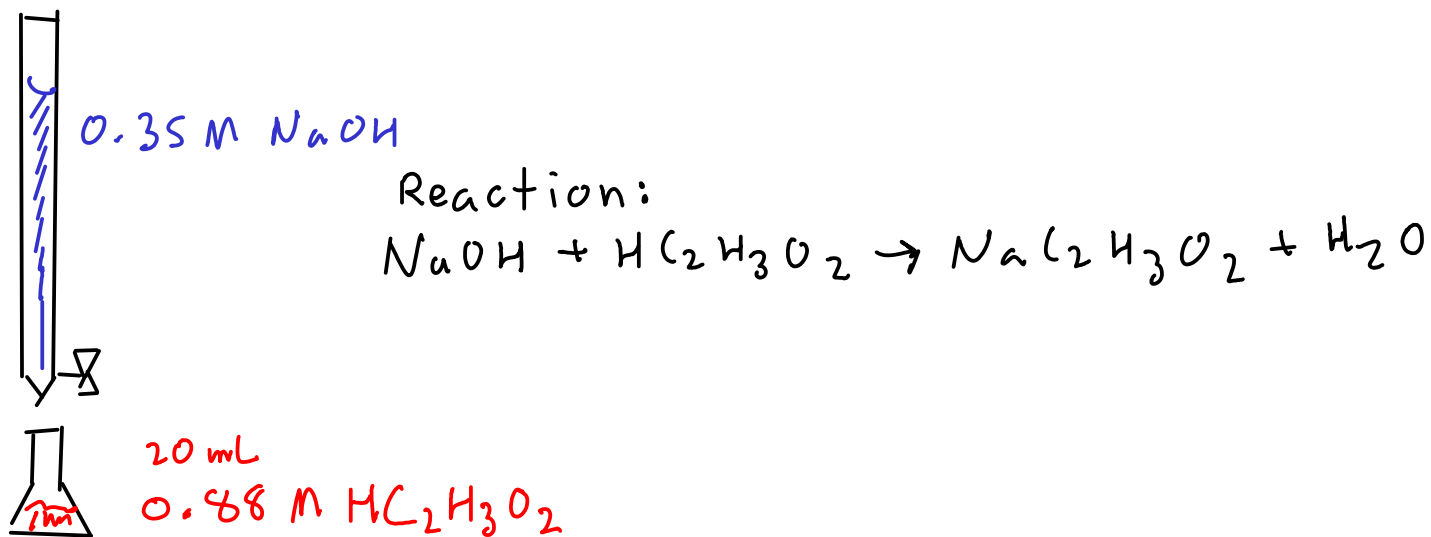


171 Titration

- 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

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

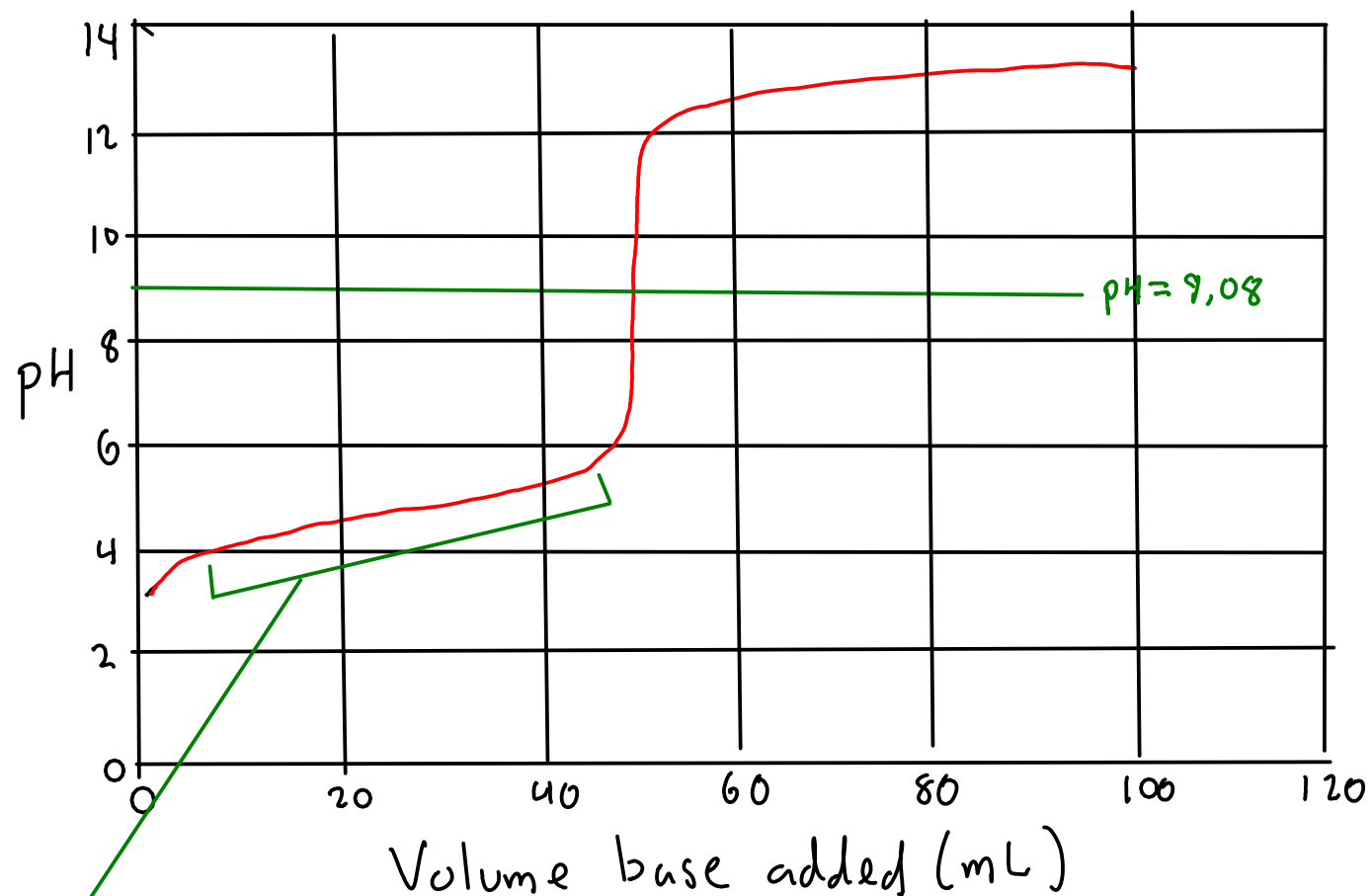
$$17.6 \text{ mmol } \text{HC}_2\text{H}_3\text{O}_2 \times \frac{\text{mol } \text{NaOH}}{\text{mol } \text{HC}_2\text{H}_3\text{O}_2} \times \frac{\text{L}}{0.35 \text{ mol } \text{NaOH}} = 50.3 \text{ mL of } 0.35 \text{ M } \text{NaOH}$$

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

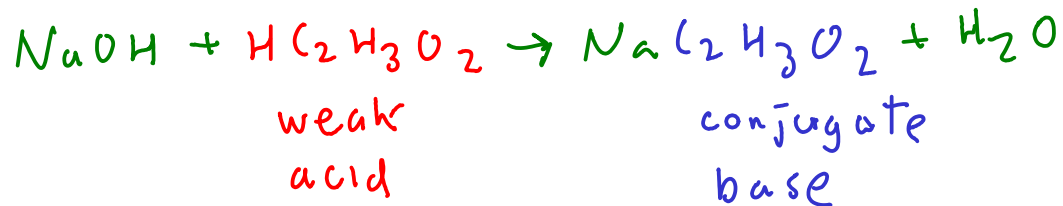
In the lab, we have used phenolphthalein indicator for vinegar titrations. Phenolphthalein changes from colorless to pink over the range of about pH 9 to pH 10. How does this indicator show where the endpoint is?

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

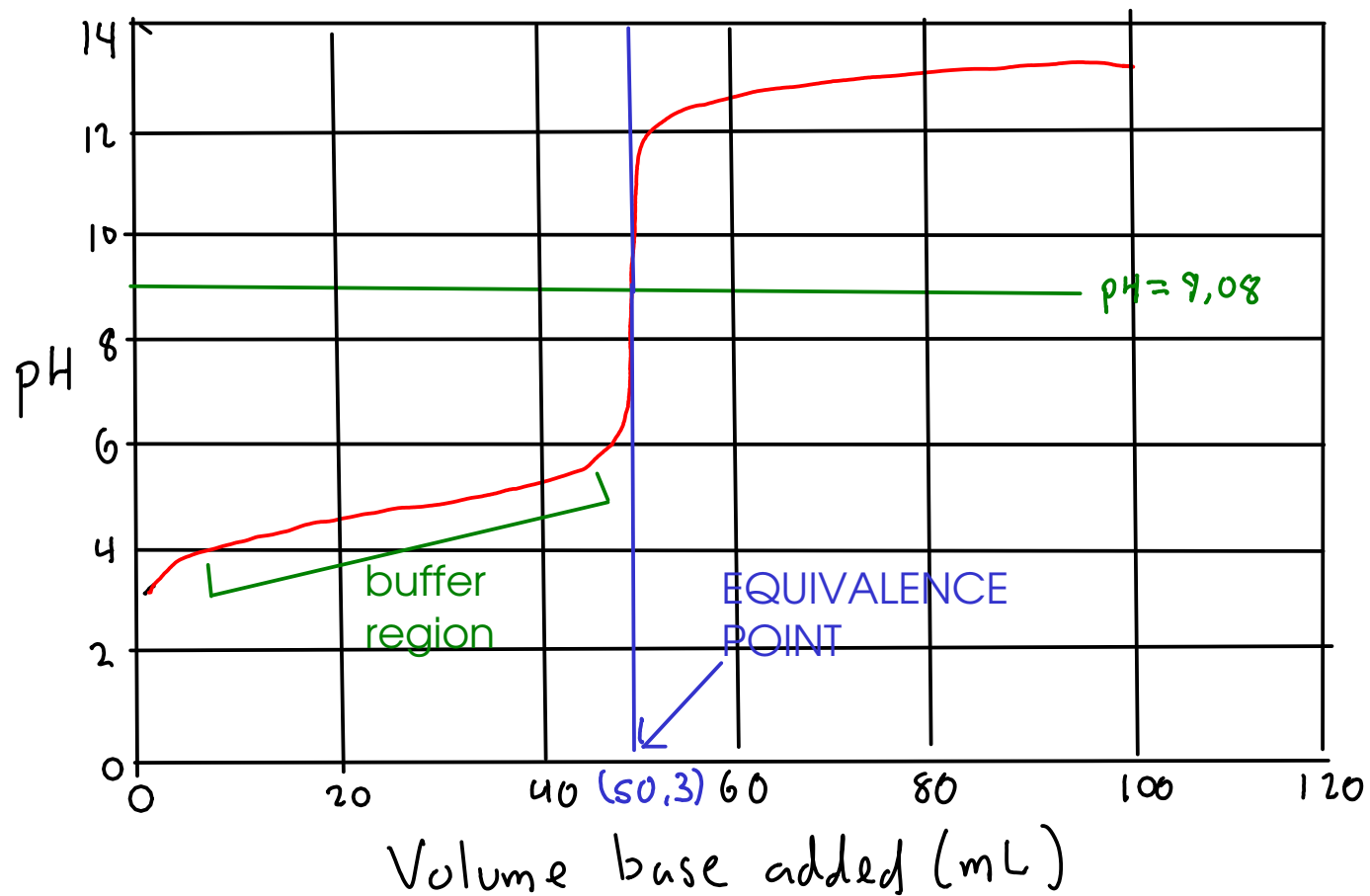
Titration curve for the titration of 20 mL of 0.88 M acetic acid with 0.35 M sodium hydroxide



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 NaOH

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

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

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

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



	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

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

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

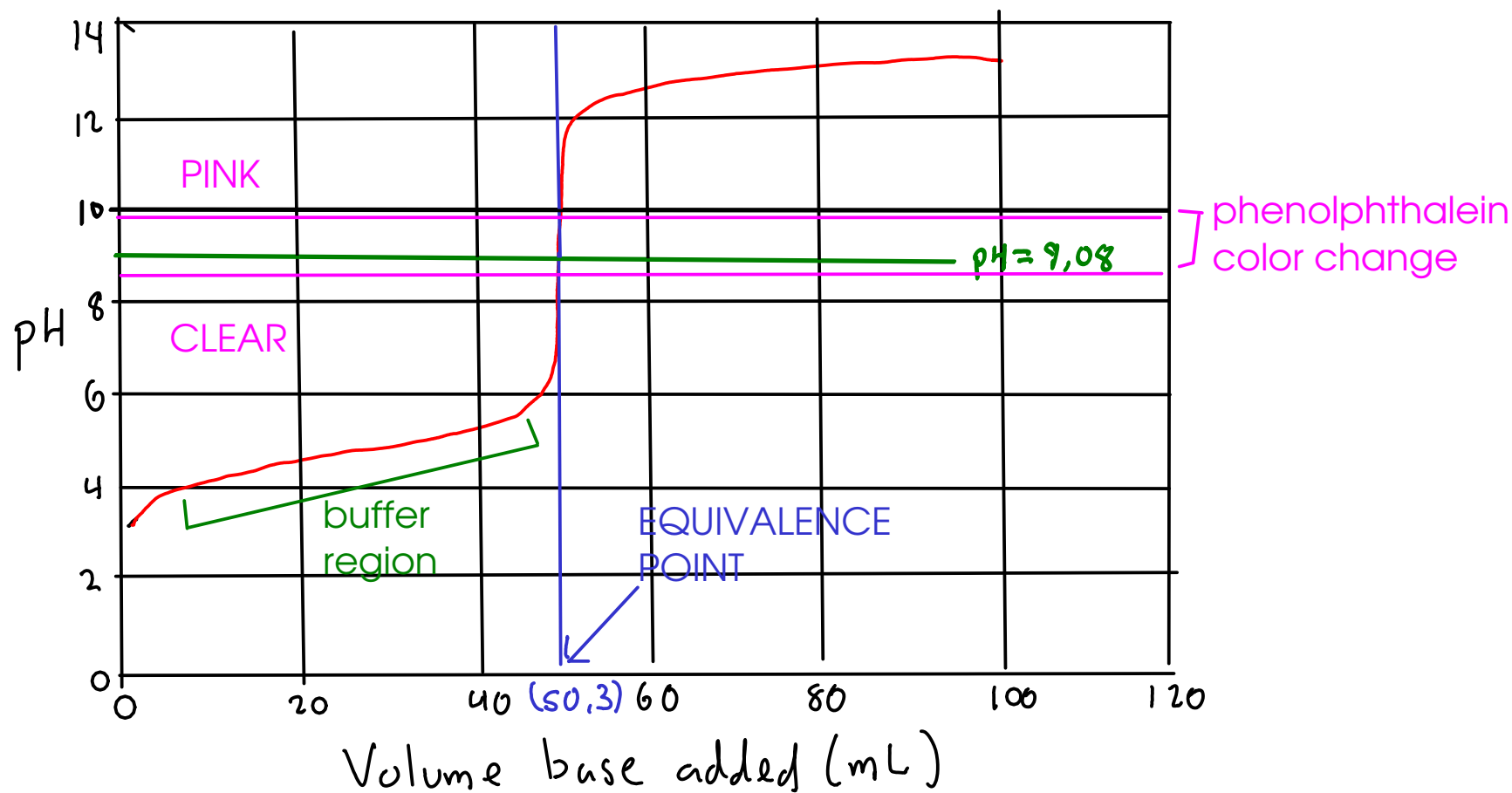
$$\frac{x^2}{0.250} = 5.88 \times 10^{-10}$$

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

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

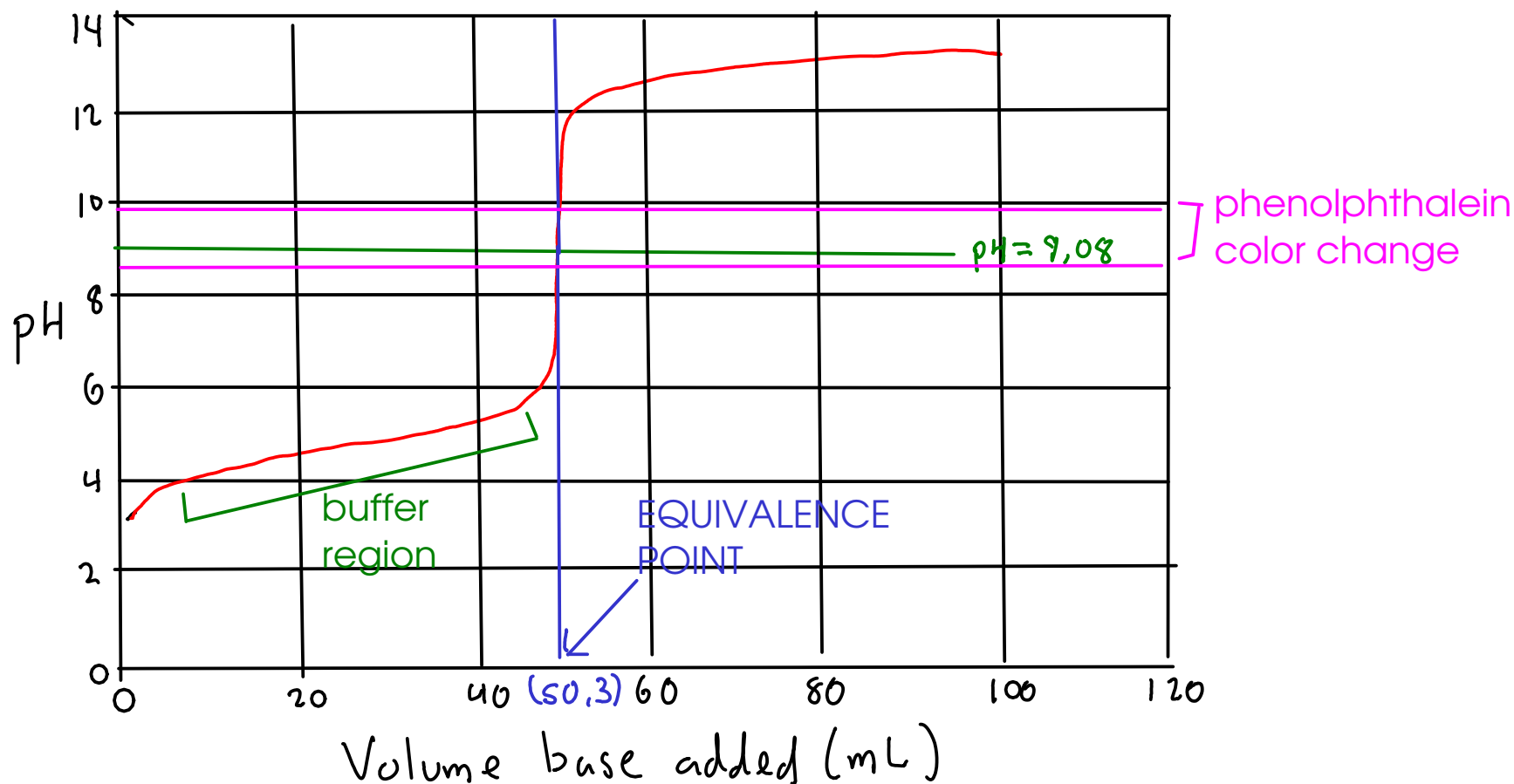
$$x = 1.21 \times 10^{-5}, \quad \text{pOH} = 4.92, \quad \text{pH} = 9.08$$

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

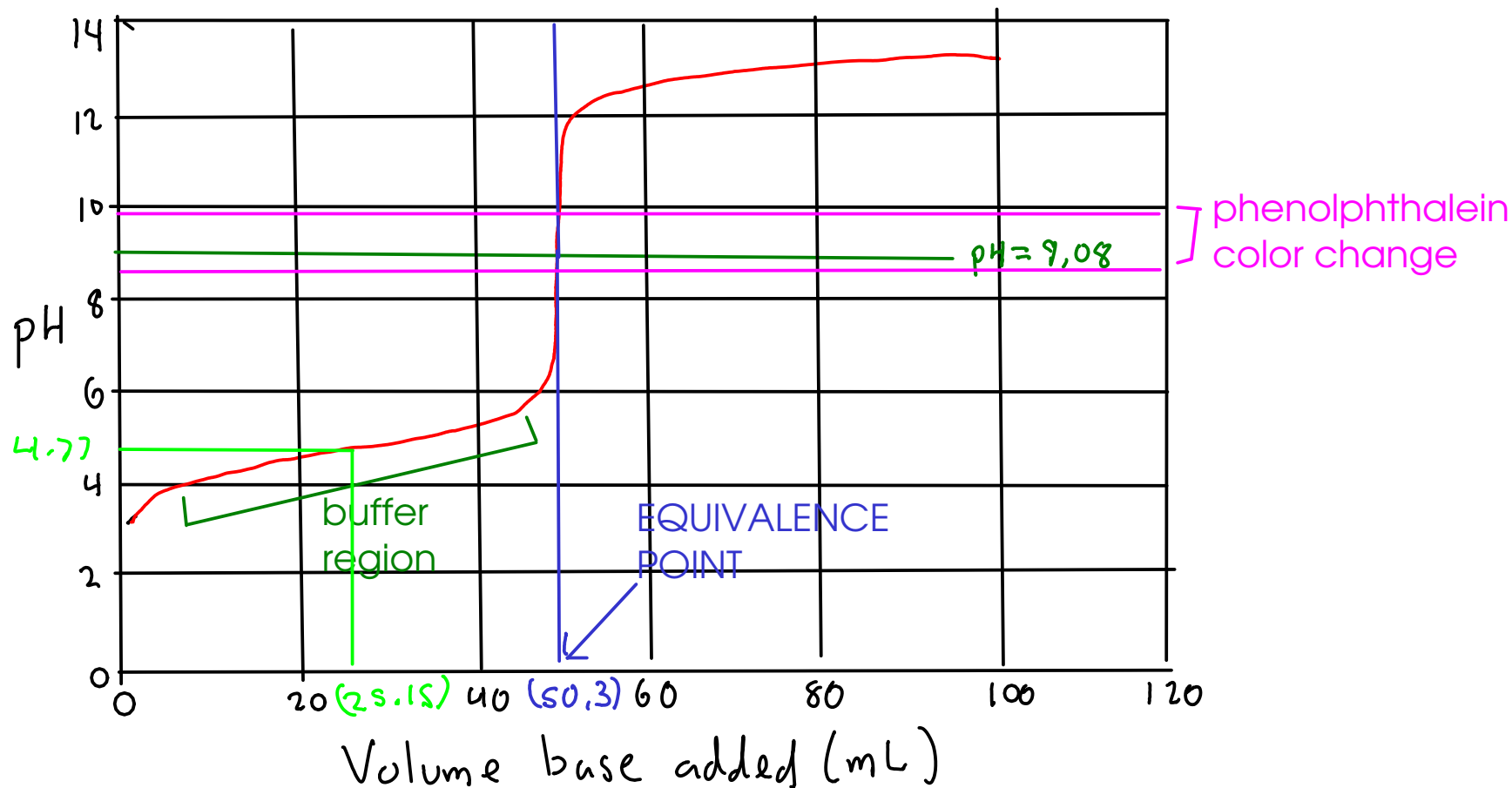


17,6 mmol $\text{HC}_2\text{H}_3\text{O}_2$
initially

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 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.

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

= 0, since the ratio = 1

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

Useful for finding acid ionization constants!

SOLUTION: Homogeneous mixture of substances Solutions contain:

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

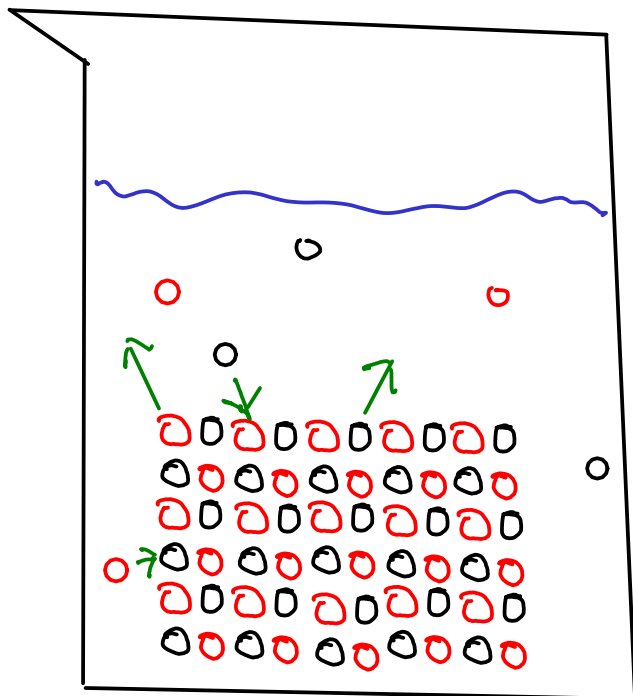
SOLVENT: Component of a solution present in greatest amount

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

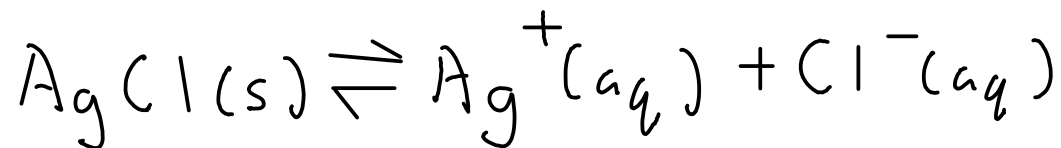
SOLUBILITY: The amount of a solute that will dissolve in a given volume of solvent

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

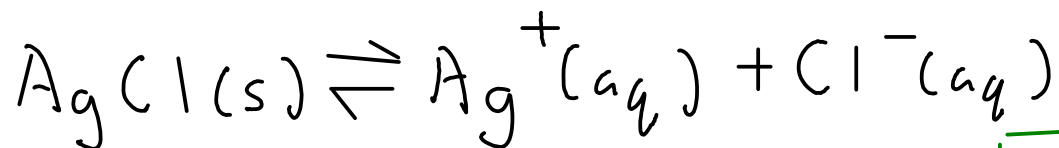
A SATURATED SOLUTION is a solute where dissolved solute exists in an EQUILIBRIUM with undissolved solute!



Example: Consider a saturated solution of silver chloride:

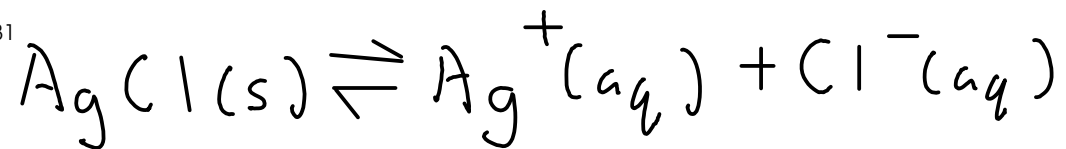


At equilibrium, the rate of dissolving equals the rate of crystallization!



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

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

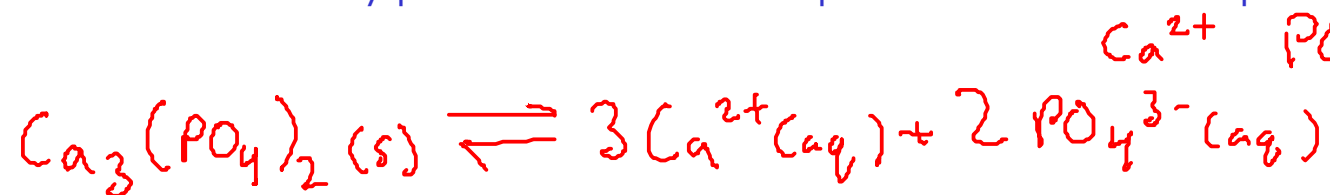


$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

↪ This equilibrium constant is given a special name - the SOLUBILITY PRODUCT CONSTANT - because the equilibrium expression for the dissolving of a salt always appears as a PRODUCT of the concentrations of the ions in the compound!

Remember, K_{sp} is an equilibrium constant, so everything that applies to equilibrium constants applies to the solubility constant - including what to do with coefficients:

What is the solubility product constant expression for calcium phosphate?



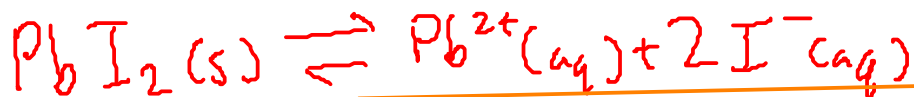
$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

182 Solubility calculations and Ksp

You can calculate the solubility of a compound if you know Ksp!

Calculate the solubility (in g/L) of lead(II) iodide at 25C. (see p A-15 in book)

$$K_{sp} = 6.5 \times 10^{-9} \quad ; \quad FW = 461.0 \text{ g/mol}$$



$$K_{sp} = 6.5 \times 10^{-9} = [\text{Pb}^{2+}][\text{I}^{-}]^2$$

We need to solve this equation, since these concentrations are related to the solubility we are trying to find!

SPECIES	INITIAL CONC	CHANGE	EQUILIBRIUM CONC
Pb^{2+}	0	+x	x
I^{-}	0	+2x	2x

$$6.5 \times 10^{-9} = (x)(2x)^2$$

$$6.5 \times 10^{-9} = 4x^3 \quad \rightarrow \quad x = 0.0011756673 = [\text{Pb}^{2+}]$$

= nominal $[\text{PbI}_2]$

So, the lead concentration equals the concentration of dissolved lead iodide!

$$\frac{0.0011756673 \text{ mol PbI}_2}{\text{L}} \times \frac{461.0 \text{ g PbI}_2}{\text{mol PbI}_2} = \boxed{0.54 \text{ g/L}} = 540 \text{ ppm} \left(\frac{\text{mg}}{\text{L}} \right)$$

ppm (parts per million) is a common unit used for small concentrations. In dilute aqueous solutions, it is equivalent to mg solute / L solution