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!

$$\overset{\text{RED}}{HA} + H_2O \rightleftharpoons H_3O^+ + \overset{\text{BLUE}}{A^-}$$

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.

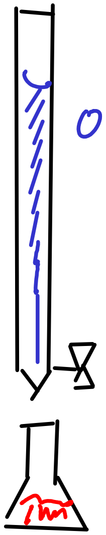
Titration

- 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?



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 0.88 M HC_2H_3O w/ 0.35 M NaOH

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

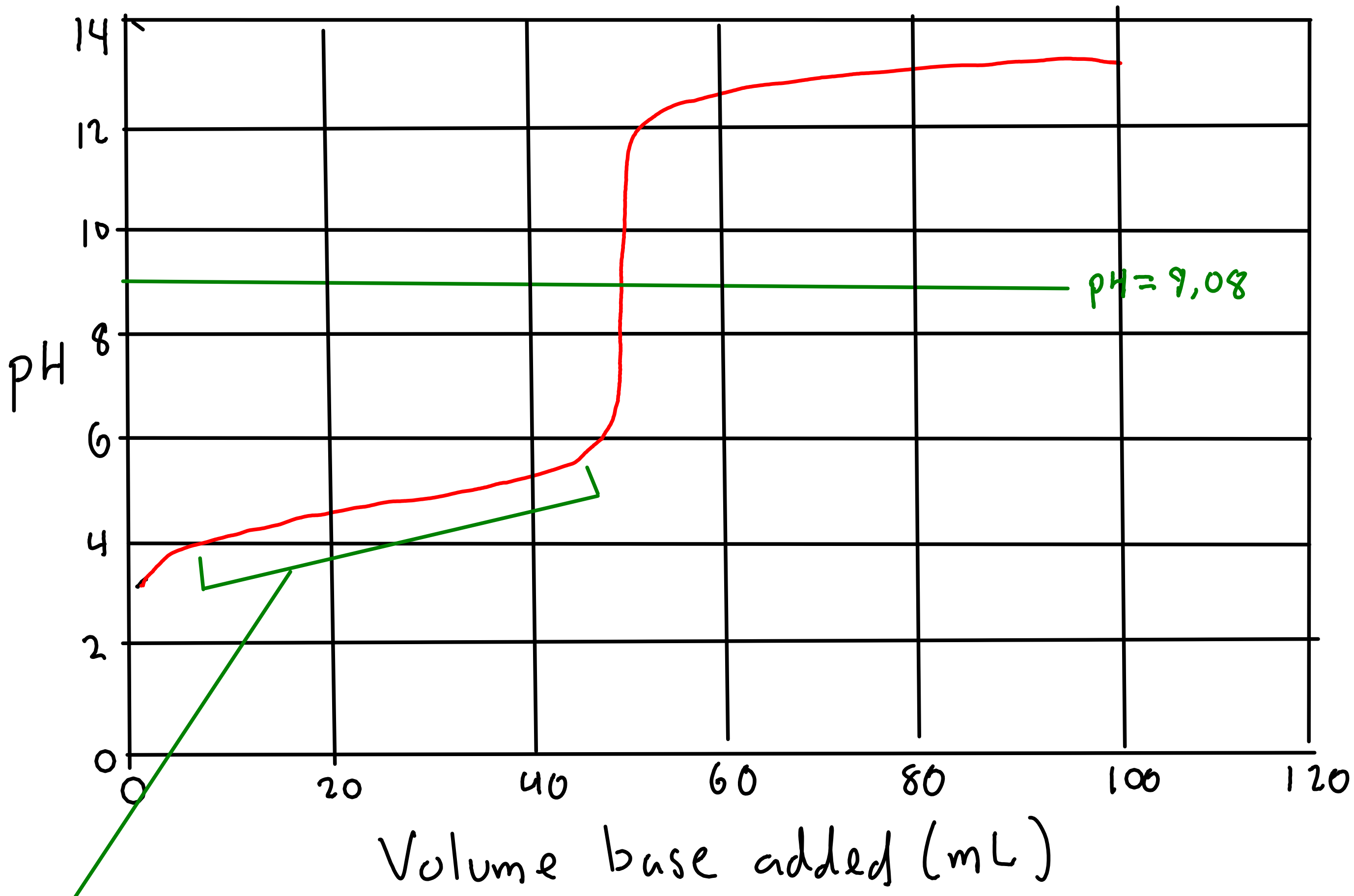
$$17.6\,mmol\ HC_2H_3O_2 \times \frac{mol\ NaOH}{mm\ HC_2H_3O_2} \times \frac{L}{0.35\,mol\ NaOH} = \boxed{\text{50.3 mL of 0.350 M NaOH}}$$

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!

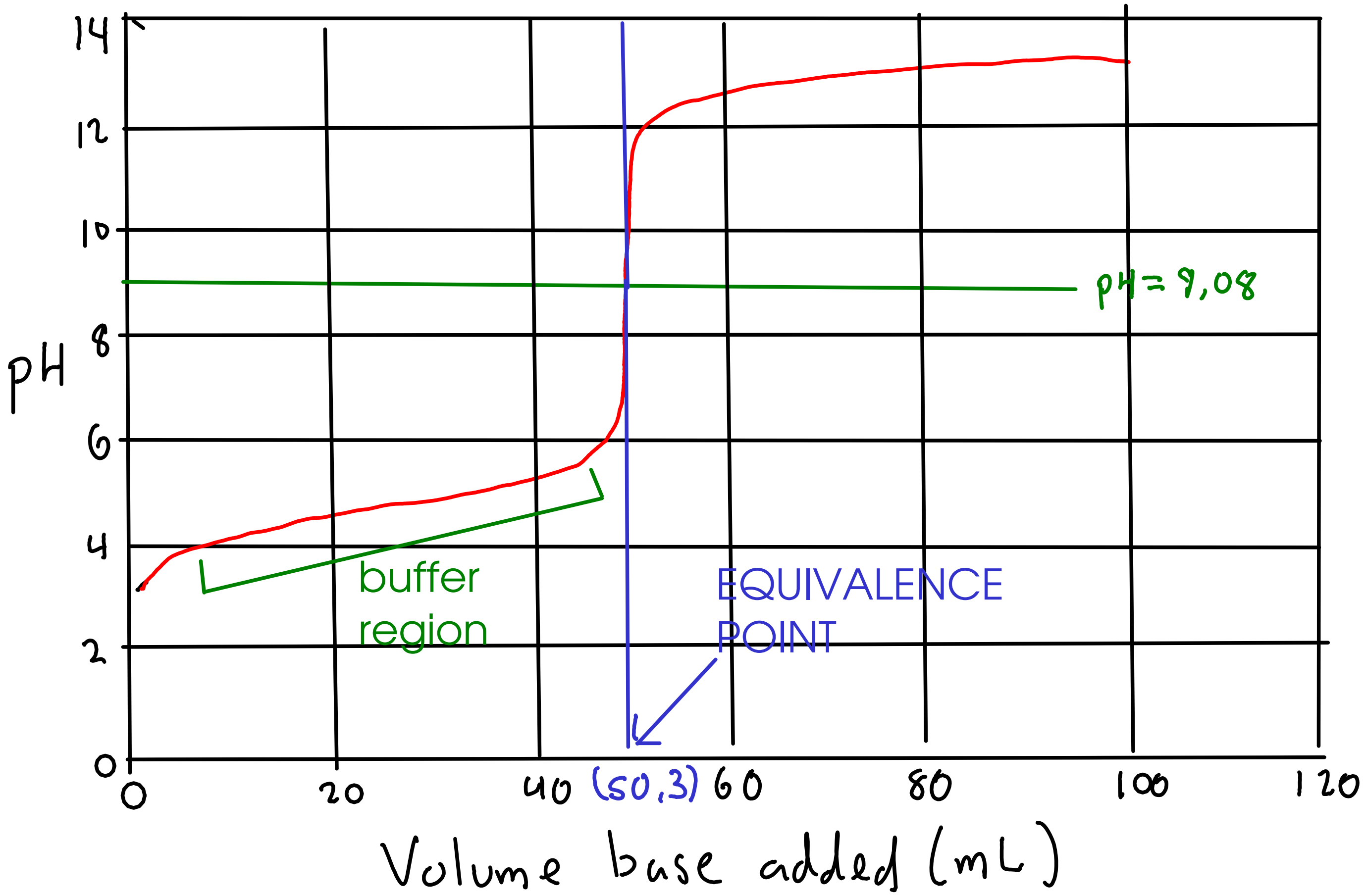
Titration curve for the titration of 20 mL of 0.88 M acetic acid with 0.35 M sodium hydroxide



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.

$$NaOH + \underset{\text{weak acid}}{HC_2H_3O_2} \rightarrow \underset{\text{conjugate base}}{NaC_2H_3O_2} + H_2O$$

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

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

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

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

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

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

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

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

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

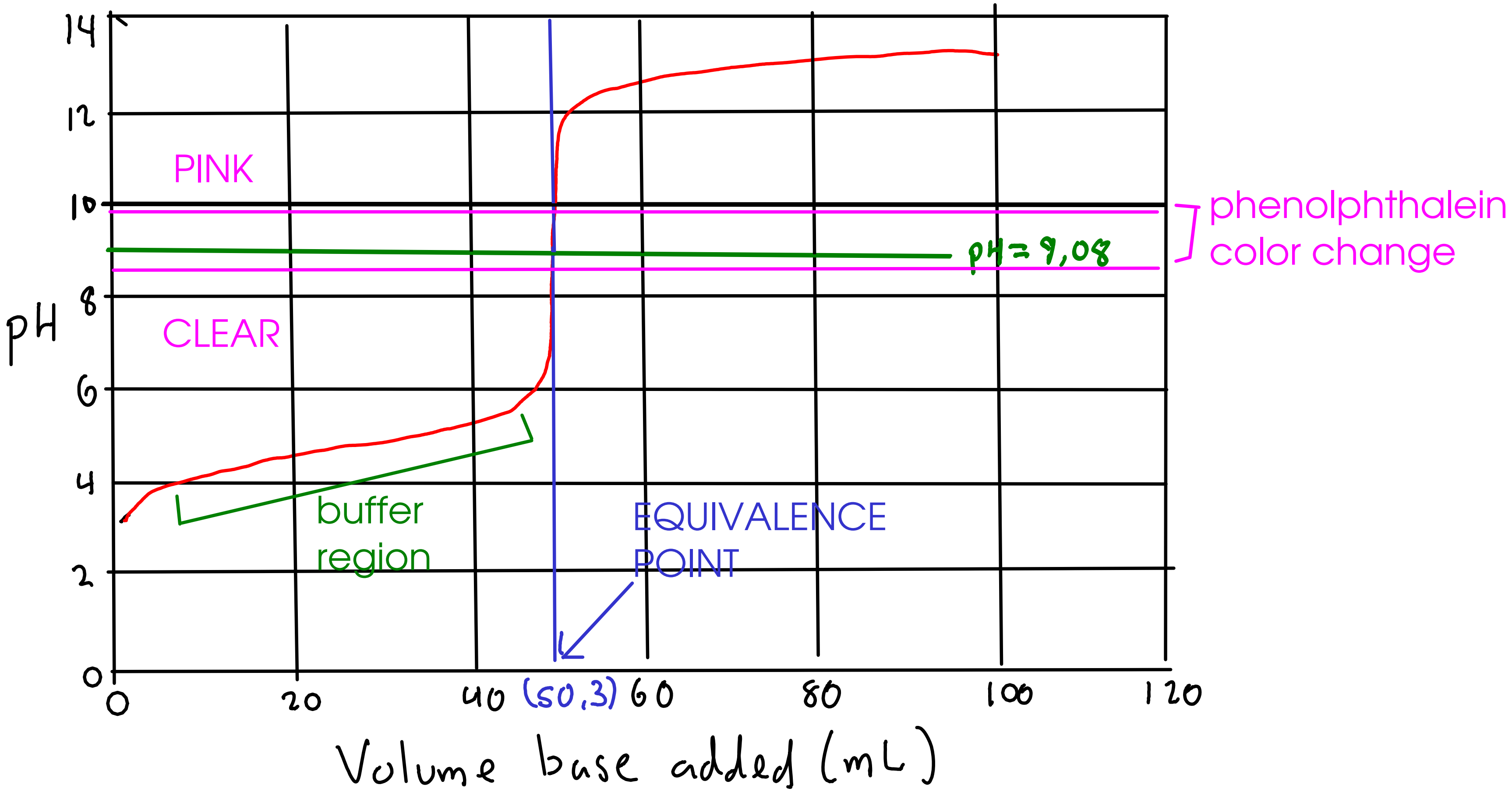
$$\frac{x^2}{0.250} = 5.88 \times 10^{-10}$$

$K_{a,\,HC_2H_3O_2} = 1.7 \times 10^{-5}$

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

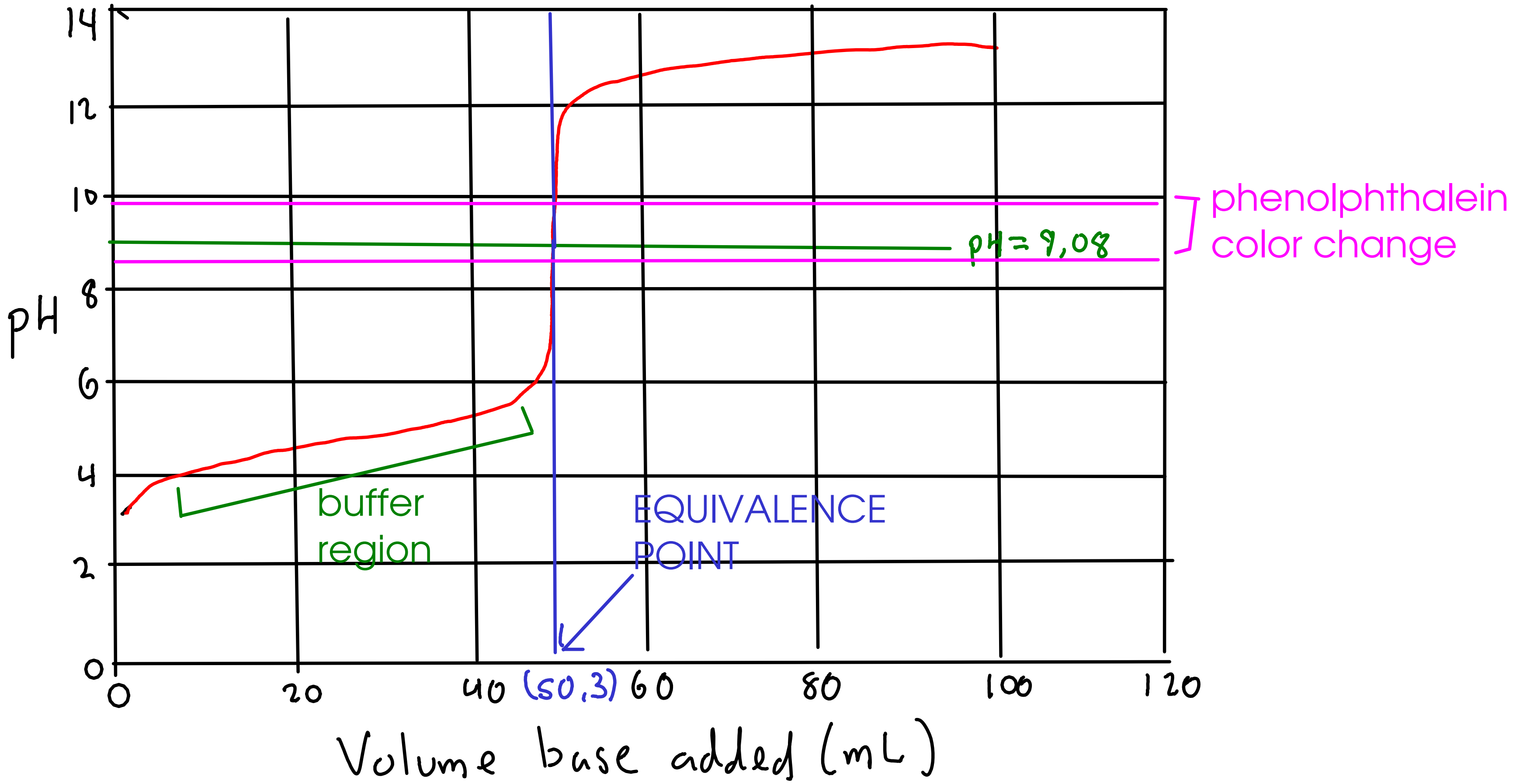
$x = 1.21 \times 10^{-5}$, $pOH = 4.92$, $\boxed{pH = 9.08}$

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

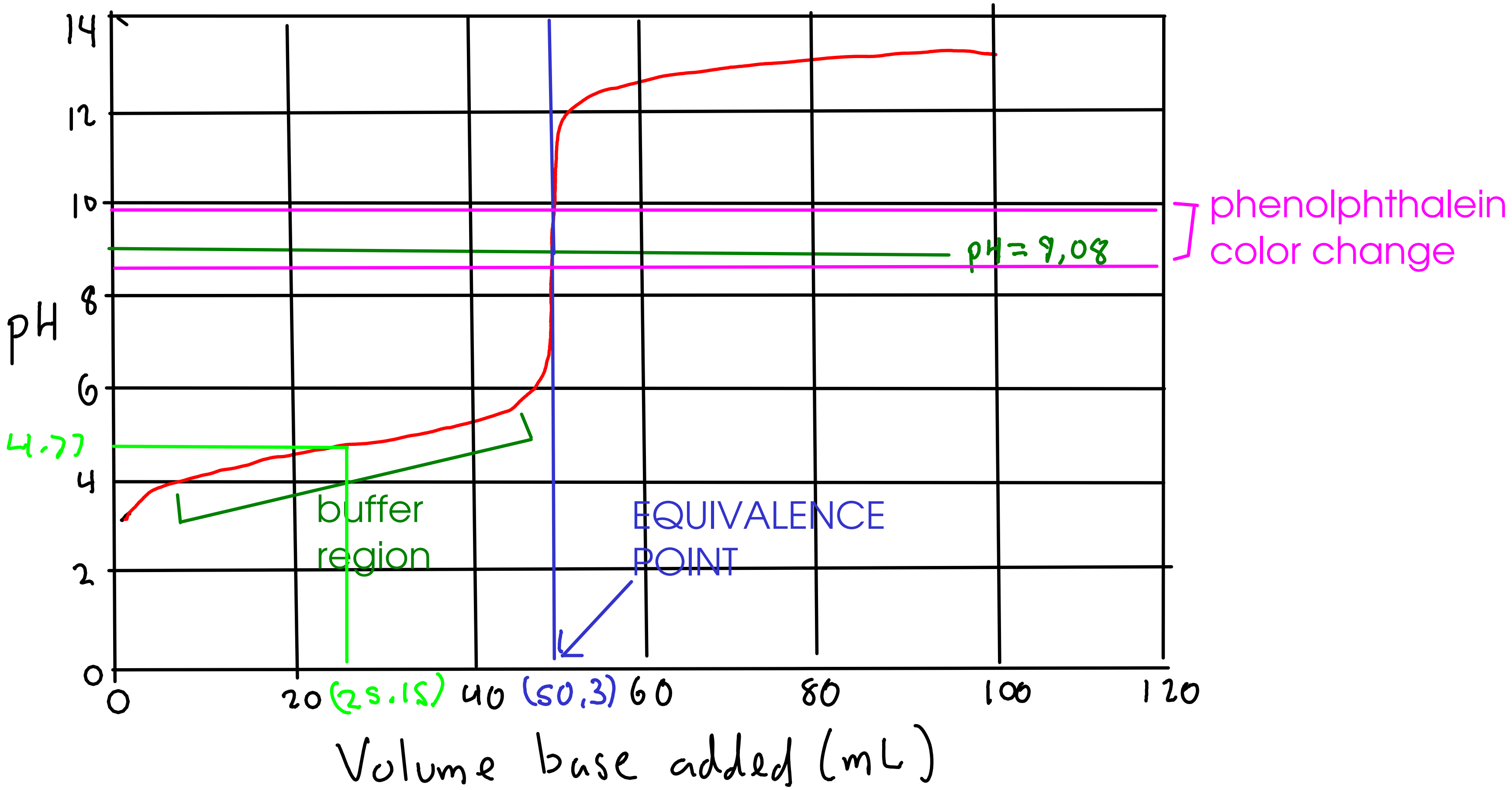
$NaOH + HC_2H_3O_2 \rightarrow NaC_2H_3O_2 + H_2O$

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.

$$pH = pK_{a,HC_2H_3O_2} + \underbrace{\log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)}_{=0,\text{ since the ratio }=1}$$

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

Useful for finding acid ionization constants!

Solubility as an equilibrium process

SOLUTION: Homegeneous mixture of substances Solutions contain:

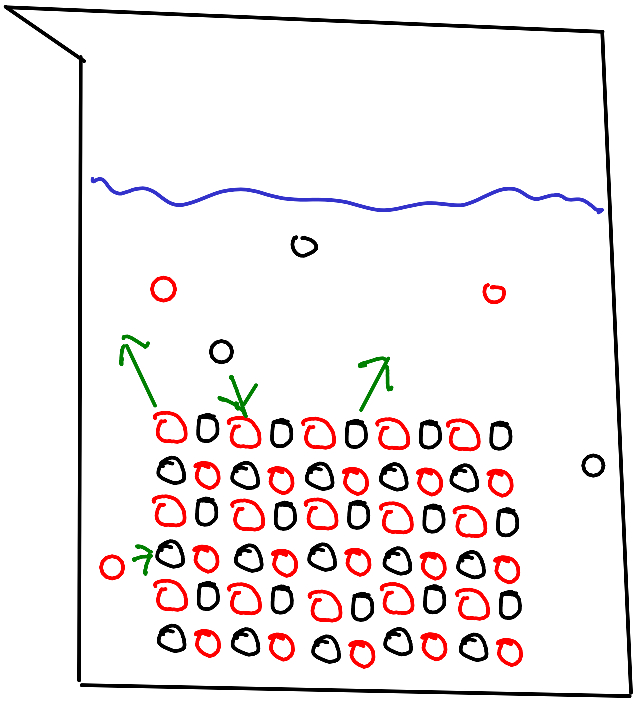
SOLUTE: Component(s) of a solution present in small amount
SOLVENT: Component of a solution present in greatest amount

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!

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

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

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

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

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

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, Ksp 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?

Ca^{2+} PO_4^{3-}

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

$$\boxed{Ksp = [Ca^{2+}]^3[PO_4^{3-}]^2}$$

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)

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

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$; $\boxed{K_{sp} = [Pb^{2+}][I^-]^2 = 6.5 \times 10^{-9}}$

We need to solve this, since it will give us equilibrium concentrations.

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

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

$4x^3 = 6.5 \times 10^{-9}$

$x = 0.0011756673 = [Pb^{2+}]$

Since the dissolved lead and dissolved lead(II) iodide concentrations are equal ...

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

$$\frac{0.0011756673 \text{ mol } Pb}{L} \times \frac{207.2 \text{ g } Pb}{\text{mol } Pb} = 0.24 \text{ g/L} = 240 \text{ ppm } Pb$$

ppm = "parts per million" - equivalent to mg/L for dilute 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 Ksp

Example: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$; $K_{sp} = 1.8 \times 10^{-10}$

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

IF...

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

Would a solution with (Ag+) = 0.014 M and (Cl-) = 0.00042 M precipitate?

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

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

Q > Ksp, so precipitation occurs!

Le Chateleir'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!

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

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

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

$$K_{sp} = 1.8\times10^{-10} = [Ag^+][Cl^-]$$

AgCl:

Ag: 1 x 107.9

Cl: 1 x 35.45

143.35 g/mol

For distilled water...

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

$$x^2 = 1.8\times10^{-10}$$

$$x = 1.341640786\times10^{-5}\ \underline{M} = [Ag^+] = [AgCl]_{dissolved}$$

$$\frac{1.341640786\times10^{-5}\ \text{mol AgCl}}{\text{L}} \times \frac{143.35\ \text{g AgCl}}{\text{mol AgCl}} = 0.0019\ g/L = \boxed{1.9\ \text{ppm AgCl}}$$

in distilled water

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

$$K_{sp} = 1,8\times10^{-10} = [Ag^+][Cl^-]$$

For 0.10 M NaCl solution...

$$NaCl \rightarrow Na^+ + Cl^-$$

Species	[Initial]	Δ	[Equilibrium]
Ag^+	0	$+x$	x
Cl^-	0.10	$+x$	$0,10+x$

$$(x)(0.10+x) = 1.8\times10^{-10}$$

$\downarrow$ $x \ll 0,10$, so $0.10+x \approx 0,10$

$$0.10x = 1.8\times10^{-10}$$

$$x = 1,8\times10^{-9} = [Ag^+] = [AgCl]_{\text{dissolved}}$$

$$\frac{1.8\times10^{-9}\text{ mol AgCl}}{\text{L}} \times \frac{143.35\text{ g AgCl}}{\text{mol AgCl}} = 2.6\times10^{-7}\text{ g/L} = 2.6\times10^{-4}\text{ ppm}$$

(0.00026 ppm)

in 0.10 M NaCl

Compare:
1.9 ppm AgCl in distilled water
0.00026 ppm AgCl in aqueous 0.10 M NaCl solution

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

pH AND SOLUBILITY

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \text{ ; } K_{sp} = 1.8 \times 10^{-11}$$

This salt's solubility is pH dependent. How?

* In a BASIC solution, the concentration of hydroxide ion in solution is high.
, so solubility is LOWER than in pure water.

* In an ACIDIC solution, we have a significant amount of hydronium, which can react with hydroxide. This lowers the hydroxide concentration and makes magnesium hydroxide MORE SOLUBLE

Generalizing

If a compound is BASIC, then it will be LESS SOLUBLE in basic solutions, and MORE SOLUBLE in acidic solutions!

If a compound is ACIDIC, then it will be MORE SOLUBLE in basic solutions, and LESS SOLUBLE in acidic solutions!

If a compound is NEUTRAL (neither acidic nor basic), then its solubility will be UNAFFECTED by pH