

BUFFERS

- resist pH change caused by either the addition of strong acid/base OR by dilution

Made in one of two ways:

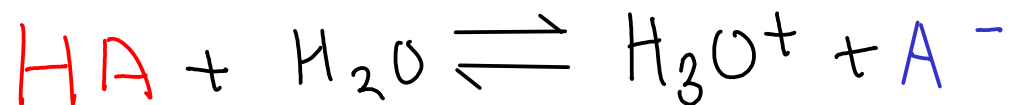
- ① Make a mixture of a weak acid and its conjugate base (as the SALT)
 $\text{HC}_2\text{H}_3\text{O}_2$ $\text{NaC}_2\text{H}_3\text{O}_2$
- ② Make a mixture of a weak base and its conjugate acid (as the SALT)
 NH_3 NH_4Cl

For a weak acid, you would:



- Add HA (weak acid)
- Add a salt containing A^- (example: NaA)

- This solution actually contains an acid and a base at equilibrium, with a significant concentration of BOTH.
- The acid in the buffer can neutralize bases, while the base can neutralize acids.



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

① Take log of both sides

② Multiply by -1

③ Rearrange, solving for pH

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

$[A^-]$... from the salt

$[HA]$... from the weak acid

- We ASSUME that the initial concentrations of both the acid and its conjugate are equal to the equilibrium concentrations. Valid IF there are significant amounts of both species initially.

$$\text{pH} = \text{p}K_{a, \text{acidic}} + \log \left(\frac{[\text{basic species}]}{[\text{acidic species}]} \right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

ex: acidic buffer



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

ex: basic buffer

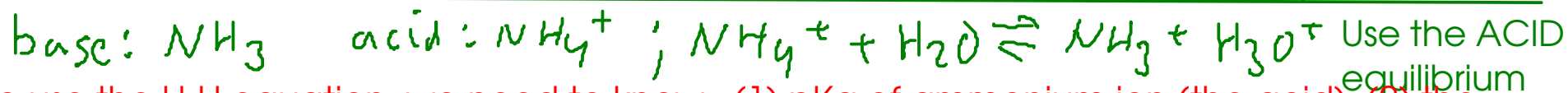


$$\text{pH} = \text{p}K_{a, \text{NH}_4^+} + \log \left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right)$$

$$\text{p}K_a + \text{p}K_b = 14,00 \quad \dots \text{ is the } -\log \text{ of } K_a \times K_b = K_w$$

Calculate the pH of a buffer made from 30.2 grams of ammonium chloride (FW = 53.492 g/mol) and 29 mL of 18.1 M ammonia diluted to 150. mL with water.

$$\text{pH} = \text{p}K_{a,\text{acidic}} + \log \left(\frac{[\text{basic species}]}{[\text{acidic species}]} \right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$



To use the H-H equation, we need to know: (1) pKa of ammonium ion (the acid), (2) the nominal concentration of ammonia (the base), and (3) the nominal concentration of the ammonium ion (the acid)

① Page A-13 doesn't list ammonium, but page A-14 lists Kb for ammonia ...

$$K_{b,\text{NH}_3} = 1.8 \times 10^{-5}, \quad \text{p}K_b = 4.74, \quad \text{so } \text{p}K_a = 14.00 - \text{p}K_b = 9.26$$

$$\text{p}K_a = 9.26$$

$$\textcircled{2} \quad [\text{NH}_3] = ? \quad M_1 V_1 = M_2 V_2; \quad (18.1 \text{ M})(29 \text{ mL}) = M_2 (150 \text{ mL})$$

$$M_2 = [\text{NH}_3] = 3.499333333 \text{ M}$$

$$\textcircled{3} \quad 30.2 \text{ g NH}_4\text{Cl} \times \frac{\text{mol NH}_4\text{Cl}}{53.492 \text{ g NH}_4\text{Cl}} = 0.5645704031 \text{ mol NH}_4\text{Cl}$$

$$M = \frac{0.5645704031 \text{ mol NH}_4\text{Cl}}{0.150 \text{ L}} = 3.763802687 \text{ M NH}_4\text{Cl}$$

$$\text{pH} = 9.26 + \log \left(\frac{3.499333333 \text{ M}}{3.763802687 \text{ M}} \right) = \boxed{9.23}$$

BUFFER SELECTION

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

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

- 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 / conjugate acid)

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



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!

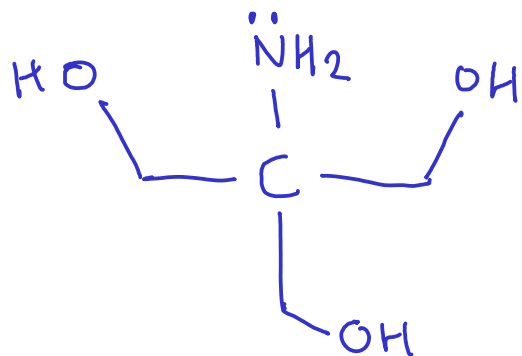
$$\text{pH} = \text{p}K_{a,\text{acidic}} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

Henderson-Hasselbalch Equation

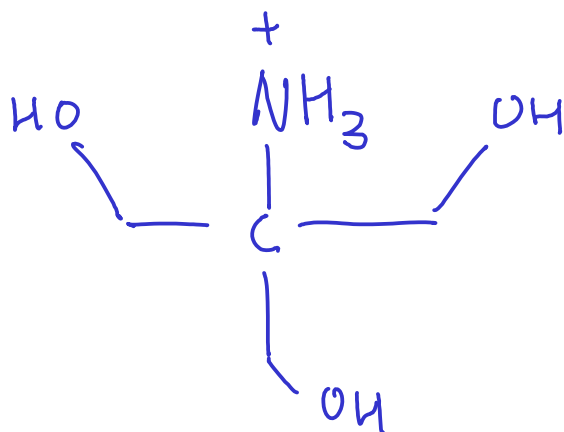
Ratio determines pH; the actual concentrations don't!

- 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⁻

$$pK_a = 8,06$$

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.

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

$$[tris]: m_1 V_1 = m_2 V_2 \quad (0,10M)(50\text{ mL}) = M_2 (100\text{ mL})$$

$$M_2 = [tris] = 0,050\text{ M}$$

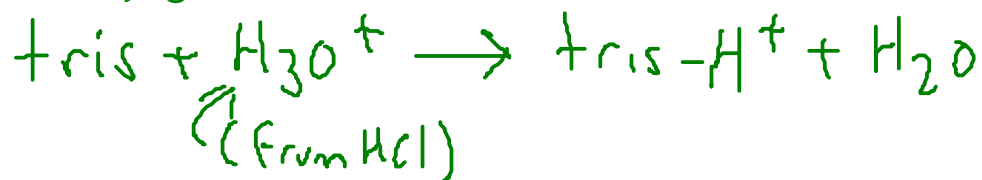
$$[tris-H^+]: (0,15\text{ M})(50\text{ mL}) = M_2 (100\text{ mL})$$

$$M_2 = [tris-H^+] = 0,075\text{ M}$$

$$pH = 8,06 + \log \left(\frac{0,050}{0,075} \right) = 7,88$$

182 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 \times 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 \times 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 \times 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)

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

The original pH was 7.88, so the pH dropped 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.

$$M_1 V_1 = M_2 V_2$$

$$(0.10 \text{ M})(5.0 \text{ mL}) = M_2 (105 \text{ mL})$$

$$0.0047619 \text{ M HCl} = M_2$$

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

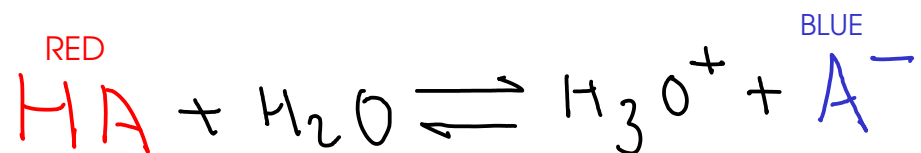
$$[\text{H}_3\text{O}^+] = 0.0047619 \text{ M}$$

$$\text{pH} = 2.32$$

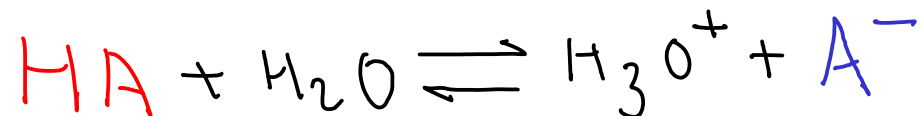
... which is a change of 4.68 pH units from water's original pH of 7.00!

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!



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?



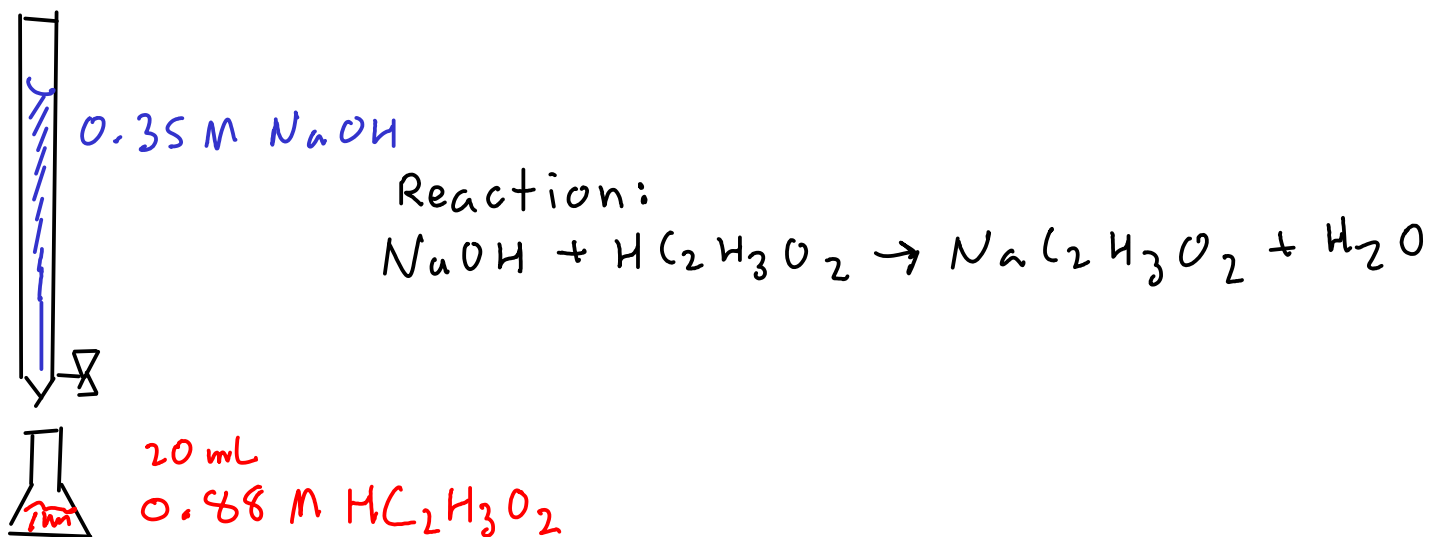
- So, the color changes when the pH of the solution is near the pKa of the indicator, BUT we can only DETECT the change when enough of the other form is present.

186 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

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

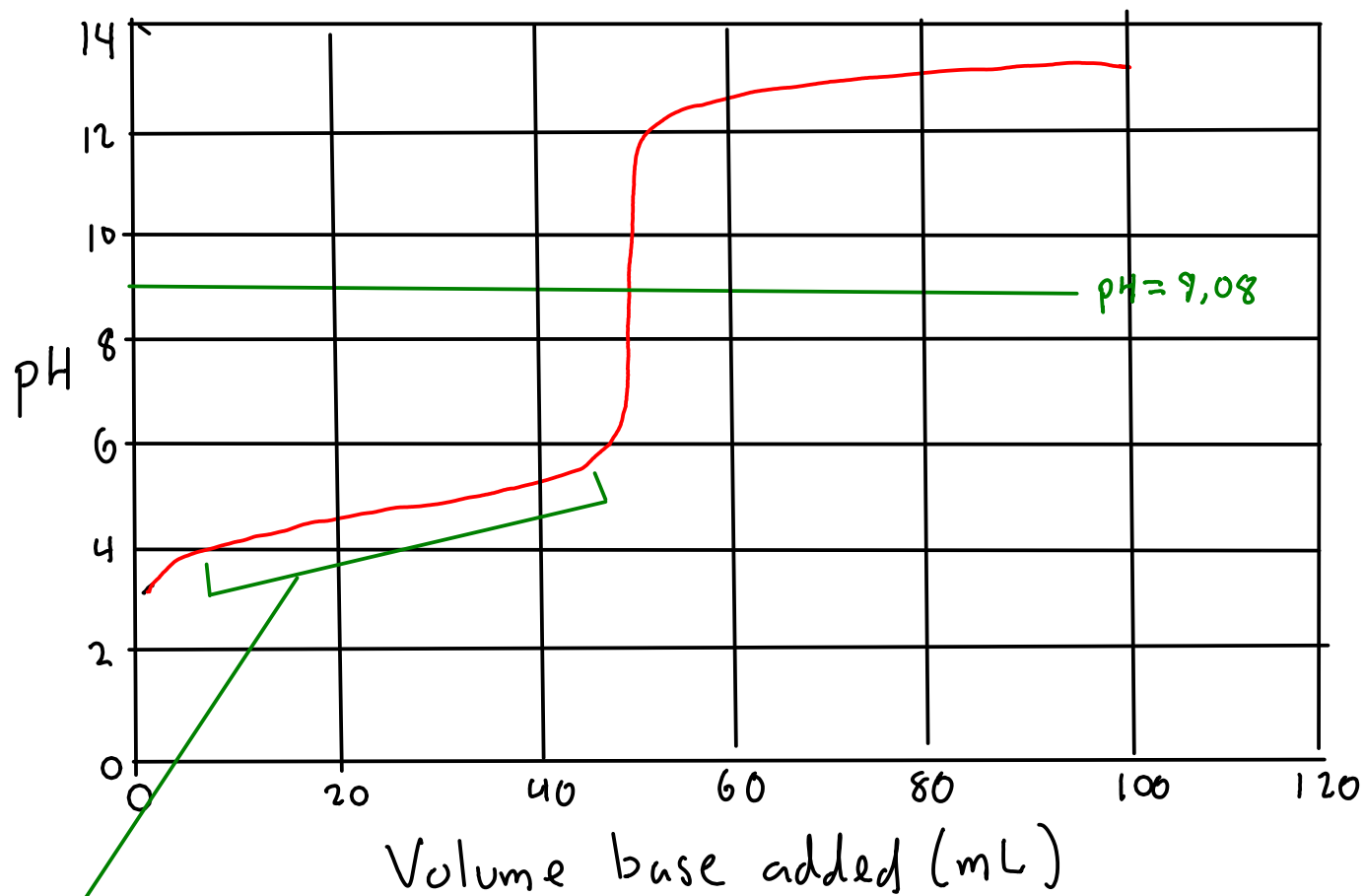
$$17.6 \text{ mmol } \text{HC}_2\text{H}_3\text{O}_2 \times \frac{\text{mol NaOH}}{\text{mmol } \text{HC}_2\text{H}_3\text{O}_2} \times \frac{\text{L}}{0.35 \text{ mol NaOH}} = 50.3 \text{ mL of } 0.350 \text{ M NaOH}$$

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

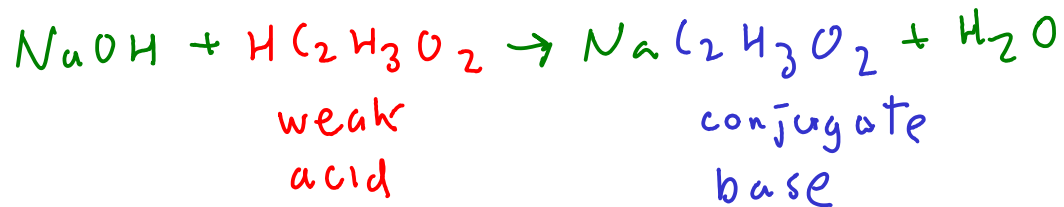
In the lab, we have used phenolphthalein indicator for vinegar titrations. Phenolphthalein changes from colorless to pink over the range of about pH 9 to pH 10. How does this indicator show where the endpoint is?

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

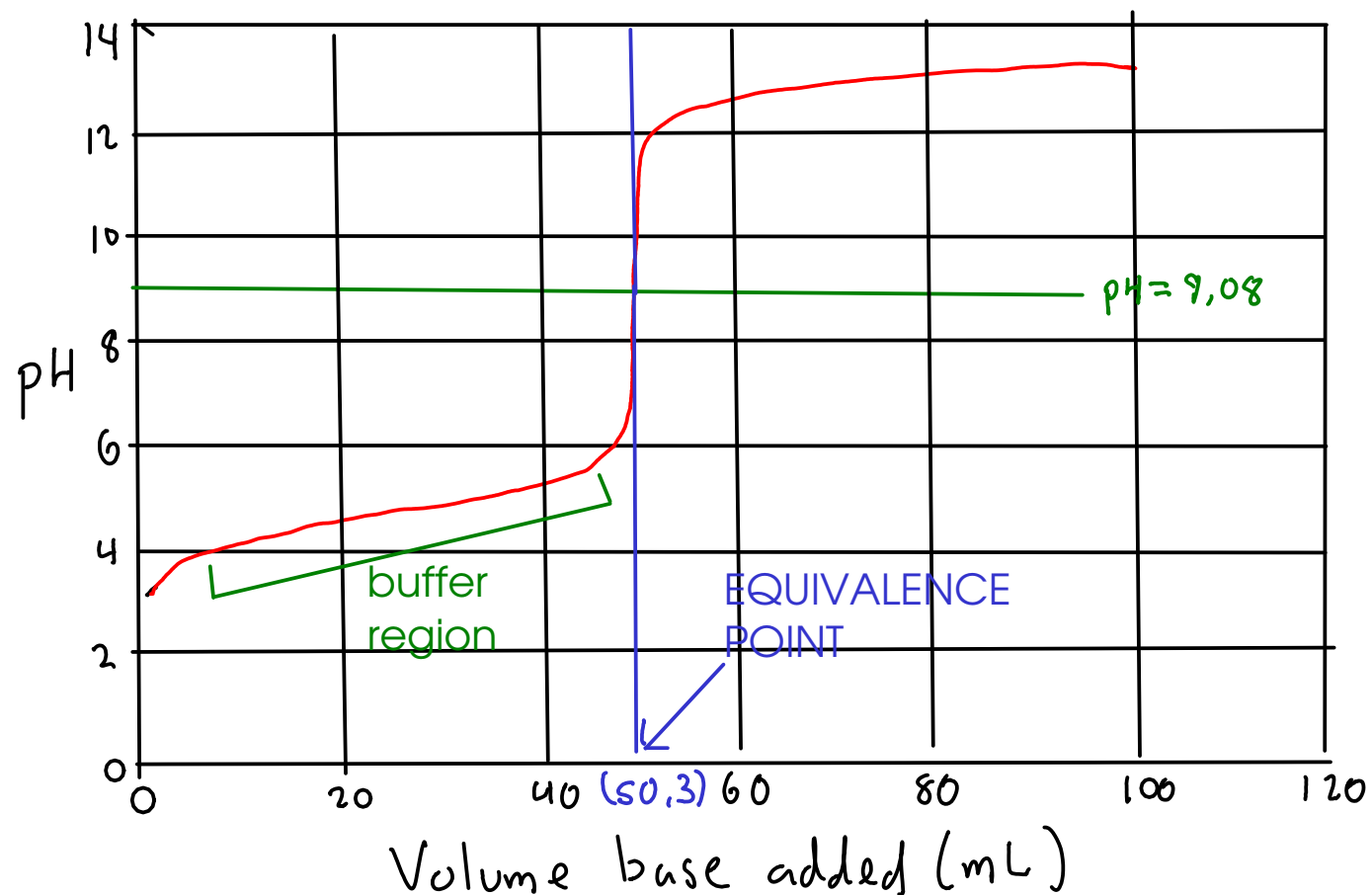
Titration curve for the titration of 20 mL of 0.88 M acetic acid with 0.35 M sodium hydroxide



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

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

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

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

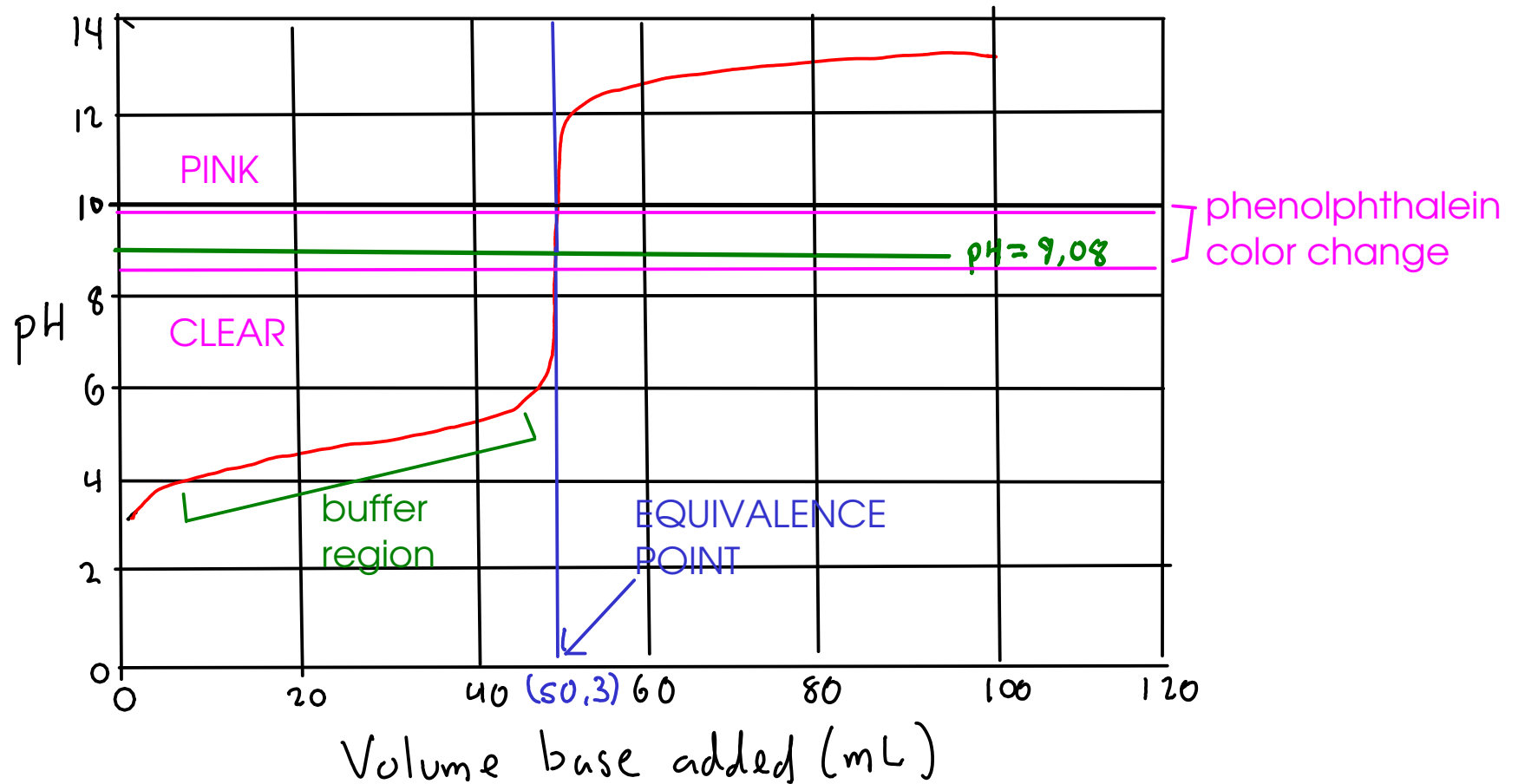
$$\text{pH} = 9.08$$

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

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

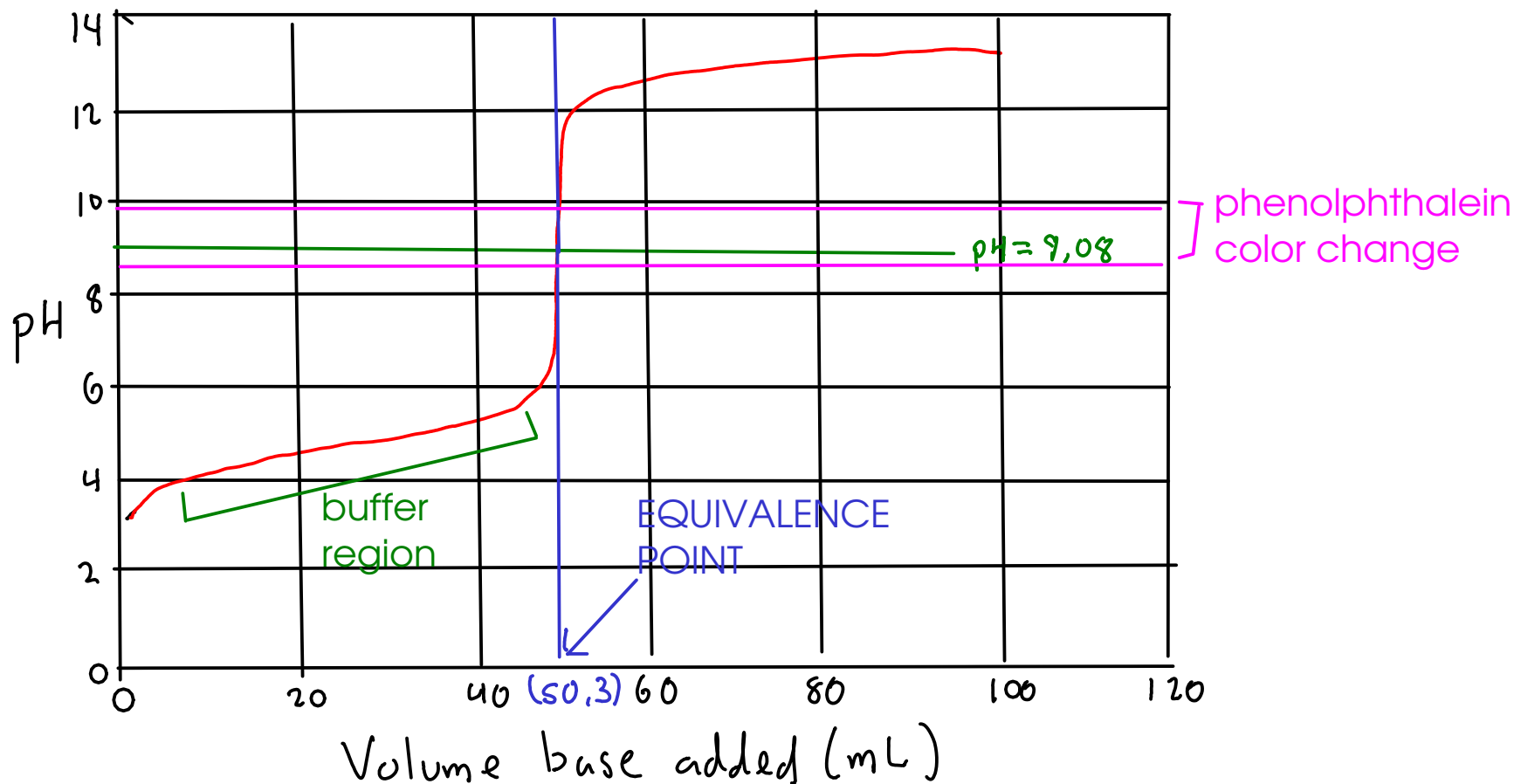
Once you figure out the concentration of acetate ion, this is simply the calculation of the pH of a salt solution!

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 acid to reach the equivalence point

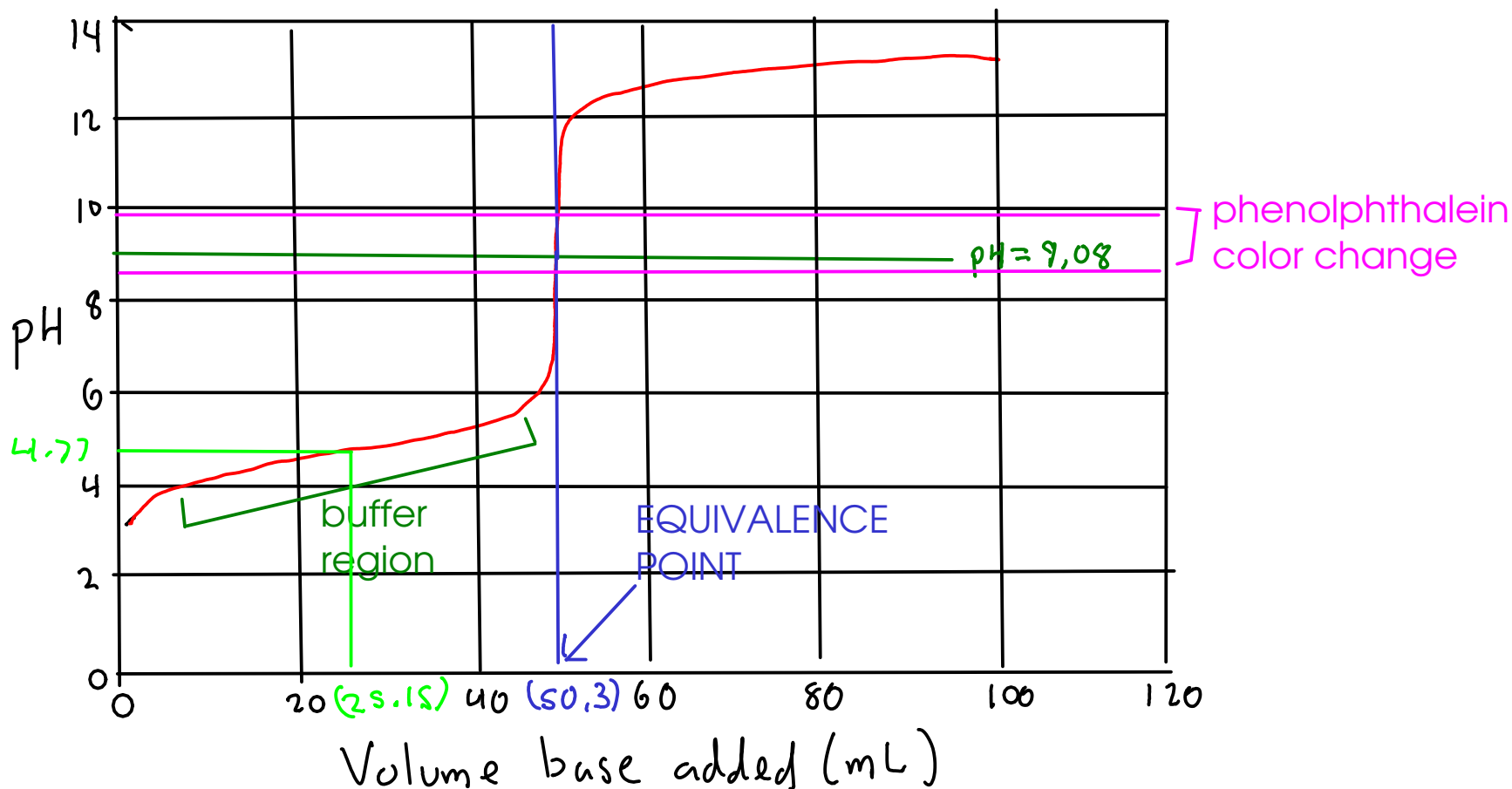


17,6 mmol $\text{HC}_2\text{H}_3\text{O}_2$
initially

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 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.

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

= 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

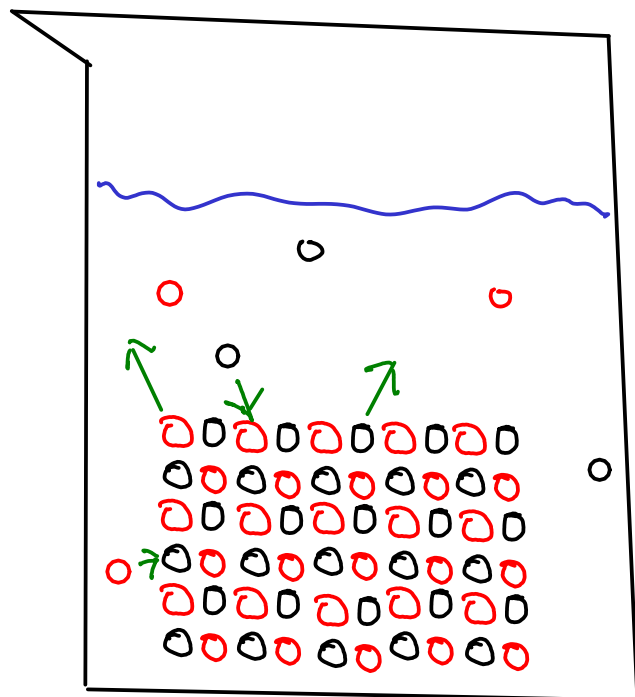
SOLVENT: Component of a solution present in greatest amount

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

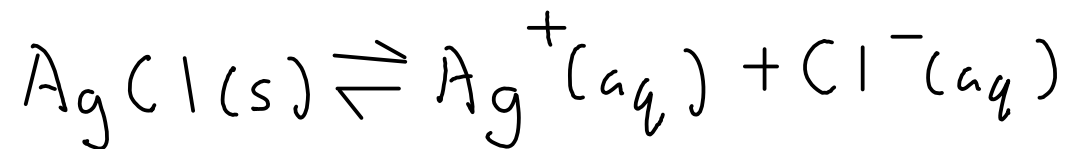
SOLUBILITY: The amount of a solute that will dissolve in a given volume of solvent

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

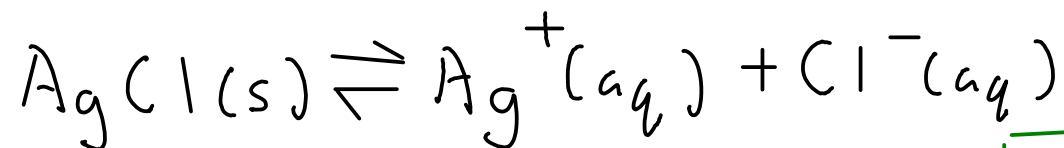
A SATURATED SOLUTION is a solution where dissolved solute exists in an EQUILIBRIUM with undissolved solute!



Example: Consider a saturated solution of silver chloride:

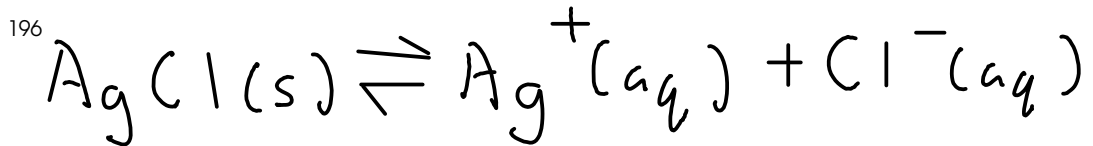


At equilibrium, the rate of dissolving equals the rate of crystallization!



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

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

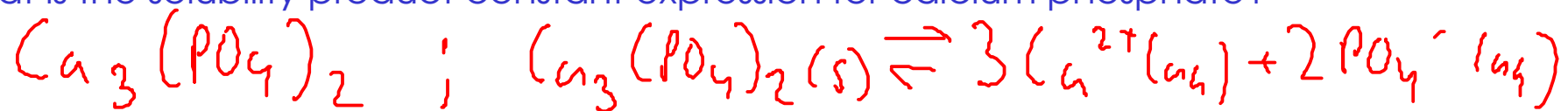


$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

↪ 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?



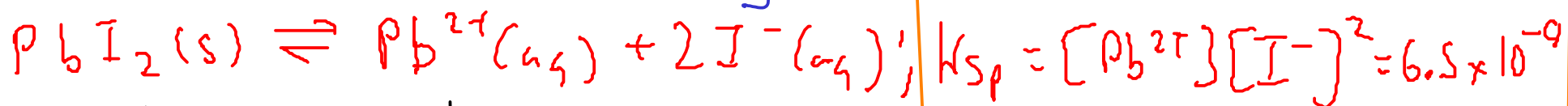
$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

197 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)

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



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

We need to solve this equilibrium to find out how much lead(II) iodide dissolved!

Define 'x' as the change in lead(II) ion concentration

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

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

Since each dissolving unit of lead(II) iodide makes a single lead ion, the dissolved lead(II) iodide concentration equals the lead(II) ion concentration!

$[Pb^{2+}] = 0.0011756673 \text{ M}$

$0.0011756673 \frac{\text{mol } PbI_2}{L} \cdot \frac{461.0 \text{ g } PbI_2}{\text{mol } PbI_2} = 0.54 \text{ g/L}$

Another common concentration unit for insoluble compounds ... ppm (parts per million):

$ppm = \frac{mg}{L}$ (for dilute aqueous solutions), so $0.54 \text{ g/L} \times \frac{mg}{10^{-3}g} = 540 \text{ ppm } PbI_2$