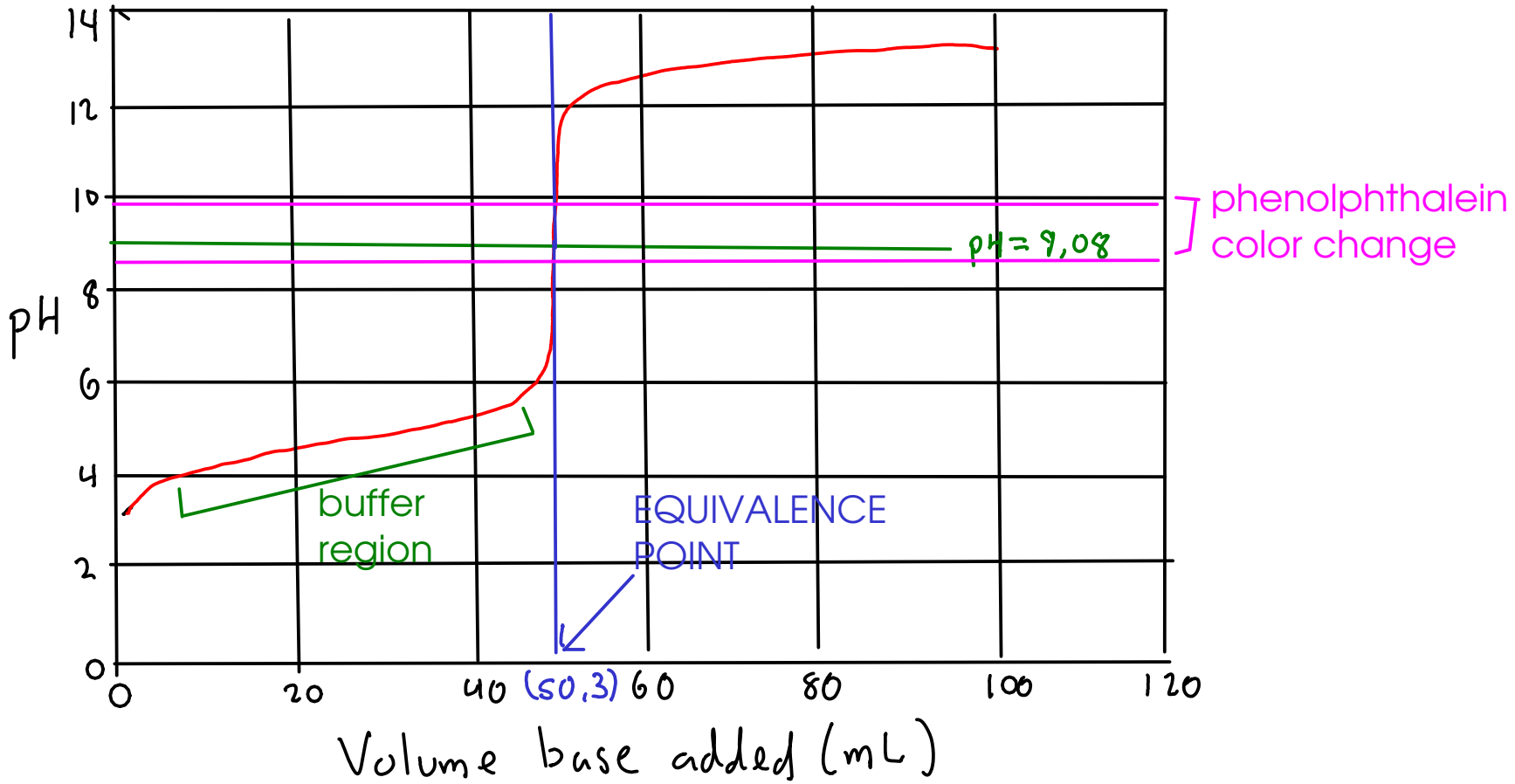
Once you figure out the concentration of acetate ion, this is simply the calculation of the pH of a salt solution!

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

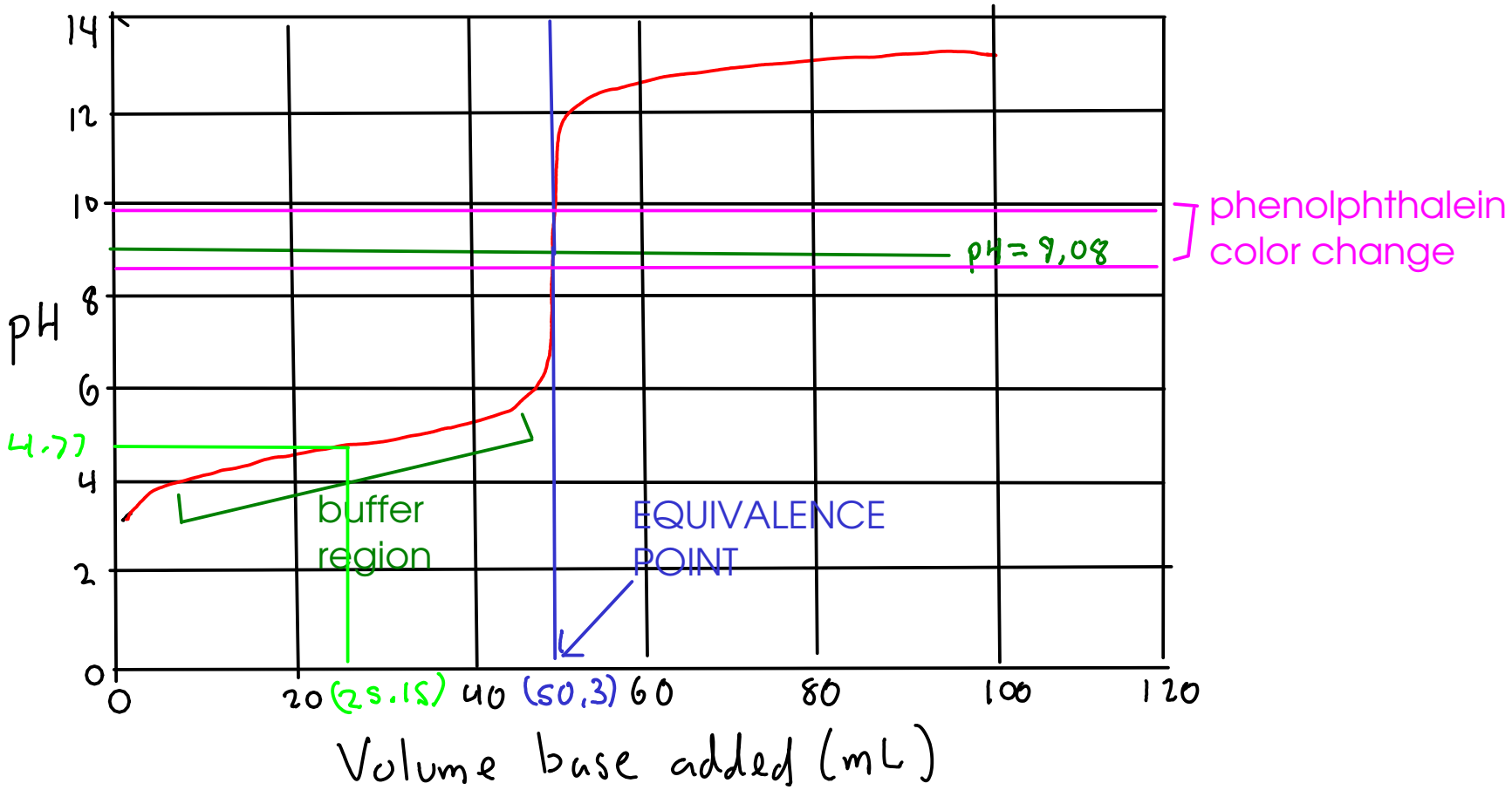
$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$

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!

Solubility as an equilibrium process

SOLUTION: Homogeneous mixture of substances Solutions contain:

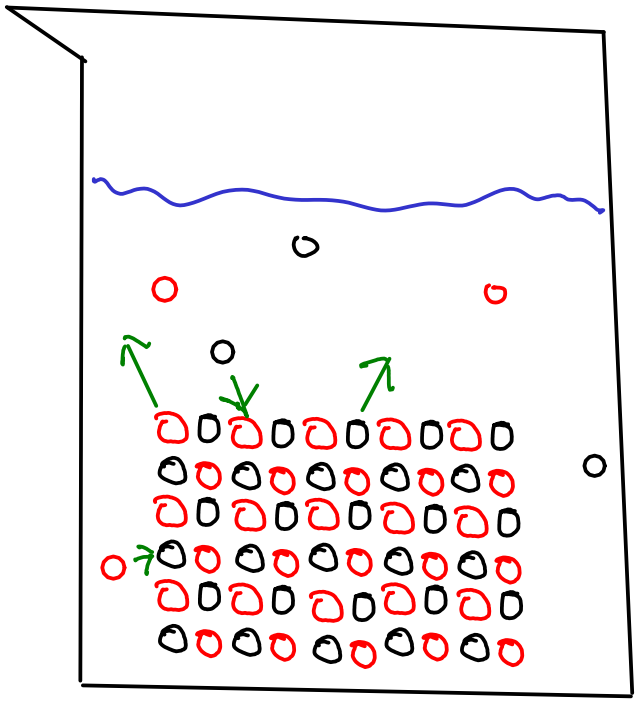
SOLUTE: Component(s) of a solution present in small amount
SOLVENT: Component of a solution present in greatest amount

We usually call water the solvent in aqueous mixtures, even if the water is present in smaller amount than another component

SOLUBILITY: The amount of a solute that will dissolve in a given volume of solvent

SATURATED SOLUTION: Contains the maximum amount of solute that it is possible to dissolve in a given volume of solvent!

A SATURATED SOLUTION is a solution where dissolved solute exists in an EQUILIBRIUM with undissolved solute!



Example: Consider a saturated solution of silver chloride:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

At equilibrium, the rate of dissolving equals the rate of crystallization!

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K_c = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

... what does this equilibrium constant tell us? That silver chloride isn't very soluble!