Calculate the pH of a buffer made from 3.2 grams of ammonium chloride and 29 mL of 18.1 M ammonia diluted to 50.0 mL with water.

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

Henderson-Hasselbalch Equation

$$3.2\ g\ NH_4Cl \times \frac{mol}{53.467\ g} = 0.059826\ mol\ NH_4Cl$$

$$\frac{0.059826\ mol\ NH_4Cl}{0.0500} = 1.1965\ M\ NH_4^+$$

$$M_1V_1 = M_2V_2$$

$$(18.1\ M)(29\ mL) = M_2(50.0\ mL)$$

$$10.498\ M\ NH_3 = M_2$$

$$pH = 9.245 + \log\left(\frac{10.498\ M}{1.1965\ M}\right)$$

Buffer pH controlled by pKa of the acidic species!

$$\log 8.773557$$

$$0.943175$$

$$pH = 9.245 + 0.943175 = \boxed{10.19}$$

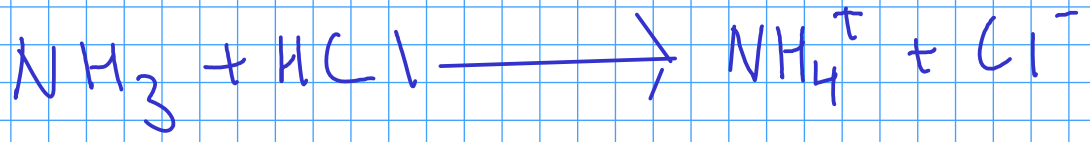
BUFFER SELECTION

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

- 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!

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



If you have more ammonia than hydrochloric 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!

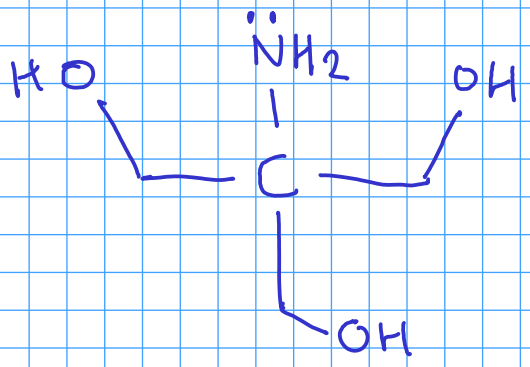
$$pH = pK_{a,\,acidic} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

Henderson-Hasselbalch Equation

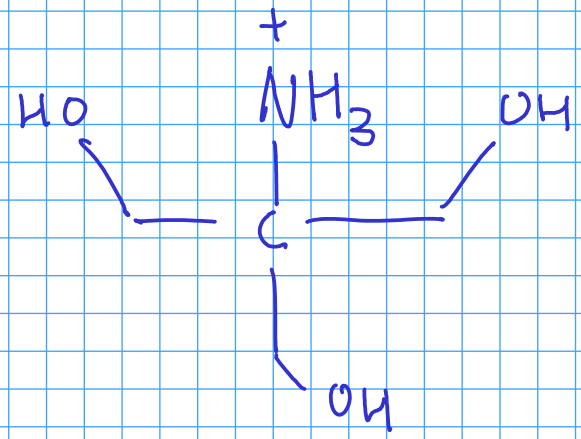
Ratio determines pH; the actual concentrations don't!

- 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^-

$pK_a = 8.06$

Calculate the pH of a buffer made from 50 mL of 0.10M tris and 50 mL of 0.15M tris-HCl

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

$$pH = 8.06 + \log\left(\frac{[\text{tris}]}{[\text{tris-HCl}]}\right)$$

$\frac{.050\ M}{.075\ M}$

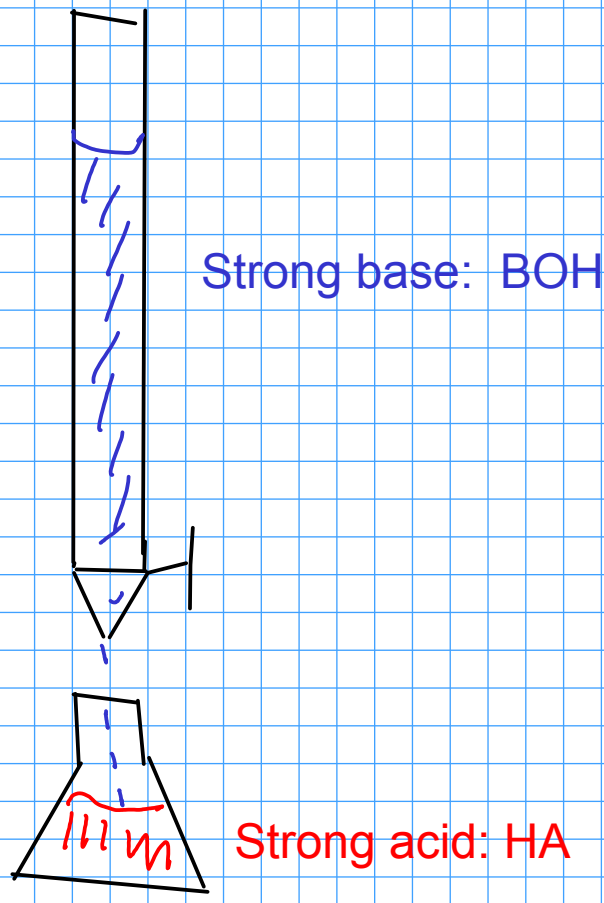
$pH = 8.06 - .176$

$pH = 7.88$

ACID-BASE TITRATIONS

- HOW do acid-base titrations really work?

- Look at the simplest case: Strong acid and strong base



Strong base: BOH

Strong acid: HA

$$HA + BOH \longrightarrow BA + H_2O$$

- This is a NEUTRALIZATION reaction.

- What controls the concentrations of hydronium ion in the flask?

Initially: (No BOH base added)

$[H_3O^+] = [HA]$ (strong acid solution!)

$$HA + H_2O \longrightarrow H_3O^+ + A^-$$

Start adding base (BOH) from the buret

$$HA + H_2O \longrightarrow H_3O^+ + A^-$$

$$BOH \longrightarrow B^+ + OH^-$$

... BUT hydronium reacts with hydroxide, so the hydronium ion concentration is determined by the amount of hydronium left over after the hydroxide from the base finished reacting with it!

Eventually, we will add enough BOH base to react away all of the original acid. This is the EQUIVALENCE POINT. What controls the hydronium concentration NOW?

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_w = [H_3O^+][OH^-]$$

$$[H_3O^+] = [OH^-] = \sqrt{K_w} = 1.0 \times 10^{-7} \quad (pH = 7)$$

If we CONTINUE to add base BOH, what controls the hydronium concentration?

$$BOH \rightarrow B^+ + OH^-$$

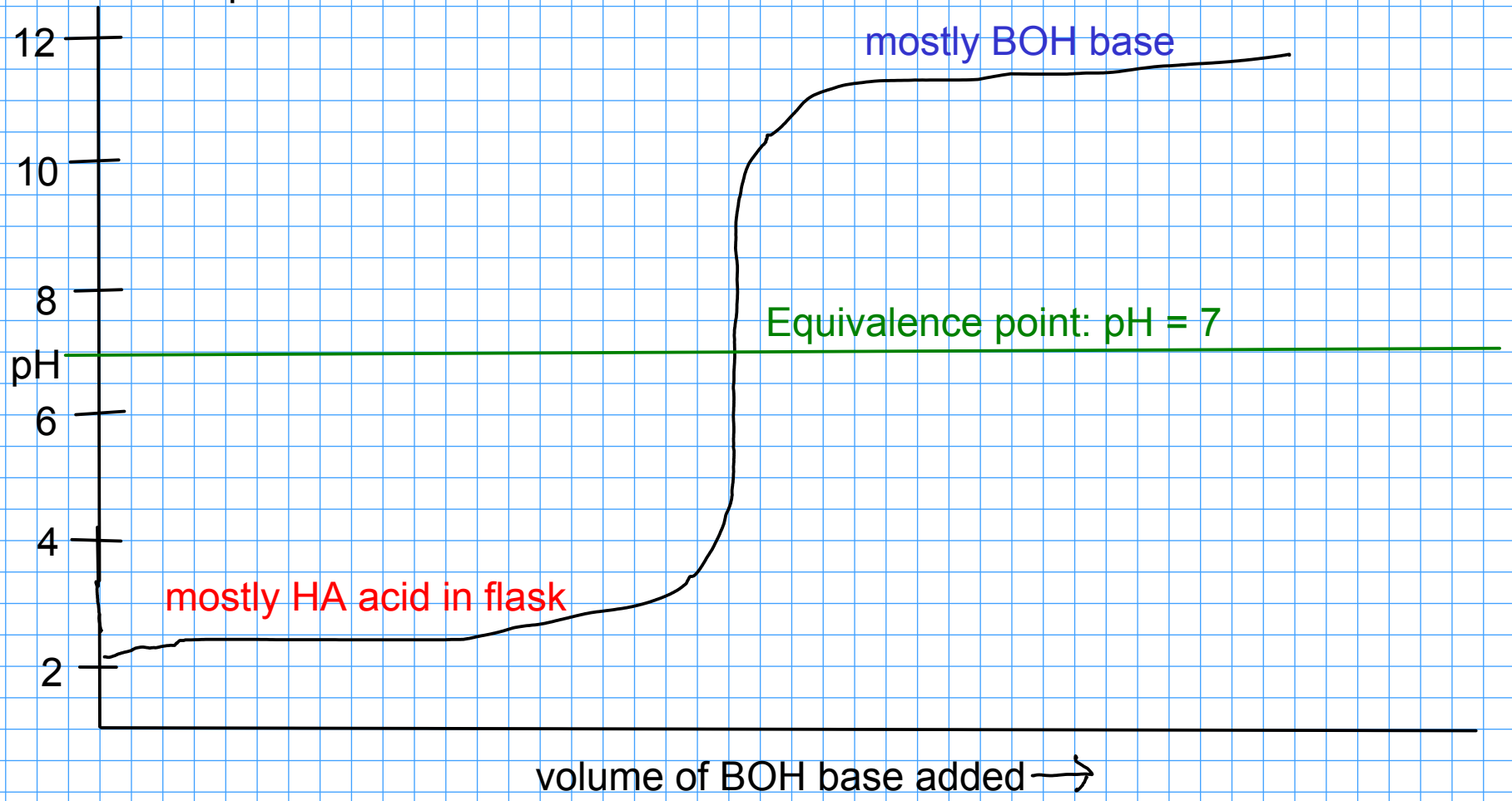
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$[H_3O^+][OH^-] = K_w$$

$[OH^-]$ = concentration of base $[BOH]$

So, how do we know (if the concentration of acid HA is actually UNKNOWN), when we have reached the EQUIVALENCE POINT?

Let's look at pH:



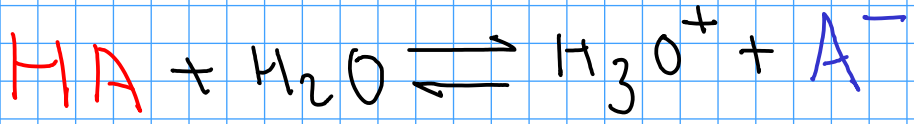
- We can make a plot like this by simply monitoring the pH during the titration with a pH meter!

INDICATORS

-Instead of using a pH meter to monitor a titration, 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?

$[HA] >> [A^-]$ ... so the SOLUTION IS RED!

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

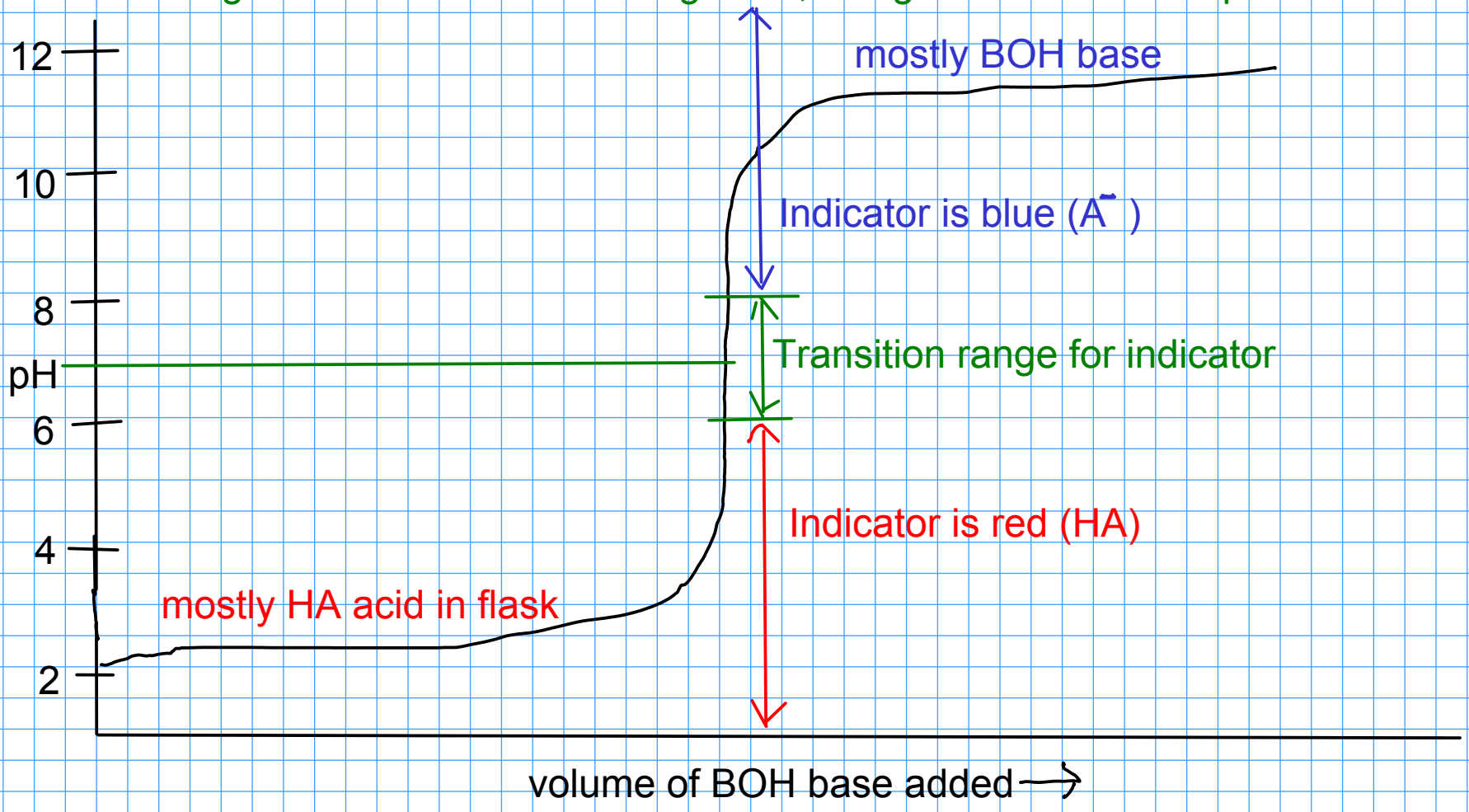
- What color is the solution>

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

- Usually, the indicator visually changes over a range of about +/- 1 pH unit around the pKa of the indicator.

Strong acid is titrated with strong base, using an indicator with pKa=7



$HA + H_2O \rightleftharpoons H_3O^+ + A^-$ Indicator equilibrium!

- Since the pH changes RAPIDLY near the equivalence point, the indicator's color changes rapidly (often with a single drop of base) from red to blue.

- Why would we ever need more than indicator?

Compare:

strong acid/strong base: $HCl + NaOH \rightarrow NaCl + H_2O$

At the equivalence point, you have a solution of sodium chloride, a neutral salt. pH = 7

weak acid/strong base $HC_2H_3O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O$

At the equivalence point, you have a solution of sodium acetate, a BASIC salt!

$NaC_2H_3O_2 \rightarrow Na^+ \quad C_2H_3O_2^-$

$C_2H_3O_2^-$ conjugate of ACETIC ACID

pH > 7

- Equivalence point's pH is NOT = 7 for this titration!

- The reason that there are so many acid-base indicators is that the pH of the equivalence point for an acid-base titration is usually not equal to 7.

TITRATION OF WEAK ACID WITH STRONG BASE

$$HA + BOH \longrightarrow H_2O + B^+ + A^-$$

weak acid

basic salt

How does the pH change during the titration?

INITIALLY

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

pH controlled by the weak acid equilibrium

AFTER ADDING BOH (base)

$$HA + BOH \rightarrow H_2O + B^+ + \boxed{A^-}$$

conjugate of HA is formed by the reaction of strong base with HA!

... we have a solution containing significant amounts of both HA and A^-

... a buffer sólution!

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

HALFWAY POINT

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

HALFWAY TO THE EQUIVALENCE POINT

... we've turned half of the HA into $\bar{A}$, so their concentrations are now equal

So, pH = pKa at the halfway point

AT THE EQUIVALENCE POINT

... we have a solution that contains only $\bar{A}$ - so the pH is determined by

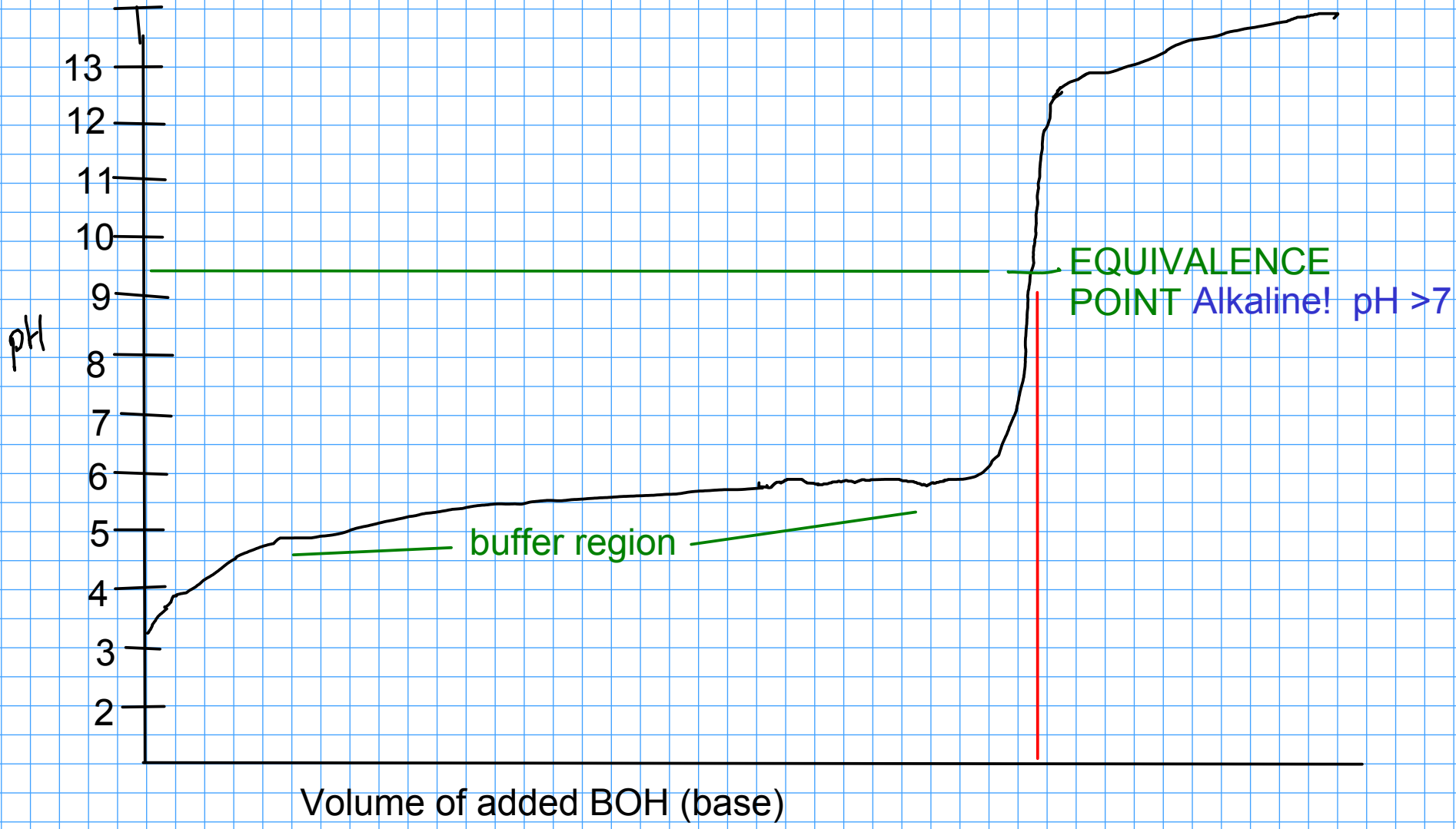
$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

basic pH!

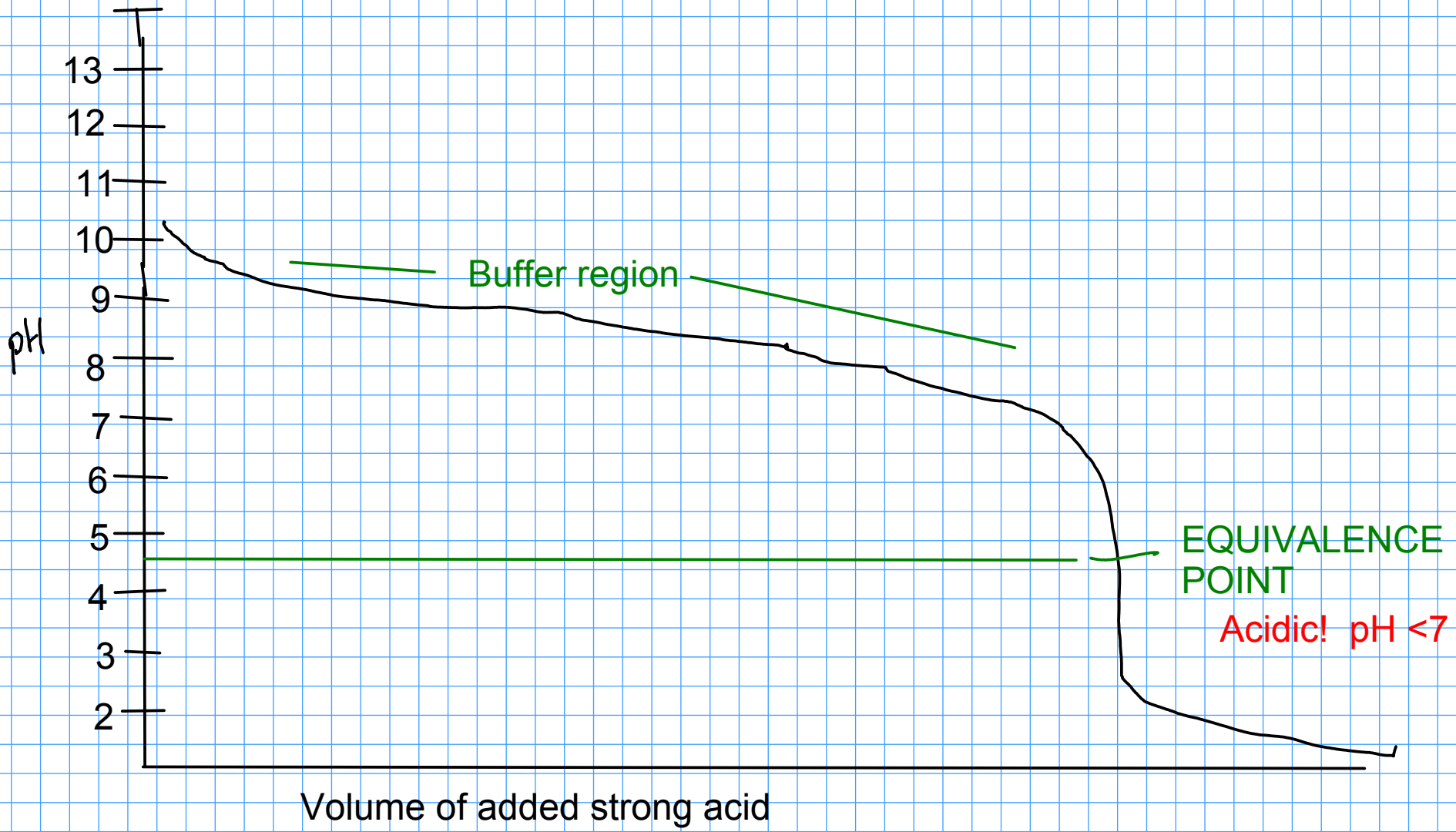
AFTER THE EQUIVALENCE POINT

... the pH will be controlled by the strong base



The WEAKER the acid, the HIGHER the pH will be at the equivalence point!

For a WEAK BASE titrated with strong acid, the pH at the equivalence point will be acidic. The weaker the base, the more acidic the equivalence point will be.



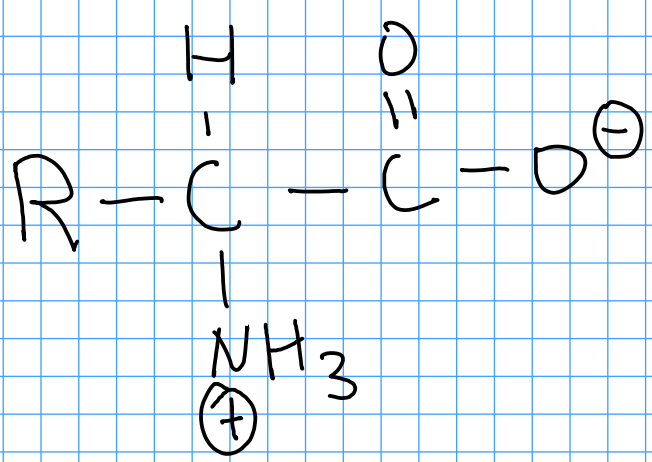
$B + HA \rightarrow BH^+ + A^-$

weak base

acidic salt

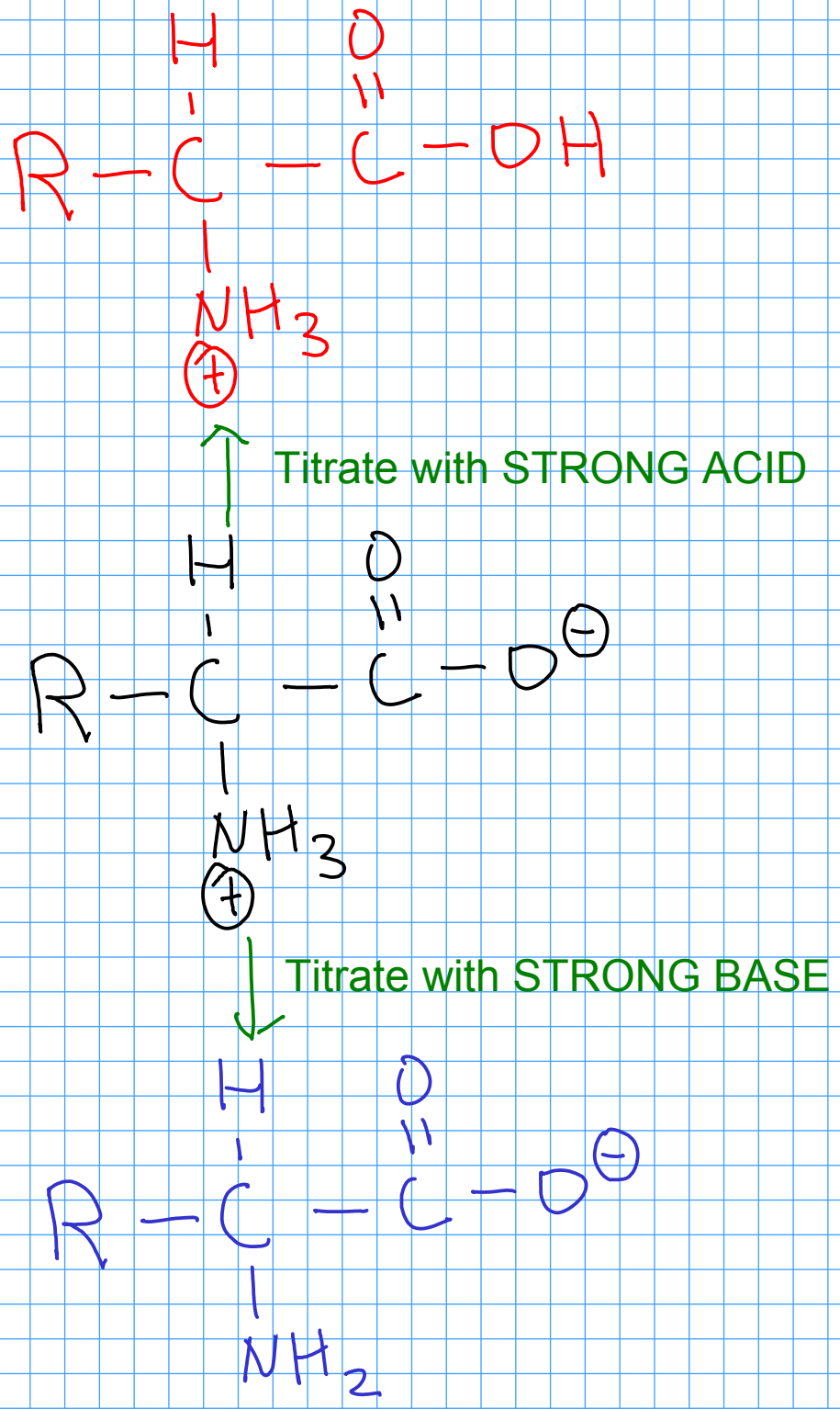
AMINO ACIDS

- amphoteric - can act as either an acid or a bsae

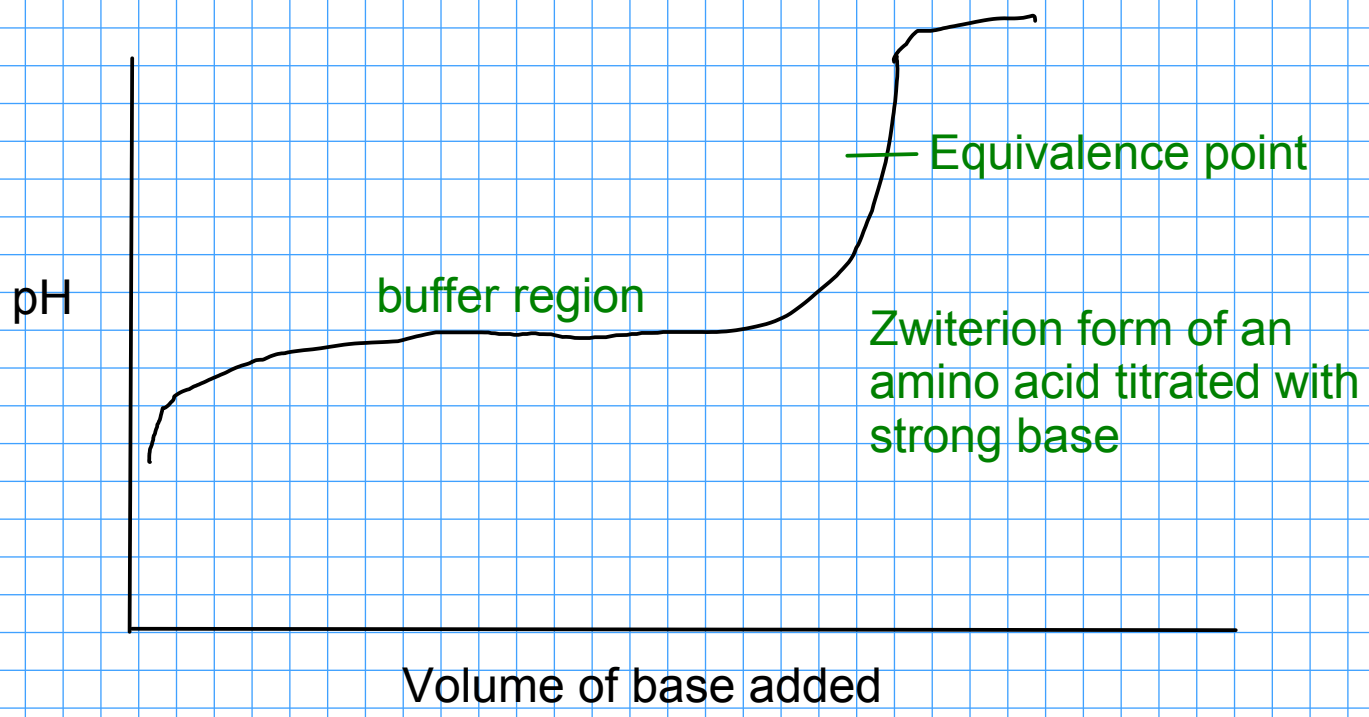


ZWITERION form - has both
a positive and negative charge

... titration? How do we titrate this? With a strong acid OR a strong base.


Titrate with STRONG ACID
Titrate with STRONG BASE

Sample titration curve for an amino acid titrated with strong base

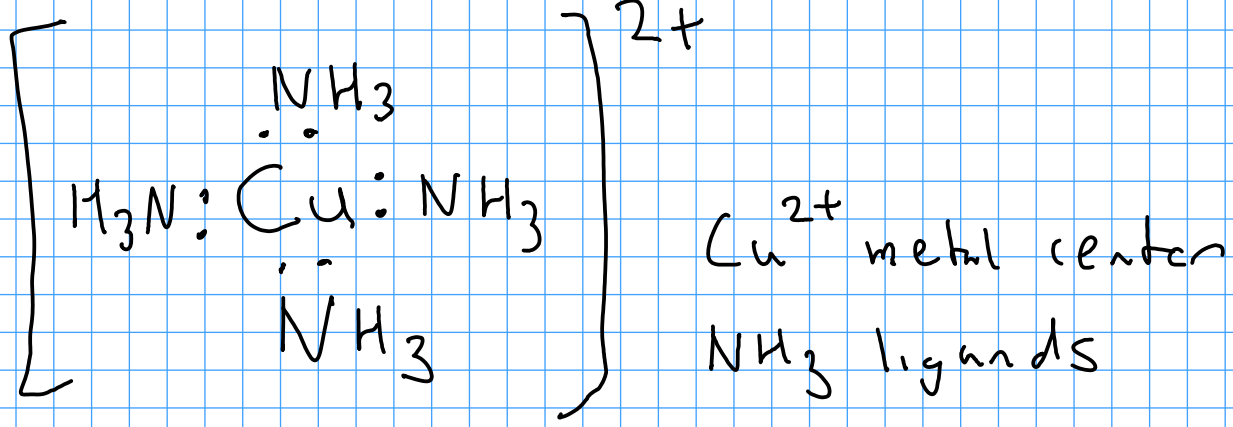


Looks similar to the titration of a regular weal acid with strong base!

COMPLEXOMETRIC TITRATIONS

- titrations involving the formation of COMPLEXES of metal ions with LIGANDS

- LIGANDS are molecules that are covalently (but weakly) bound to a metal center



DEEP BLUE color in solution

- The formation of this complex is a Lewis acid-base reaction. It is ALSO an EQUILIBRIUM process

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

$$K_F = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4}$$

FORMATION CONSTANT
or STABILITY CONSTANT
for this comples

$$Cu(NH_3)_4^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$$

$$K_d = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{+}]}$$

DISSOCIATION constant

You can calculate concentrations of these species in solution using similar math to solving acid-base equilibria.

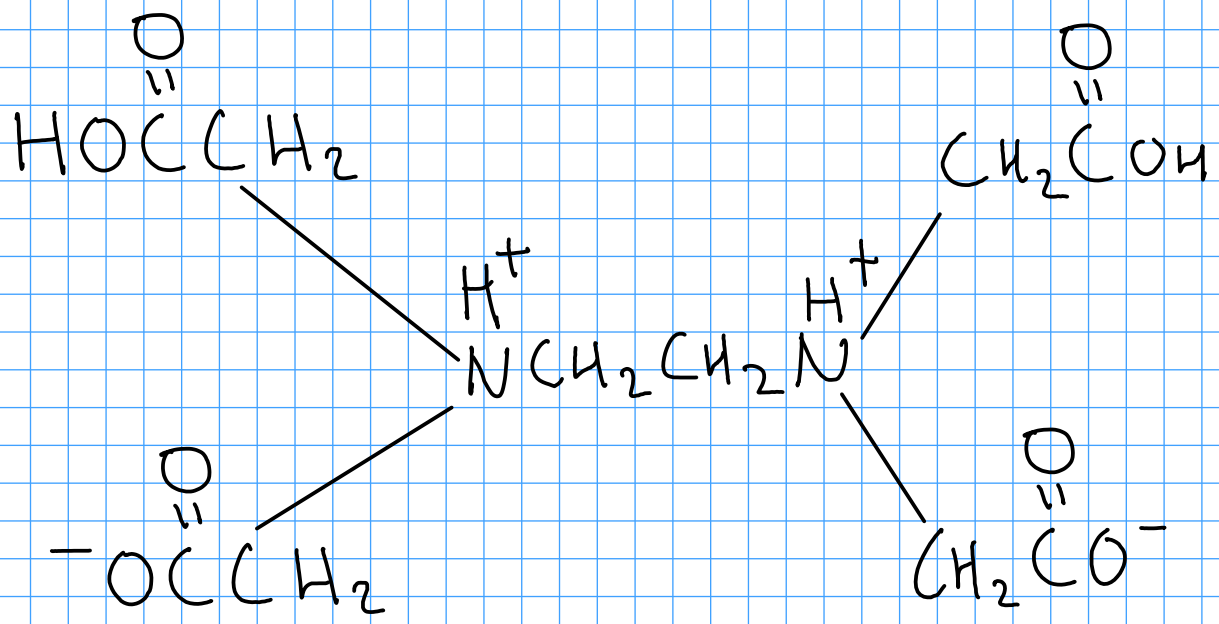
CHELATING AGENTS

- complexing agents which have two or more groups that can bind to / complex with a metal.

- complexes with these are called CHELATES

EDTA

- ethylenediaminetetraacetic acid

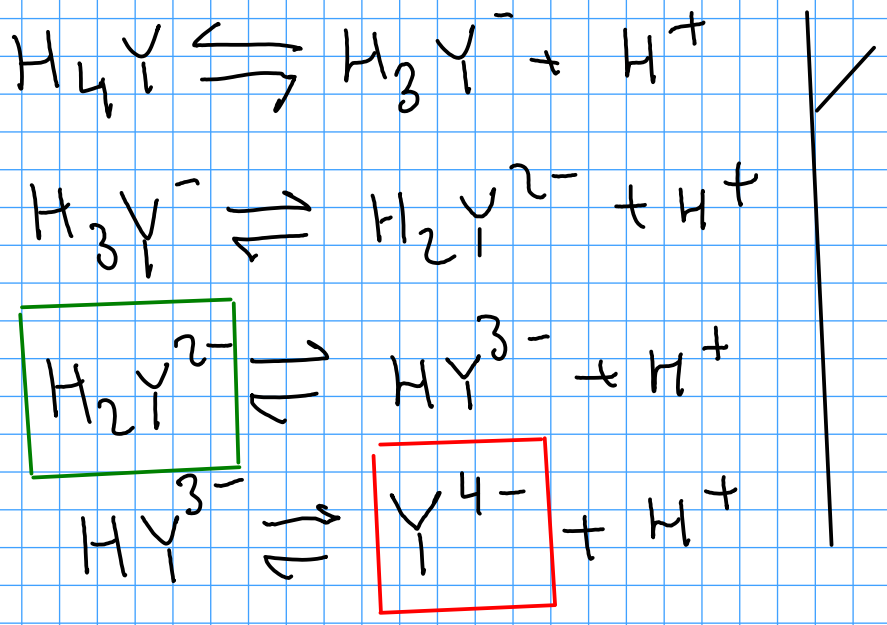


- EDTA is a polyprotic acid with FOUR ionizable protons!

" H_4Y " ... abbreviation

- To use EDTA, we make solutions of the salt Na_2H_2Y

H_2Y^{2-} in solution



Equilibria for EDTA in aqeous solution

Only the completely deprotonated (Y^{4-}) form complexes with metal ions!

We added a basic buffer to force the equilibrium to produce more of the deprotonated form of EDTA

We used pH 10 buffer instead of an excess of strong base (like NaOH) to avoid precipitating out our ions as hydroxides

INDICATORS FOR EDTA

- How do we tell when the chelate actually forms, since it's colorless?

- Use an indicator - Eriochrome Black T - which is highly colored AND forms complexes with metal ions!

Black T – Metal complex

RED

EDTA replaces Black T in the complex at the end of the titration

EDTA binds more tightly to the metal than Black T does!

Black T (free)

BLUE