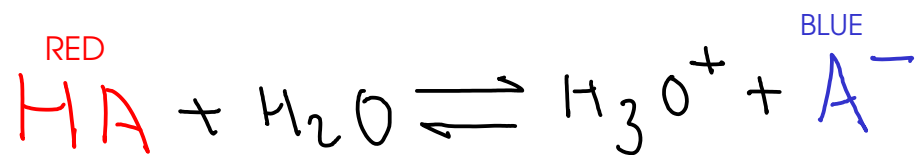
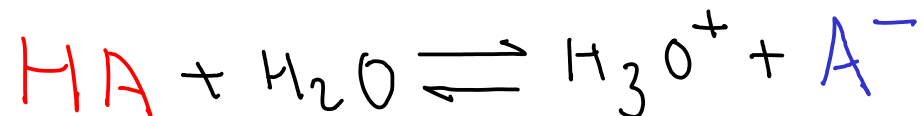


INDICATORS

- 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!



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!

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

When does the color of the indicator change?

If the pH is \ll pKa, then the log term above must be both large AND negative!

- What color is the solution?



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

- What color is the solution?



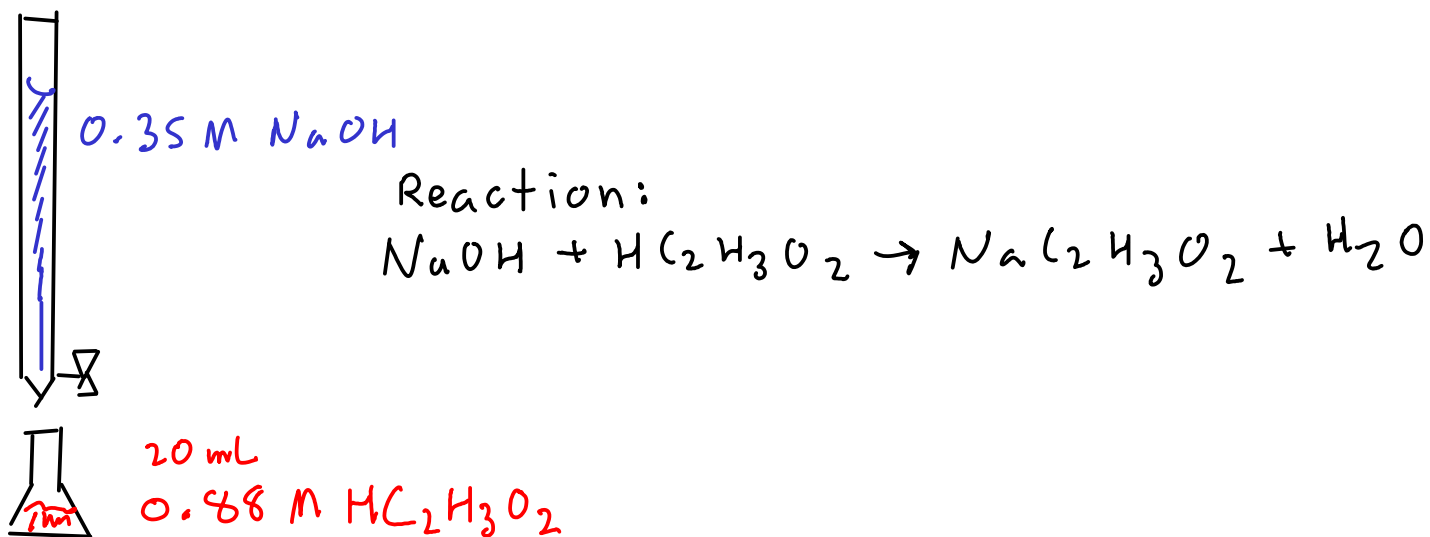
- So, the color changes when the pH of the solution is near the pKa of the indicator, BUT we can only DETECT the change when enough of the other form is present.

178 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

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

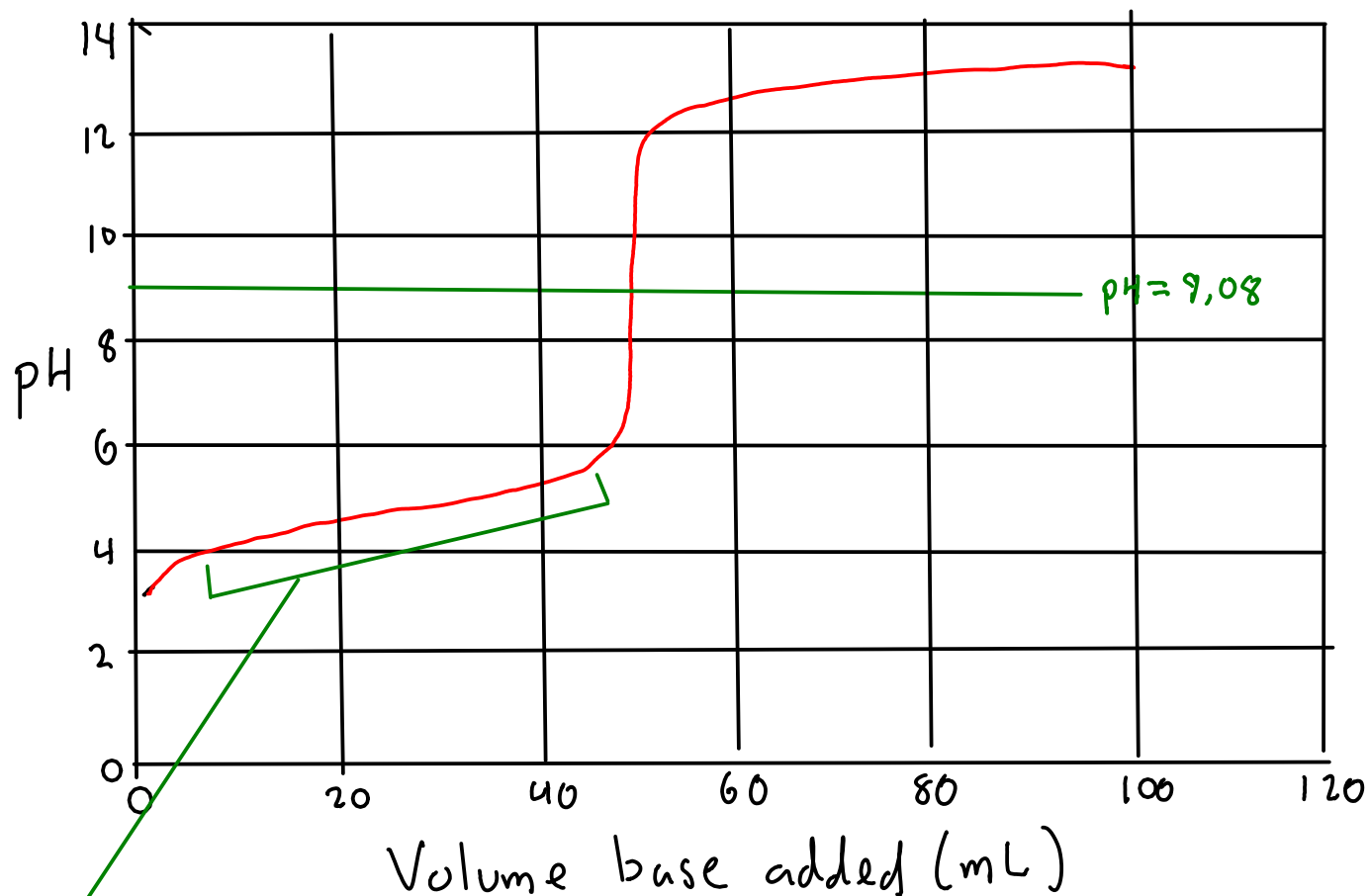
$$17.6 \text{ mmol } \text{HC}_2\text{H}_3\text{O}_2 \times \frac{\text{mol NaOH}}{\text{mmol } \text{HC}_2\text{H}_3\text{O}_2} \times \frac{\text{L}}{0.35 \text{ mol NaOH}} = 50.3 \text{ mL of } 0.350 \text{ M NaOH}$$

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

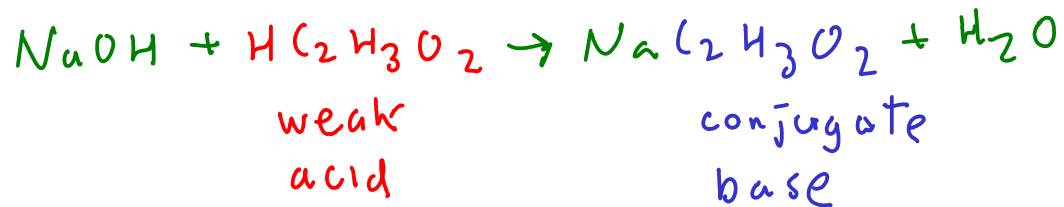
In the lab, we have used phenolphthalein indicator for vinegar titrations. Phenolphthalein changes from colorless to pink over the range of about pH 9 to pH 10. How does this indicator show where the endpoint is?

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

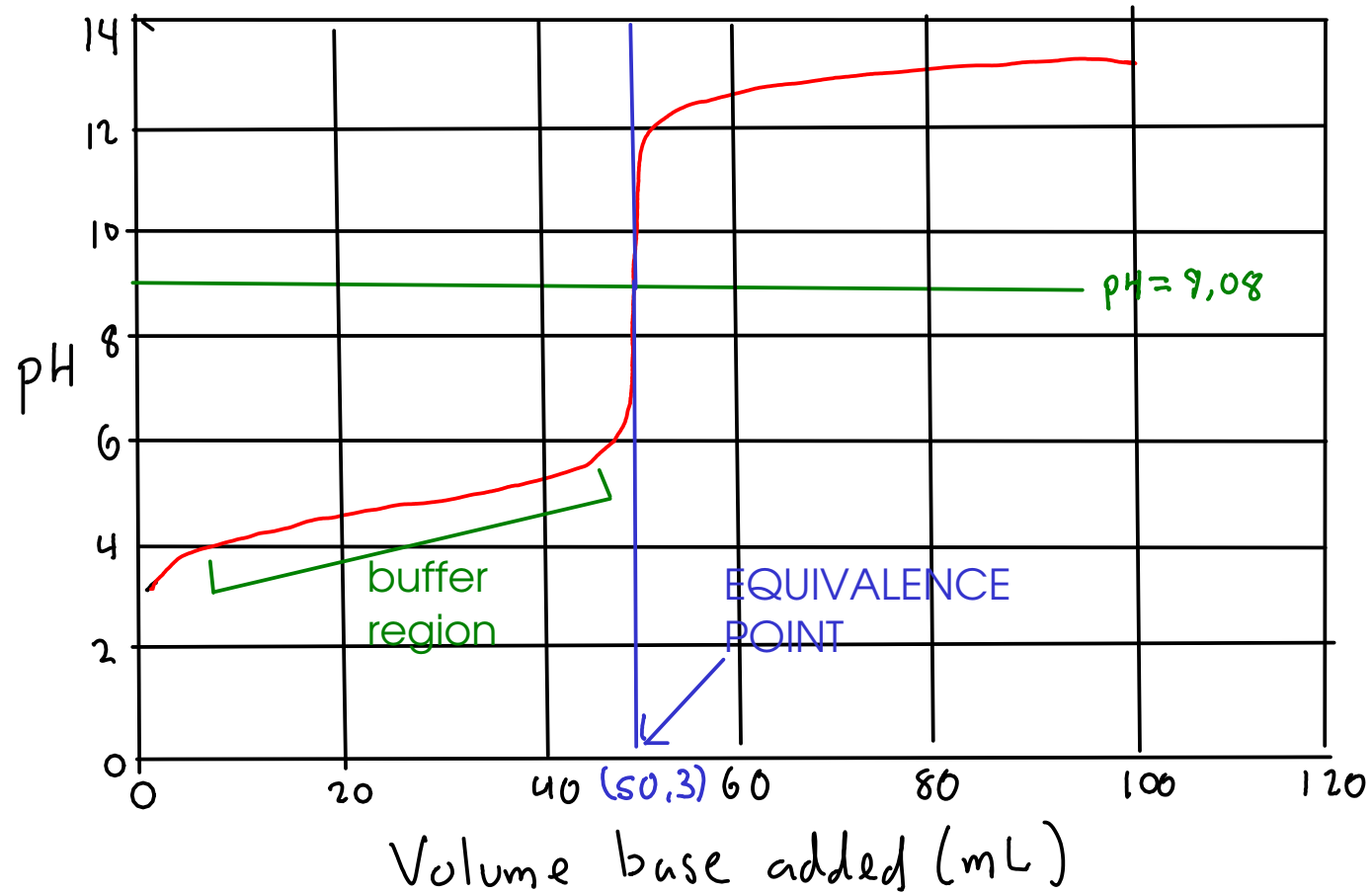
Titration curve for the titration of 20 mL of 0.88 M acetic acid with 0.35 M sodium hydroxide



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.

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.

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



	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

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

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

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

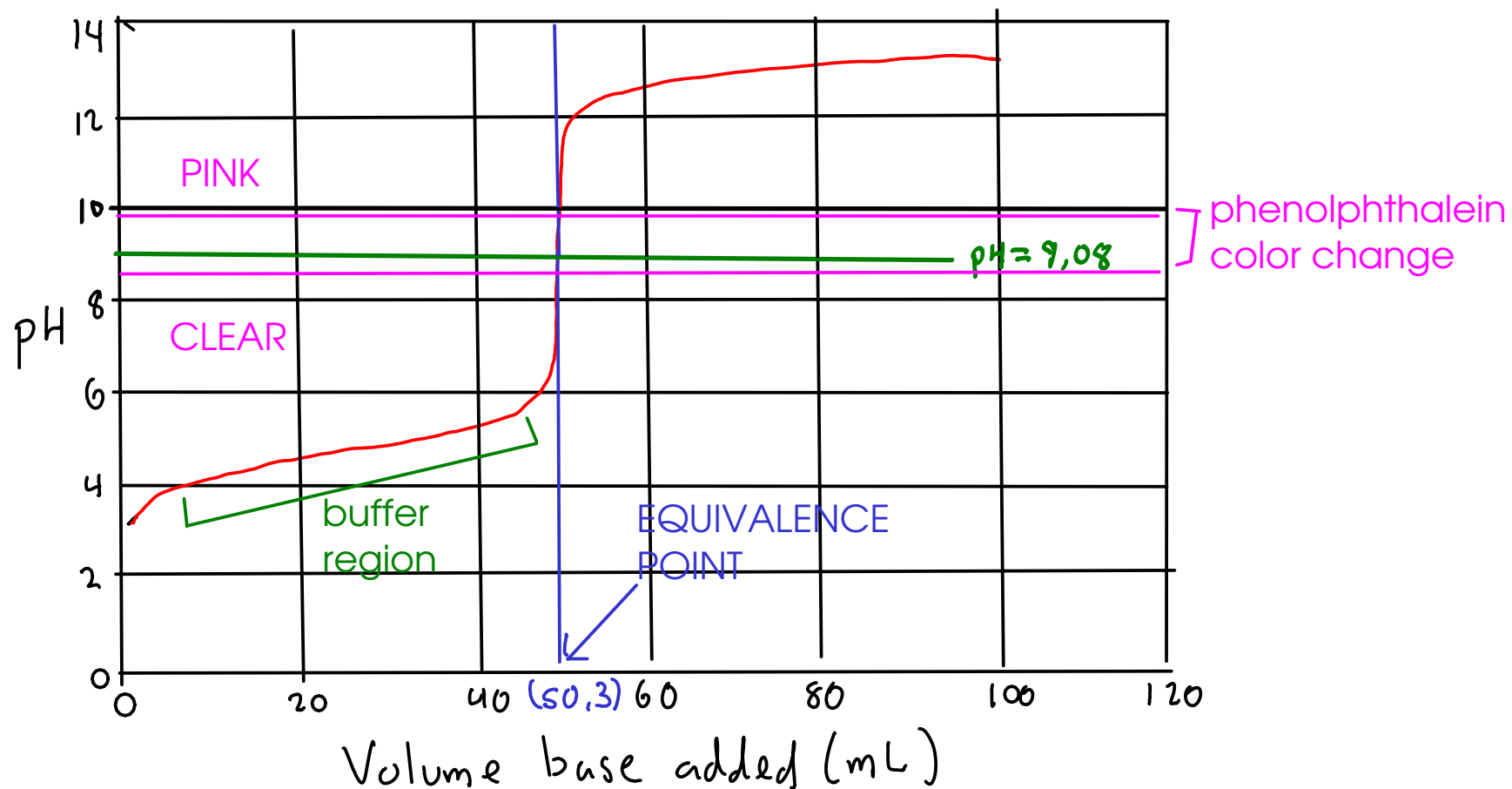
$$\text{pH} = 9.08$$

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

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

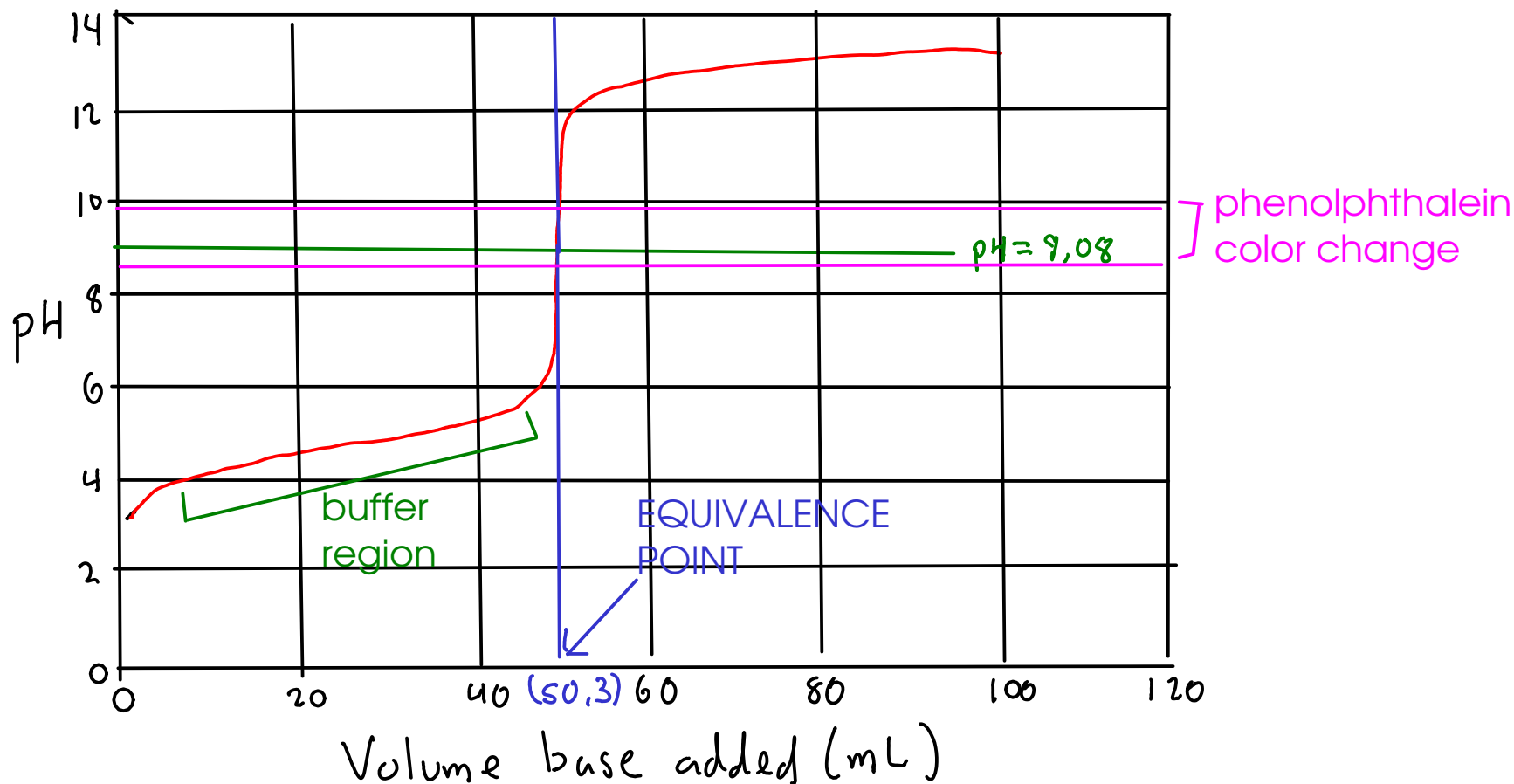
Once you figure out the concentration of acetate ion, this is simply the calculation of the pH of a salt solution!

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 base to reach the equivalence point

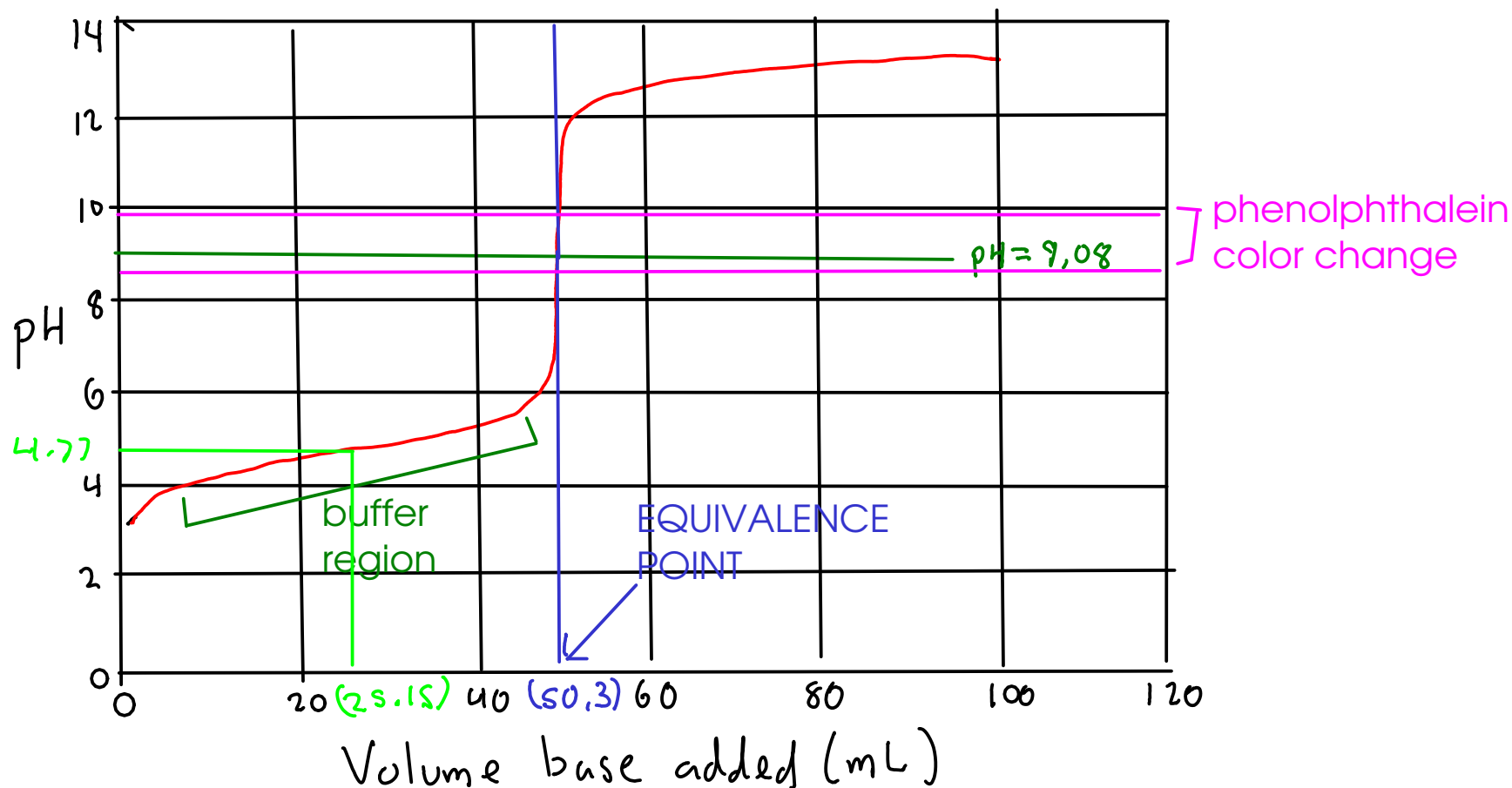


17,6 mmol $\text{HC}_2\text{H}_3\text{O}_2$
initially

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.

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

$\underbrace{\hspace{15em}}_{= 0, \text{ since the ratio} = 1}$

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

Useful for finding acid ionization constants!

SOLUTION: Homogeneous mixture of substances Solutions contain:

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

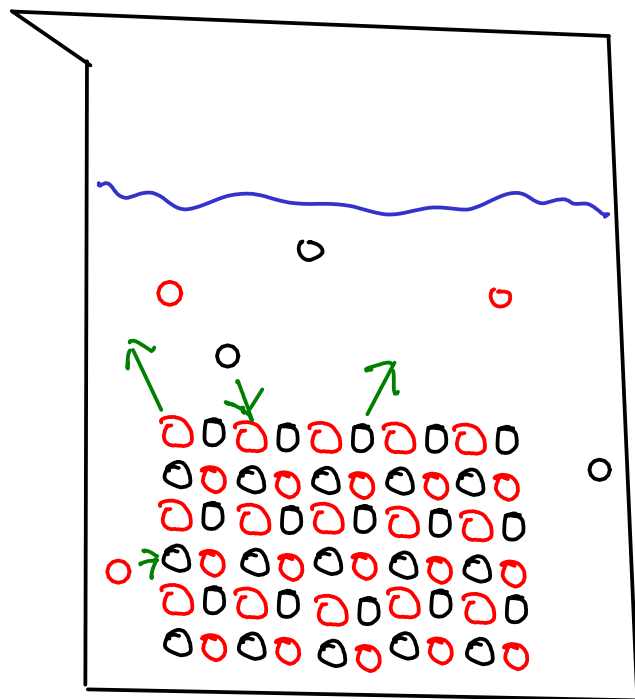
SOLVENT: Component of a solution present in greatest amount

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

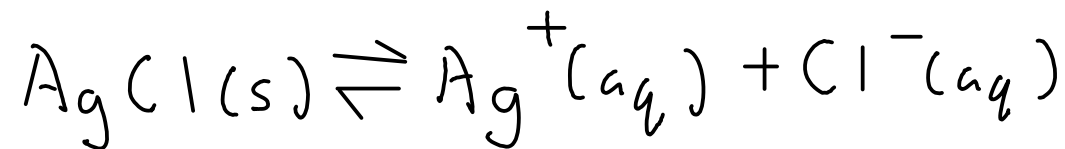
SOLUBILITY: The amount of a solute that will dissolve in a given volume of solvent

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

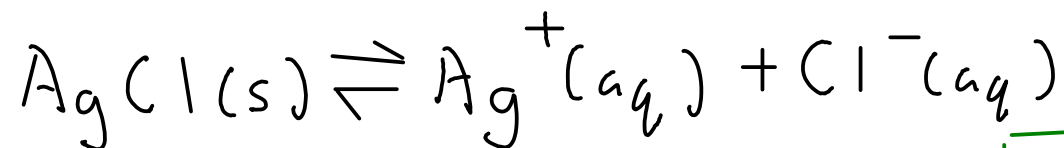
A SATURATED SOLUTION is a solution where dissolved solute exists in an EQUILIBRIUM with undissolved solute!



Example: Consider a saturated solution of silver chloride:

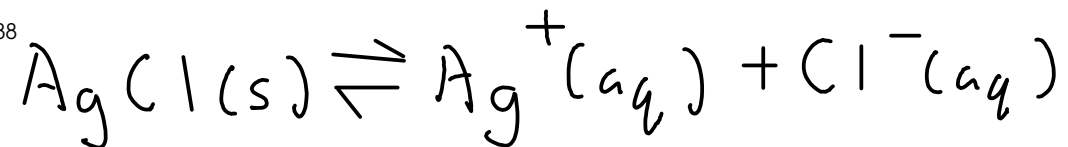


At equilibrium, the rate of dissolving equals the rate of crystallization!



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

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

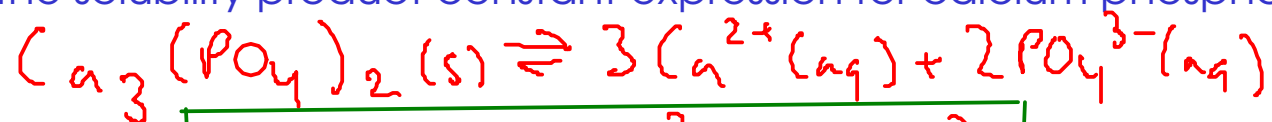


$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

↶ 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?



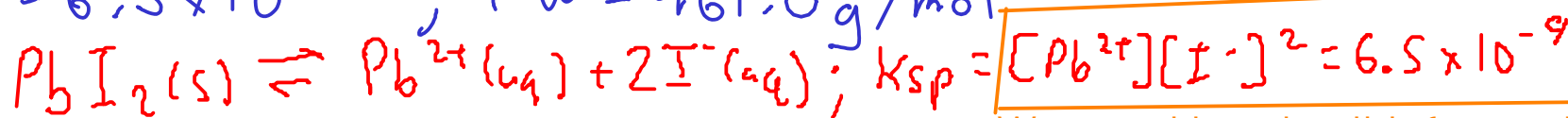
$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

189 Solubility calculations and K_{sp}

You can calculate the solubility of a compound if you know K_{sp}!

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

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



We need to solve this for equilibrium concentration of the ions

Species	[Initial]	Δ	[Equilibrium]
Pb^{2+}	0	+x	x
I^{-}	0	+2x	2x

Define 'x' as the change in concentration of Pb ion.

$(x)(2x)^2 = 6.5 \times 10^{-9}$
 $4x^3 = 6.5 \times 10^{-9}$ | $x = 0.0011756673 = [Pb^{2+}] = [PbI_2]_{\text{dissolved}}$

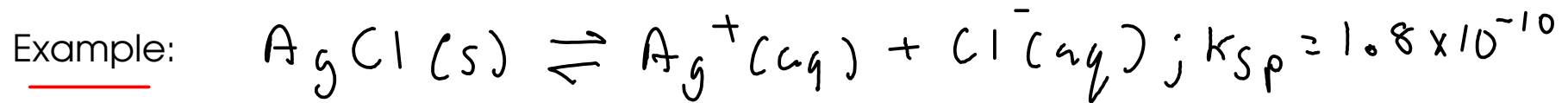
Since the dissolved lead iodide concentration equals the lead ion concentration ...

$\frac{0.0011756673 \text{ mol } PbI_2}{L} \times \frac{461.0 \text{ g } PbI_2}{\text{mol } PbI_2} = 0.54 \text{ g/L} = 540 \text{ ppm } PbI_2$

ppm: Parts Per Million. Common unit for solubility of "insoluble" compounds. It's equivalent to mg/L for aqueous solutions.

Precipitation - also known as the reaction quotient

To predict whether a salt at a given concentration will precipitate out, calculate the reaction quotient Q and compare it to the K_{sp}



$$Q = [Ag^+][Cl^-]$$

IF...

- * $Q < K_{sp}$; the reaction proceeds to produce more products (dissolved ions), so more solid is able to dissolve: NO PRECIPITATION
- * $Q > K_{sp}$; the reaction proceeds to produce more reactants (solid), so solid falls out of solution: PRECIPITATION OCCURS
- * $Q = K_{sp}$; the reaction is at equilibrium. PRECIPITATION IS JUST BEGINNING

Would a solution with $[Ag^+] = 0.014 \text{ M}$ and $[Cl^-] = 0.00042 \text{ M}$ precipitate?

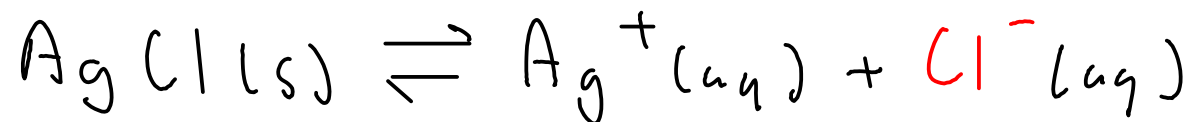
$$Q = [Ag^+][Cl^-] = (0.014)(0.00042) = 5.88 \times 10^{-6}$$

$$Q = 5.88 \times 10^{-6} > 1.8 \times 10^{-10}$$

Since $Q > K_{sp}$, PRECIPITATION OCCURS!

¹⁹¹ Le Chateleur's Principle

The "common ion effect" affects the solubility of a compound in solution. The presence of one of the ions in a salt in the solution will REDUCE THE SOLUBILITY of that salt!

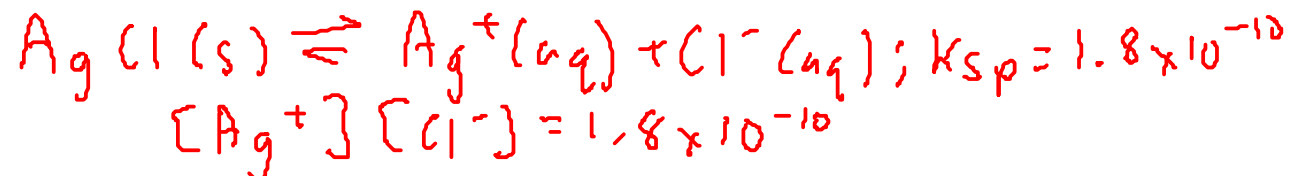


Silver chloride is much less soluble in a solution of 0.1 M NaCl than it is in distilled water. Why? The presence of CHLORIDE ION forces the solubility equilibrium back to the left, meaning less silver chloride can dissolve!

Solubility can also be affected by pH - depending on the acidic or basic properties of the salt!

A second example: Salicylic acid in the characterization lab

Calculate the solubility of AgCl (FW = 143.35 g/mol) in distilled water. Then, calculate the solubility of AgCl in 0.10 M NaCl solution. Report both answers in parts per million (mg/L)



For distilled water ...

Species	[Initial]	Δ	[Equilibrium]
Ag^+	0	+x	x
Cl^-	0	+x	x

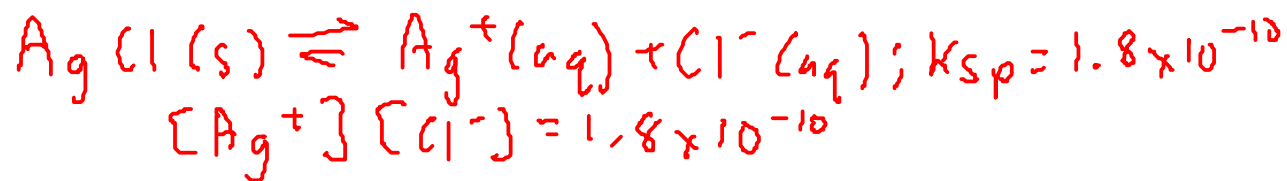
$$(x)(x) = 1.8 \times 10^{-10}$$

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.341640786 \times 10^{-5} \text{ M} = [\text{Ag}^+] = [\text{AgCl}]_{\text{dissolved}}$$

$$\frac{1.341640786 \times 10^{-5} \text{ mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} = 0.0019 \text{ g/L} = 1.9 \text{ ppm}$$

1.9 ppm
AgCl,
distilled
H₂O



For solubility in 0.10 M NaCl solution...

Species	[Initial]	Δ	[Equilibrium]
Ag^+	0	+x	x
Cl^-	0.10	+x	0.10+x

$$(x)(0.10+x) = 1.8 \times 10^{-10}$$

↓ We know that 'x' << 0.10, so $0.10 + x \approx 0.10$

$$0.10x = 1.8 \times 10^{-10}$$

$$x = 1.8 \times 10^{-9} \text{ M} = [\text{Ag}^+] = [\text{AgCl}] \text{ dissolved}$$

$$\frac{1.8 \times 10^{-9} \text{ mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} = 2.6 \times 10^{-7} \text{ g/L} = 2.6 \times 10^{-4} \text{ ppm AgCl}$$

in 0.10 M NaCl

(0.00026 ppm)

Compare:

1.9 ppm AgCl in distilled water

0.00026 ppm in 0.10 M NaCl

Conclusion: The presence of a common ion greatly DECREASES solubility!