VOLUMETRIC ANALYSIS (TITRATION)

Many different kinds of titration, can be loosely classified by the kind of reaction used:

① Acid-base titration

② Precipitation titration

③ Complexometric titration

④ Redox (oxidation-reduction) titration

REACTIONS FOR TITRATION

- these characteristics apply to all types of titration

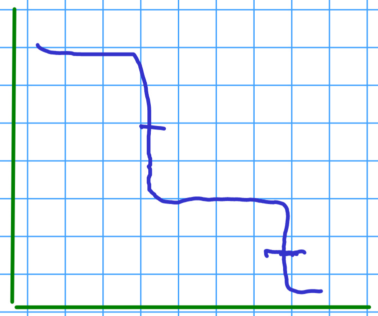
① STOICHIOMETRIC - react in a well-defined way with analyte

② NO SIDE REACTIONS - All interferants must be removed prior to titration

③ CLEAR ENDPOINT - must give a well-defined change in some property of the solution at the end of the titration

④ RAPID REACTION

⑤ EQUIVALENCE POINT SHOULD COINCIDE WITH ENDPOINT



⑥ QUANTITATIVE reaction - equilibrium point lies far towards PRODUCTS

high K_c !

PRIMARY STANDARDS

- highly pure materials used to accurately determine ("standardize") the concentration of a less-pure material.

Examples:

KHP (potassium acid phthalate) - a primary-standard ACID

$HOOC-C_6H_4-COO^-K^+$

sodium carbonate - a primary standard BASE

Na_2CO_3

$CO_3^{2-} + 2H^+ \rightarrow \underset{\text{weak acid}}{H_2CO_3}$

PRIMARY STANDARD QUALITIES

- Pirmary standards should have these characteristics:

① Available at 100.00% purity

② Stable over time and at various temperatures (ex: high-temperature drying)

③ Readily available

④ High formula weight

solid at room temp
non-volatile

TITRATION CALCULATIONS

- To perform titration calculations, we need to know:

① A BALANCED EQUATION for the titration

② An accurate CONCENTRATION OF TITRANT

③ VOLUME OF TITRANT (usually in mL)

④ AMOUNT OP SAMPLE (may be volume or mass)

TITRATION CALCULATIONS

- Once we have the required information, we then:

① Find the mmol (millimoles) of titrant used $mL \times \underline{M} = mmol$

② Relate the mmol titrant to mmol analyte using the balanced equation

$H_2SO_4 + 2NaOH \rightarrow 2H_2O + Na_2SO_4$

2 mmol NaOH = 1 mmol H_2SO_4

③ Find mmol analyte

④ Convert mmol analyte to desired measurement (mass or moles)

⑤ Report mass, mass percentage, or concentration of analyte, depending on SOP requirements

STANDARDIZATION

- It's often not possible to directly use a primary standard for your analysis. If this is the case, you'll need to STANDARDIZE the titrant you actually DO use!

What;'s that mean? Use the titrant to titrate a known quantity of a STANDARD, then calculate the concentration of the titrant!

To STANDARDIZE a solution, you'll need to find:

$$\text{mmol} = \frac{\text{mg}}{\text{FW}}$$

① mmol of STANDARD used (usually from a mass and a formula weight)

② mmol TITRANT - use the balanced equation to relate the STANDARD with the TITRANT

③ $$\frac{\text{mmol TITRANT}}{\text{mL TITRANT}} = \text{M titrant (molarity)}$$

A COMMON TITRATION PROBLEM

- Ideally, we'd like to use only titration reactions that proceed RAPIDLY.

- However, not all potentially usable reactions proceed rapidly.

- A process called BACK-TITRATION is useful for dealing with slow reactions.

BACK-TITRATION

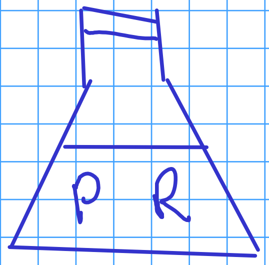
add lots of "R"!

$\textcircled{A} + R \rightarrow P$ slow

- How is this done?

① Add a measured amount of a REAGENT to the sample. The added amount is IN EXCESS of the amount needed to completely react the analyte

② Allow this reaction to go to completion.



③ TITRATE the EXCESS REAGENT using a FAST reaction with a distinct ENDPOINT

$\underline{R} + \underline{T} \rightarrow Q$ Fast!

BACK-TITRATION CALCULATIONS

$A + R \rightarrow P$

- To determine the amount of analyte in a back-titration procedure, do this:

$R + T \rightarrow Q$

① Find the TOTAL mmol of ADDED REAGENT

total R

② Find the mmol TITRANT

T

③ Relate mmol TITRANT to mmol EXCESS REAGENT using the balanced equation between TITRANT and REAGENT

$R + T \rightarrow Q$

④ Find mmol EXCESS REAGENT

leftover R

⑤ mmol REACTED REAGENT = mmol TOTAL REAGENT - mmol EXCESS REAGENT

⑥ Relate mmol REACTED REAGENT with mmol ANALYTE using the balanced equation between ANALYTE and REAGENT

$A + R \rightarrow P$

⑦ Convert the mmol ANALYTE to desired form, depending on SOP

NORMALITY AND TITRATION

- Normality is similar to molarity, but gives the concentration of a solution in terms of MOLES OF REACTING UNITS than actual moles of a substance

- Normality is an attempt to cut STOICHIOMETRY out of routine calculations.

$$\boxed{N = \frac{\text{eq}}{\text{L}} = \frac{\text{meq}}{\text{mL}}}$$

, where "eq" means "number of equivalents"

moles of
reacting units

$$\boxed{\text{equivalent weight} = \frac{\text{Formula weight of substance}}{\text{number of equivalents per mole of substance}}}$$

equivalent weight
is similar to formula
weight!

$$\boxed{\text{eq} = \frac{\text{mass}}{\text{equivalent weight}}}$$

similar to calculation of moles
from mass using formula weight

Where's the stoichiometry? Buried in the calculation of the equivalent weight and the number of equivalents!

NORMALITY AND TITRATIONS

- Once concentrations are expressed in N, chemical calculations proceed as if all reagents react in a 1:1 ratio!

... but how do you actually determine what a "reacting unit is?"

REACTING UNITS FOR TITRATIONS

- two of the more common titration types are ACID-BASE titrations and REDOX titrations!

① ACID-BASE

- the REACTING UNIT is the PROTON (in other words, the H^+ ion)

- if the reagent is an ACID, how many reactive protons does it have?

H_2SO_4: two reactive protons

$HC_2H_3O_2$: one reactive proton

H_3PO_4: three reactive protons

- if the reagent is a BASE, how many protons is it able to react with?

NaOH: reacts with one proton

$Ca(OH)_2$: reacts with two protons

NH_3: reacts with one proton

REACTING UNITS FOR TITRATIONS

② REDOX

- the REACTING UNIT is the ELECTRON (e^-)

- For a REDUCING AGENT, how many electrons does the reagent give up?

$Na \rightarrow Na^+ + 1e^-$: one electron

- For an OXIDIZING AGENT, how many electrons does the reagent accept?

$Br_2 + 2e^- \rightarrow 2Br^-$: two electrons

TITRATION CALCULATIONS WITH NORMALITY

- Normailty is supposed to make routine calculations simpler!

① Find the concentration of TITRANT in normality units (N). This involves determining REACTING UNITS if it has not already been done.

② Find the EQUIVALENT WEIGHT of the analyte

③ Since titrant "T:" and analyte "A" react in a 1:1 ratio by equivalents, then find the composition in percent A (%A) by simple dimensional analysis

$$\boxed{\%A = \frac{\overbrace{N_T \times \text{eq wt A} \times mL_T}^{= mg_A}}{\text{mg sample}}}$$

This relationship is true for ALL titrations when you use normality units!

$$\boxed{ppm_A = \frac{mg_A}{\text{L sample}}}$$

ACID/BASE EQUILIBRIUM

- Several scientific theories exist that define acid-base chemistry

- These theories differ in the way that acids, bases, and their associated reactions are defined.

- Typically, the newer theories include MORE chemicals under the umbrella of "acid-base chemistry"!

FOUR ACID-BASE THEORIES IMPORTANT TO ANALYTICAL CHEMISTS

① Arrhenius theory

② Solvent systems theory

③ Bronsted-Lowry theory

④ Lewis theory

ARRHENIUS THEORY

- The oldest model of acid-base chemistry!
- Only applicable to systems where WATER is the solvent!

ACIDS are substances that ionize in water to increase the concentration of HYDRONIUM ION

$$HA + H_2O \rightleftharpoons \underline{H_3O}^+ + A^-$$

Hydronium ion

or, for simplicity: $HA \overset{H_2O}{\rightleftharpoons} \underline{H}^+ + A^-$

"Hydrogen ion" - doesn't really exist as a free ion in water, but a convenient simplification!

ARRHENIUS THEORY

BASES are substances that ionize in water to increase the concentration of HYDROXIDE ION

For soluble metal hydroxides:

$$MOH \overset{H_2O}{\rightleftharpoons} M^+ + \underline{OH^-}$$

Hydroxide ion

For other Arrhenius bases:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

An Arrhenius acid base reaction can be represented by:

$$\boxed{H_3O^+ + OH^- \rightleftharpoons 2H_2O}$$

"neutralization"

or, using hydrogen ion instead of hydronium

$$H^+ + OH^- \rightleftharpoons H_2O$$

SOLVENT SYSTEMS THEORY

- Typically used for systems where water is NOT the solvent!

ACIDS are substances that ionize to increase the concentration of the CATION of the solvent

BASES are substances that ionize to increase the concentration of the ANION of the solvent

Compare this to Arrhenius theory! What if we apply solvent system theory to a system with water?

$$H_2O \rightleftharpoons H^+ + OH^-$$

anion of solvent

cation of solvent

- the acid would increase H^+
- the base would increase OH^-

Familiar?

BRONSTED-LOWRY THEORY

- Bronsted-Lowry theory views acid-base reactions as PROTON (H^+) TRANSFER reactions!

ACIDS are PROTON DONORS

BASES are PROTON ACCEPTORS

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

acid

base

conjugate acid of NH_3

conjugate base of HCl

A CONJUGATE PAIR is an acid and a base that differ by a proton!

BRONSTED-LOWRY THEORY

IN WATER...

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

acid

conjugate base
of HA

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

base

conjugate acid
of B

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

In the red reactions, water functions as a base. In the blue reactions, water functions as a base!

LEWIS THEORY

- Lewis theory treats acid-base chemistry as electron-transfer chemistry involving pairs of electrons

- Lewis acid-base reactions form new covalent bonds (of interest to organic chemists!)

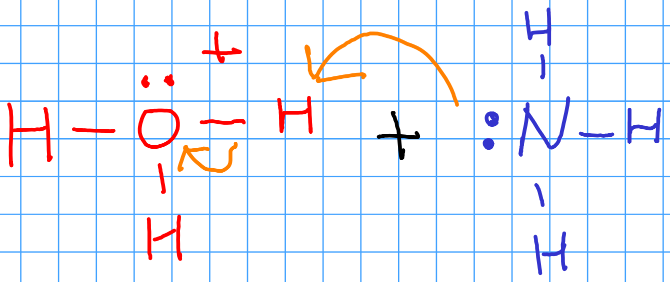
ACIDS are ACCEPTORS of electron pairs

BASES are DONORS of electron pairs

LEWIS THEORY

Example: ammonia and hydrochloric acid

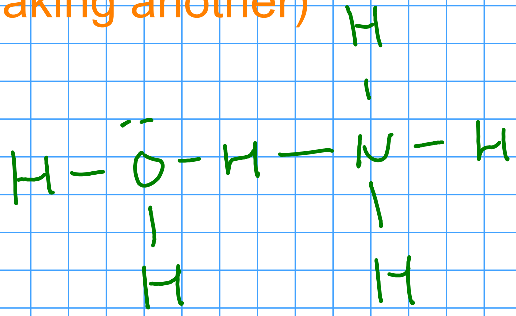
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

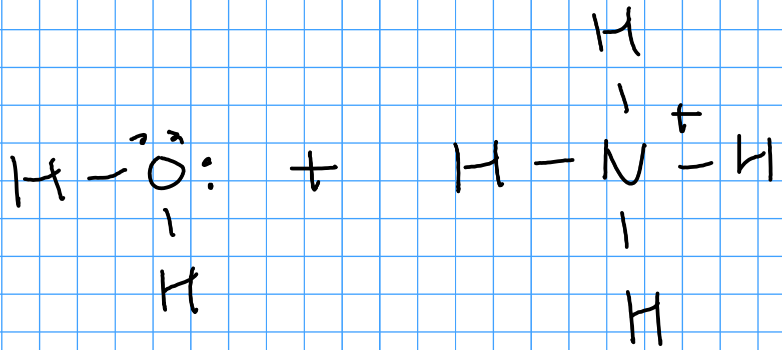


hydronium ion
(Lewis acid)

ammonia
(Lewis base)

Ammonia donates
a pair of electrons to
a hydrogen on hydronium
ion, forming a new covalent
bond (and breaking another)





water

ammonium ion

overall, $H_3O^+ + NH_3 \rightleftharpoons NH_4^+ + H_2O$

WATER CHEMISTRY

- Water self-ionizes!

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

or

$$H_2O \rightleftharpoons H^+ + OH^-$$

This is an equilibrium reaction!

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

[X] = molar concentration of "X"

In aqueous solution, [H_2O] is essentially constant, so we roll that into K.

$$\boxed{K_w = [H_3O^+][OH^-] = 1.0\times10^{-14}}$$

WATER CHEMISTRY

- The self-ionization of water has a small equilibrium constant. What does this imply?

THE CONCNETRATION OF HYDROXIDE AND HYDRONIUM ION IN PURE WATER IS VERY SMALL!

How small?

$$2H_2O \rightleftharpoons \underline{H_3O^+ + OH^-}$$

In pure water, the concentration of hydroxide and hydronium must be equal, since they are formed at the same time and at the same ratio from the ionization reaction of water.

$$K_w = [H_3O^+][OH^-] = 1\times10^{-14}$$

Let "z" = $[H_3O^+] = [OH^-]$

$$z^2 = 1\times10^{-14}$$

$$\boxed{z = 1\times10^{-7}\ \underline{m}}$$

"p" NOTATION

- "p" notation helps us deal with the very small numbers we encounter when working with acids, bases, and water.

- based on log base 10

"p" means $-\log_{10}$

log ~~ln~~

So,

$$\boxed{pH = -\log_{10}[H_3O^+]}$$

$$\boxed{pOH = -\log_{10}[OH^-]}$$

"p" NOTATION

- Apply "p" notation to the water self-ionization reaction!

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

becomes ...

$$\boxed{pK_w = pH + pOH = 14.00}$$

Taking the "p" (negative log base ten) of the equilibrium constant is often used for BUFFER SOLUTIONS, which we'll discuss later!

ACIDITY AND ALKALINITY

- At pH = 7, pH = pOH. The solution is considered NEUTRAL

Also, $[H^+] = [OH^-]$!

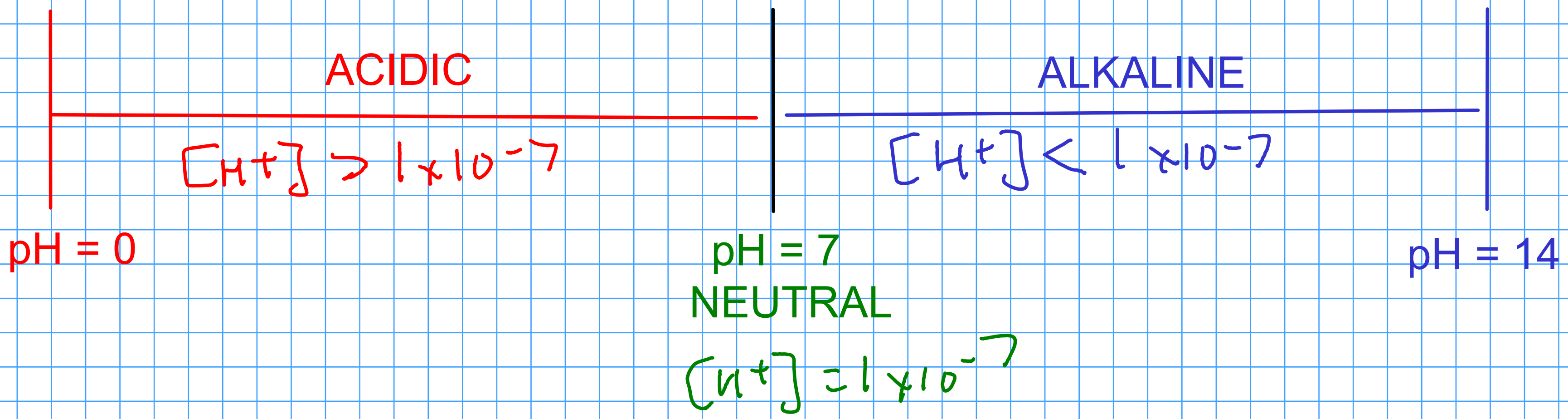
- At pH <7, pH < pOH. The solution is considered ACIDIC

Also, $[H^+] > [OH^-]$!

- At pH > 7, pH > pOH. The solution is considered ALKALINE (BASIC)

Also, $[H^+] < [OH^-]$!

The pH scale...



ACIDIC

$[H^+] > 1\times10^{-7}$

ALKALINE

$[H^+] < 1\times10^{-7}$

pH = 0

pH = 7

NEUTRAL

$[H^+] = 1\times10^{-7}$

pH = 14

pH AND TEMPERATURE

$$\boxed{pK_w = pH + pOH = 14.00}$$

This equation is valid at room temperature, specifically 25° C.

Equilibrium constants depend on TEMPERATURE, and change with temperature.

So, the "neutral" pH (where the concentration of hydroxide and hydronium ions are equal) CHANGES with changing temperatures

This change is important at temperatures greatly different from 25° C.

As an example, consider average "normal" human body temperature: 37° C

At 37°C, $pK_w = 13.60$

pH of neutral solution $= \underline{\underline{6.8}}$

SIMPLE pH CALCULATIONS: STRONG ELECTROLYTES

- With strong acids and bases, the acid or base completely ionizes in water. So, we only have to worry about the effect of the acid or base on the water equilibrium itself.

- Since the equilibrium constant for the self-ionization of water is so small, the strong acid or base will overpower the hydronium (for acids) or hydroxide (for bases) produced by the water.

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

Consider 0.025 $\underline{M}$ HNO_3

Assume all H_3O^+ comes from acid!

$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

So, $[H_3O^+] = 0.025\ \underline{M}$

$pH = 1.\underline{60}$

significant digits are after decimal!

$pOH = 14.00 - pH$

$pOH = 12.40$

Consider 0.0125 $\underline{M}$ NaOH

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

Assume all OH^- comes from base

$KOH \rightarrow K^+ + OH^-$

$[OH^-] = 0.0125\,\underline{M}$

$pOH = 1.90$

$pH = 14.00 - pOH$

$pH = 12.10$

$[H^+] = 1 \times 10^{-12.10}$

$[OH^-]$ from H_2O

ACID-BASE EQUILIBRIUM IN WATER

- Like other ELECTROLYTES, acids and bases IONIZE to some extent in water

- STRONG electrolytes ionize completely. Acids and bases that ionize completely in water are called STRONG ACIDS and STRONG BASES

- WEAK electrolytes ionize partially, remaining mostly non-ionized. Acids and bases that ionize only partially in solution are called WEAK ACIDS and WEAK BASES.

- Most acids and bases are WEAK!

Common strong acids

HCl

HNO_3

H_2SO_4 (only 1st proton)

HBr

HI

Common strong bases

$NaOH$
KOH
alkali metal hydroxides

$Ca(OH)_2$

For a WEAK ACID, equilibrium does not lie far to the right. The ionization equilibrium of the acid itself is important!

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

$$\underbrace{K_a}_{\text{acid ionization constant}} = \frac{[H_3O^+][A^-]}{\underbrace{[HA]}_{\text{[HA] = concentration of undissociated acid}}}$$

Again, water's concentration will not change significantly, so it is folded into the ionization constant

For a WEAK BASE, equilibrium does not lie far to the right. The ionization equilibrium of the base itself is important!

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$\underbrace{K_b}_{\text{base ionization constant}} = \frac{[BH^+][OH^-]}{[B]}$$

WEAK ELECTROLYTES

- In solutions of weak acids or bases, the UNDISSOCIATED form is present in significantly high concentration.

- The pH of a solution of weak acid will be HIGHER than the pH of a strong acid solution with the same nominal concentration!

- The pH of a solution of weak base will be LOWER than the pH of a strong basesolution with the same nominal concentration!

Consider a 0.100M solution of the WEAK ACID HNO_2

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = 5.1 \times 10^{-4}$$

values for Ka are determined experimentally

What is the pH of the solution?

To find the pH, we need to determine the concnetration of hydronium, $[H_3O^+]$

... so we need to solve the equilibrium expression. But we don't know all of the concentrations AT EQUILIBRIUM to do so!

... but they ARE related!

ignore H_2O equil.

initial	change	at equilibrium
$[H_3O^+] = 0$	$+x$	x
$[NO_2^-] = 0$	$+x$	x
$[HNO_2] = 0.100$	$-x$	$0.100 - x$

$x = [HNO_2]$ that dissociates

$$5.1 \times 10^{-4} = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$5.1 \times 10^{-4} = \frac{(x)\ (x)}{(0.100 - x)}$$

$$5.1 \times 10^{-4} = \frac{x^2}{0.100 - x}$$

Quadratic equation!

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\downarrow$$

Assume that x << 0.100 (this is a weak acid)

$$5.1 \times 10^{-4} = \frac{x^2}{0.100}$$

$$x^2 = .00051$$

$$x = 7.14 \times 10^{-3} = [H_3O^+]$$

$$pH = \boxed{2.15}$$

Compare:

- Weak acid HNO_2 : pH of 0.10 M solution = 2.15

- Strong acid: pH of 0.10 M solution = 1.00

The stronger the acid, the lower the pH of a solution of given concentration will be!

Consider an 0.100 M solution of the weak base ammonia:

NH_3 ; $K_b = 1.75 \times 10^{-5}$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = 1.75 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

What is the pH?

	initial	Δ	equilibrium
$[NH_4^+]$	0	$+x$	x
$[OH^-]$	0	$+x$	x
$[NH_3]$	$.100$	$-x$	$.100 - x$

$$1.75 \times 10^{-5} = \frac{x^2}{.100 - x}$$

x = amount of NH_3 that ionizes

Plug in and solve for "x"!

$$1.75\times10^{-5} = \frac{x^2}{.100 - x}$$

Quadratic!

$x \ll 0.100$ Assume $.100 - x \approx .100$

$$1.75\times10^{-5} = \frac{x^2}{.100}$$

$$1.322\times10^{-3} = x = [OH^-]$$

$$-\log(x) = pOH$$

$$2.88 = pOH$$

$$pH + pOH = 14.00$$

$$\boxed{pH = 11.12}$$

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

Compare pH to the pH of an 0.100 M solution of the strong base NaOH:

$pH_{,NH_3} = 11.12$

$NaOH \longrightarrow Na^+ + OH^-$

$[OH^-] = 0.100$

$pOH = 1.00$

$pH + pOH = 14.00$

$\boxed{pH = 13.00}$

The higher the Ka or Kb value, the stronger the acid or base!

SALTS

- Compounds that result from the reaction of an acid and a base.

- Strong electrolytes (completely dissociate in water) IF SOLUBLE (not all salts dissolve appreciably)

- Most ionic compounds are considered salts (they can be made by some reaction between the appropriate acid and base)

- Salts have acidic and basic properties!

    - Salts made from WEAK ACIDS tend to form BASIC solutions

    - Salts made from WEAK BASES tend to form ACIDIC solutions

$$\underset{\text{acid}}{H_2CO_3} + 2H_2O \rightleftharpoons 2H_3O^+ + \underset{\text{conj base}}{CO_3^{-2}}$$

Na_2CO_3

SALT OF A WEAK ACID

$$NaA \longrightarrow Na^+ + A^-$$

The salt dissolves completely!

$$\underline{A^-} + H_2O \rightleftharpoons HA + OH^-$$

... but the ionization of the salt's anion is an EQUILIBRIUM!

The anion is a BASE. It can accept a proton from water to form the weak (therefore stable as a molecule!) acid HA

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

This is the base ionixation contant for $\bar{A}$

Since A^- and HA are a conjugate pair, the ionization constants are related!

$$K_w = (K_{a,HA})(K_{b,A^-})$$

You will generally not find both the Ka AND Kb for a conjugate pair in the literature, since one can be easily converted to the other!

SALT OF A WEAK BASE

NH_4Cl

$$BHCl \longrightarrow BH^+ + Cl^-$$

The salt dissociates completely!

$$BH^+ + H_2O \rightleftharpoons \underline{B} + H_3O^+$$

... but this ionization is an EQUILIBRIUM process!

$$K_a = \frac{[B][H_3O^+]}{[BH^+]}$$

Acid ionization constant for BH^+

$$K_w = (K_{a,BH^+})(K_{b,B})$$

Find the pH for salt solutions just like you would find pH for any other weak acid or weak base solutions. Only trick is to find out whether the salt is actually acidic or basic!

0.100 M NH_4Cl ... Find pH

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

Acidic, basic, neutral?

weak base: stable in H_2O

NH_4^+: $NH_4^+ + H_2O \rightleftharpoons \boxed{NH_3} + H_3O^+$ ✓

Cl^-: $Cl^- + H_2O \rightleftharpoons \boxed{HCl} + OH^-$ ✗

strong acid, unstable in H_2O

does not exist as HCl molecule

The conjugate of a strong acid or base is NEUTRAL - does not affect pH!

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

ps40, Harris

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.69 \times 10^{-10}$$

	initial	Δ	equilibrium
$[NH_3]$	0	$+x$	x
$[H_3O^+]$	0	$+x$	x
$[NH_4^+]$	.100	$-x$	$.100 - x$

"x" = amount of NH_4^+ that reacts

$$\frac{x^2}{.100 - x} = 5.69 \times 10^{-10}$$

$$\Big\downarrow \; x \ll .100$$

$$\frac{x^2}{.100} = 5.69 \times 10^{-10}$$

$$x = 7.54 \times 10^{-6}$$

$$7.54 \times 10^{-6} = [H_3O^+]$$

$$\boxed{5.12 = pH}$$

compare to pH = 1 for strong
pH = 2.15 for HNO_2

0.100 M $NaC_2H_3O_2$, Find pH

$$NaC_2H_3O_2 \longrightarrow \underline{Na^+} + \underline{C_2H_3O_2^-}$$

conjugate of $HC_2H_3O_2$

neutral

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

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = ?$$

$$K_{a,\ HC_2H_3O_2} = 1.75 \times 10^{-5}$$

$$K_a \times K_b = K_w$$

$$(1.75 \times 10^{-5})(K_b) = (1.00 \times 10^{-14})$$

$$K_b = 5.71 \times 10^{-10}$$

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = 5.71 \times 10^{-10}$$

	initial	Δ	equilibrium
$[HC_2H_3O_2]$	0	$+x$	x
$[OH^-]$	0	$+x$	x
$[C_2H_3O_2^-]$	0.100	$-x$	$0.100 - x$

"X" = amount of acetate that reacts

$$\frac{x^2}{.100 - x} = 5.71 \times 10^{-10}$$

$\downarrow$ $.100 - x \approx .100$, $x << .100$

$$\frac{x^2}{.100} = 5.71 \times 10^{-10}$$

$$x = 7.56 \times 10^{-6} = [OH^-]$$

$x = 7{,}56 \times 10^{-6} = [OH^-]$

$pOH = 5{,}12$

$pH + pOH = 14{,}00$

$\boxed{pH = 8{,}88}$

K_a:

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

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

K_b:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

0.150 M NH_4NO_3, find pH

$$NH_4NO_3 \longrightarrow \underline{NH_4^+} + \underline{NO_3^-}$$

NO_3^-: conjugate of HNO_3 ← strong acid

NH_4^+: conjugate of NH_3 ← weak base

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$K_{a,NH_4^+} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.69 \times 10^{-10}$$

	initial	Δ	equilibrium
$[NH_3]$	0	$+X$	X
$[H_3O^+]$	0	$+X$	X
$[NH_4^+]$	.150	$-X$	$.150 - X$

X = amount of NH_4^+ that reacts

$$\frac{x^2}{.150 - x} = 5.69 \times 10^{-10}$$

$\downarrow$ $x \ll .150$,5o $.150 - x \approx .150$

$$\frac{x^2}{.150} = 5.69 \times 10^{-10}$$

$$x = 4.24 \times 10^{-6} = [H_3O^+]$$

$$\boxed{pH = 5.03}$$

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)

② Make a mixture of a weak base and its conjugate acid (as the SALT)

For a weak acid, you would:

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

- 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.

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

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

① Take log of both sides

② Multiply by -1

③ Rearrange, solving for pH

$$\Big\downarrow$$

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

Henderson-Hasselbalch Equation

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

$[HA]$ .. from 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.

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

Henderson-Hasselbalch Equation

ex: $HC_2H_3O_2 / NaC_2H_3O_2$

$$pH = pK_{a,\,HC_2H_3O_2} + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

NH_3 / NH_4NO_3

$$pH = pK_{a,\,NH_4^+} + \log\left(\frac{[NH_3]}{[NH_4^+}\right)$$

$$pK_a + pK_b = 14{,}00$$

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

$$3{,}2\ g\ NH_4Cl \times \frac{mol}{53{,}467\ g} = 0{,}059826\ mol\ NH_4Cl$$

$$\frac{0{,}059826\ mol\ NH_4Cl}{0{,}0500} = 1{,}19655\ M\ NH_4^+$$

$$M_1V_1 = M_2V_2$$

$$(18{,}1\ M)(29\ mL) = M_2(50{,}0\ mL)$$

$$10{,}498\ M\ NH_3 = M_2$$

$$pH = 9{,}245 + \log\left(\frac{10{,}498\ M}{1{,}19655\ M}\right)$$

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!

$$NH_3 + HCl \longrightarrow NH_4^+ + Cl^-$$

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!

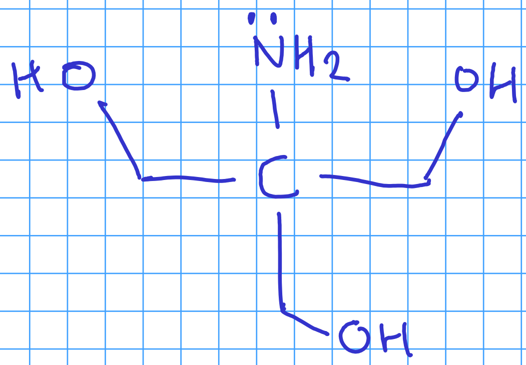
$$pH = pK_{a,\text{acidic}} + \log\left(\frac{[\text{basic species}]}{\underline{[\text{acidic species}]}}\right)$$

Henderson-Hasselbalch Equation

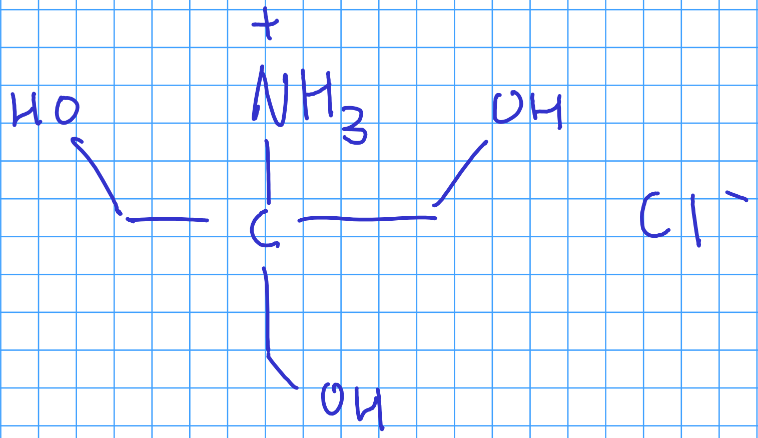
Ratio determines pH; the actual concentrations don't!

- 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)

$$\boxed{pKa = 8{,}06}$$

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

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

$$pH = 8{,}06 + \log\left(\frac{[\text{tris}]}{[\text{tris-HCl}]}\right) \qquad \frac{.050\ M}{.075\ M}$$

$$pH = 8{,}06 - .176$$

$$\boxed{pH = 7{,}88}$$

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?

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

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

$$[H_3O^+] = [OH^-] = \sqrt{K_w} = 1{,}0\times10^{-7}\ (pH=7)$$

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

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

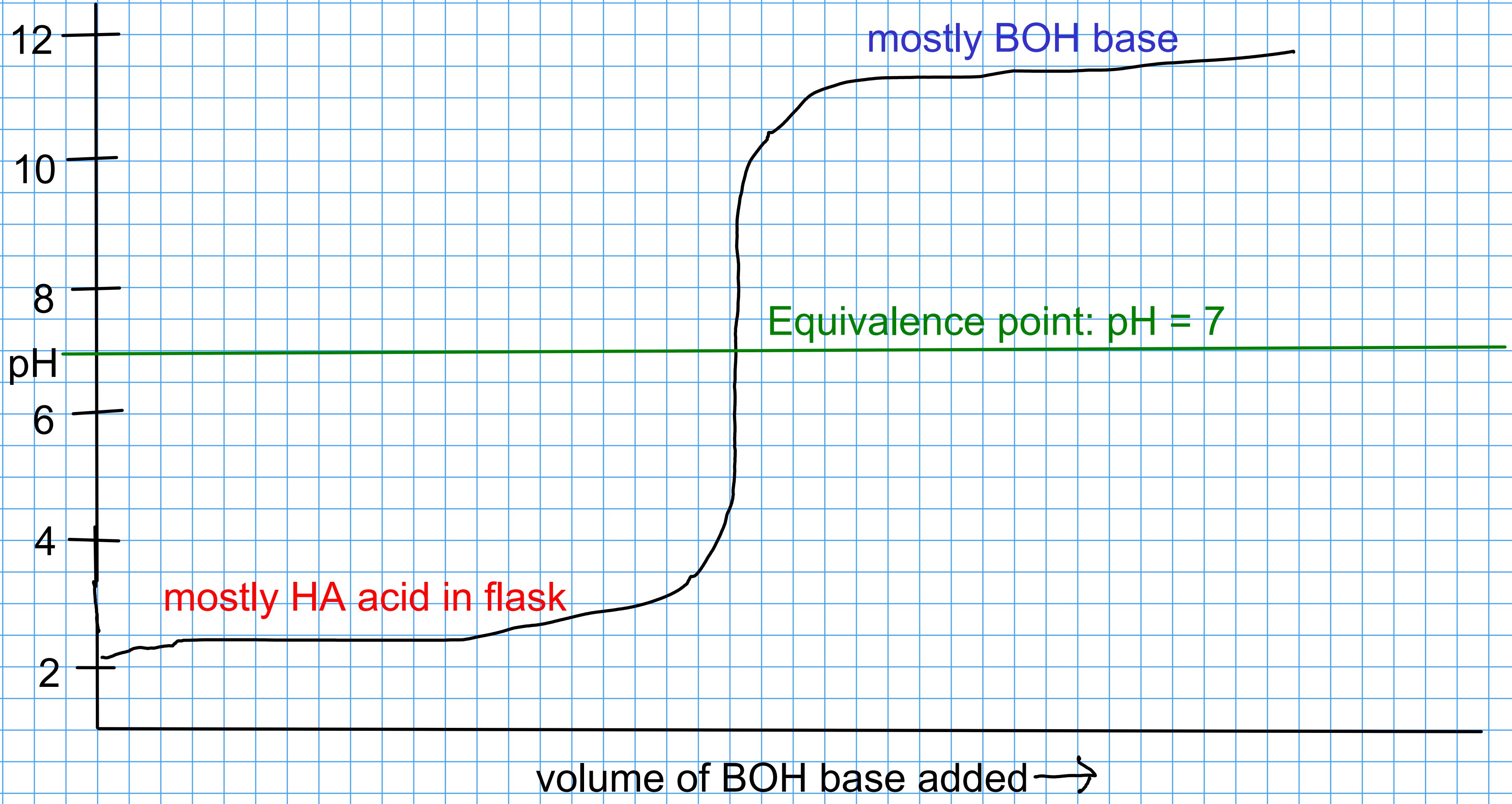
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

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

$\uparrow$ = 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!

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

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?

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

... 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>

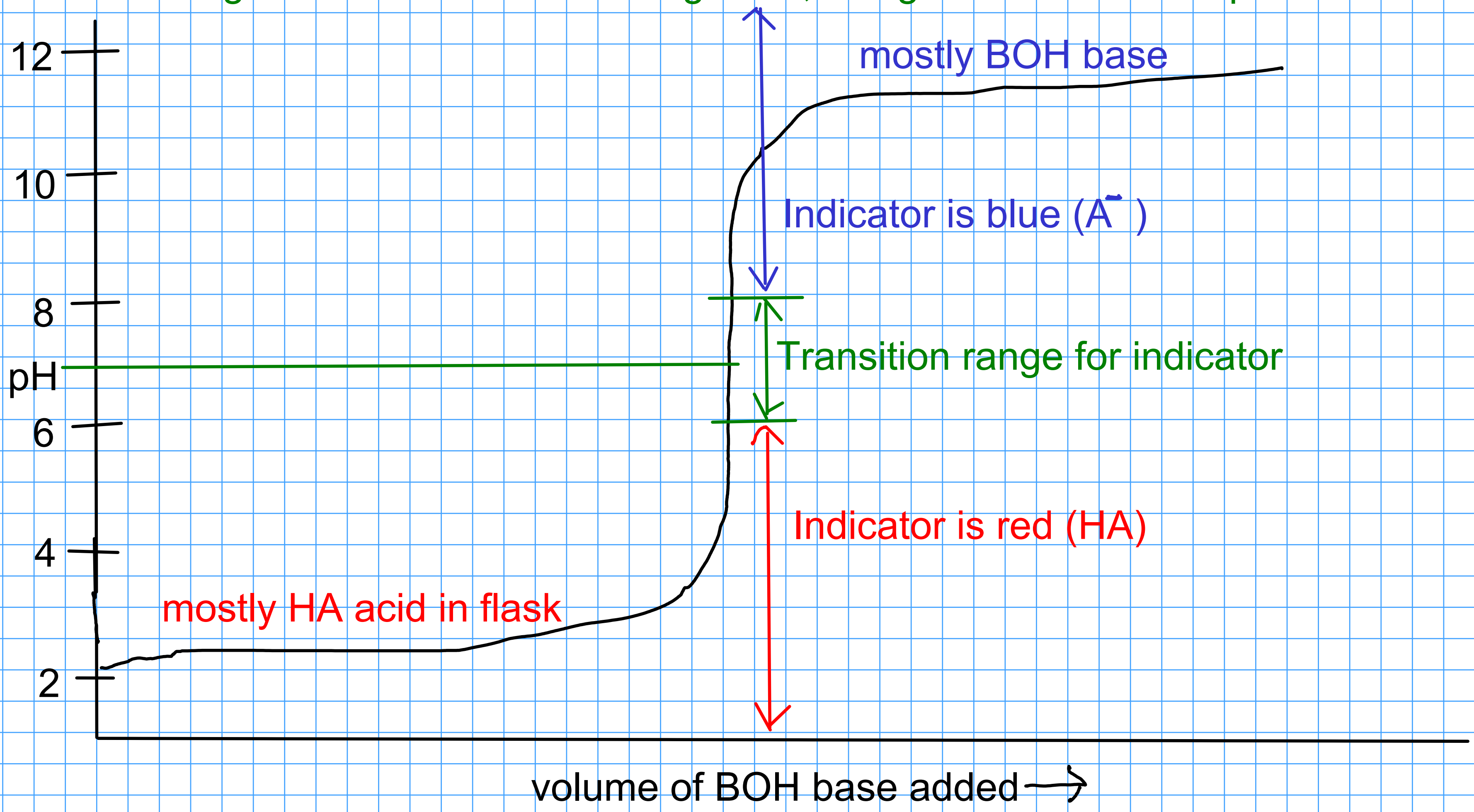
$$[A^-] >> [HA]$$

... 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!

$$NaC_2H_3O_2 \rightarrow Na^+ \quad \underbrace{C_2H_3O_2^-}_{\text{conjugate of ACETIC ACID}}$$

$pH > 7$

- 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

$$\underline{HA} + BOH \longrightarrow H_2O + B^+ + \underline{A^-}$$

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)

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

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 solution!

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

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 Ā , so their concentrations are now equal

So, pH = pKa at the halfway point

AT THE EQUIVALENCE POINT

... we have a solution that contains only Ā - so the pH is determined by

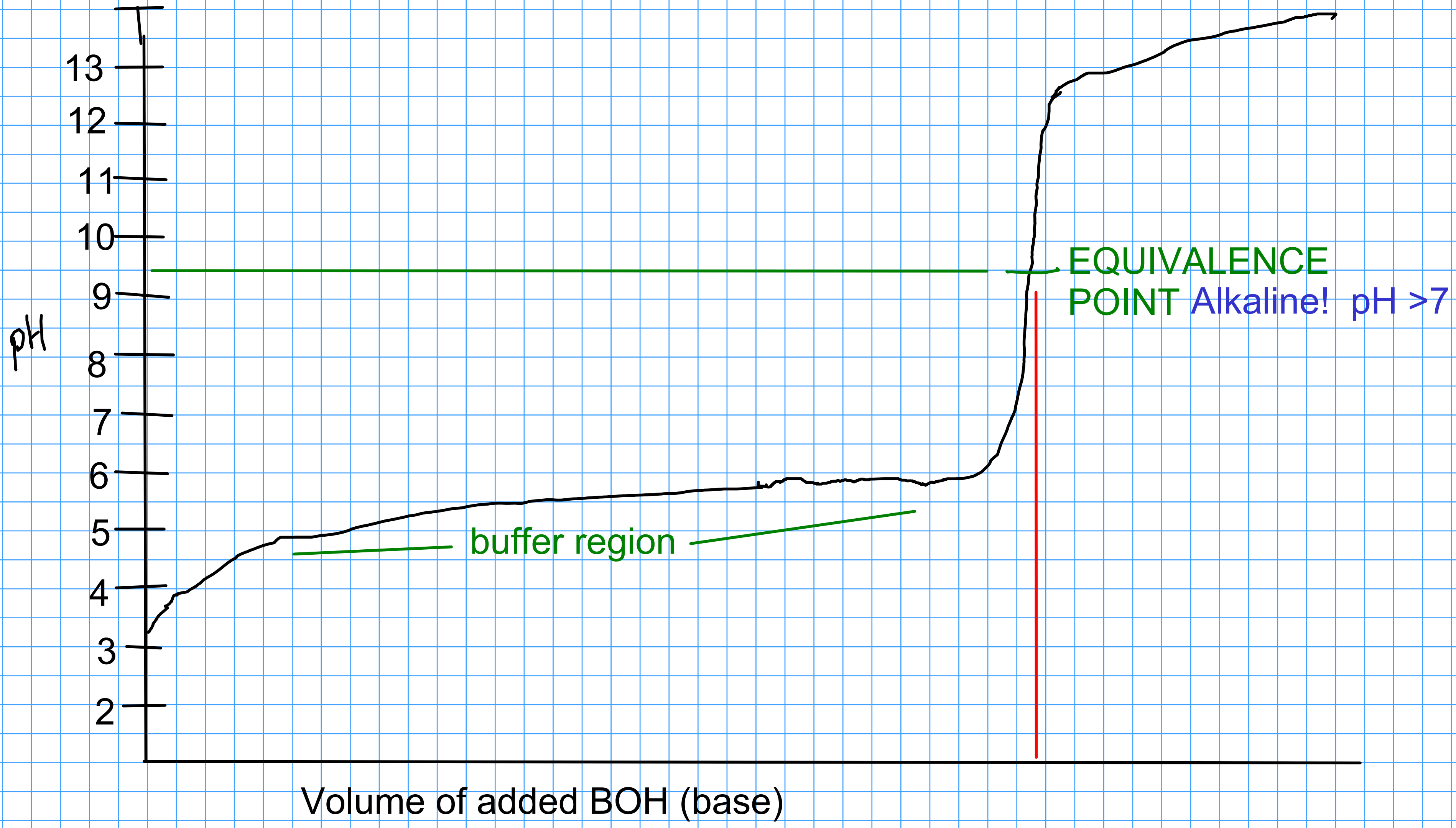
$$A^- + H_2O \rightleftharpoons HA + OH^-$$

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

basic pH!

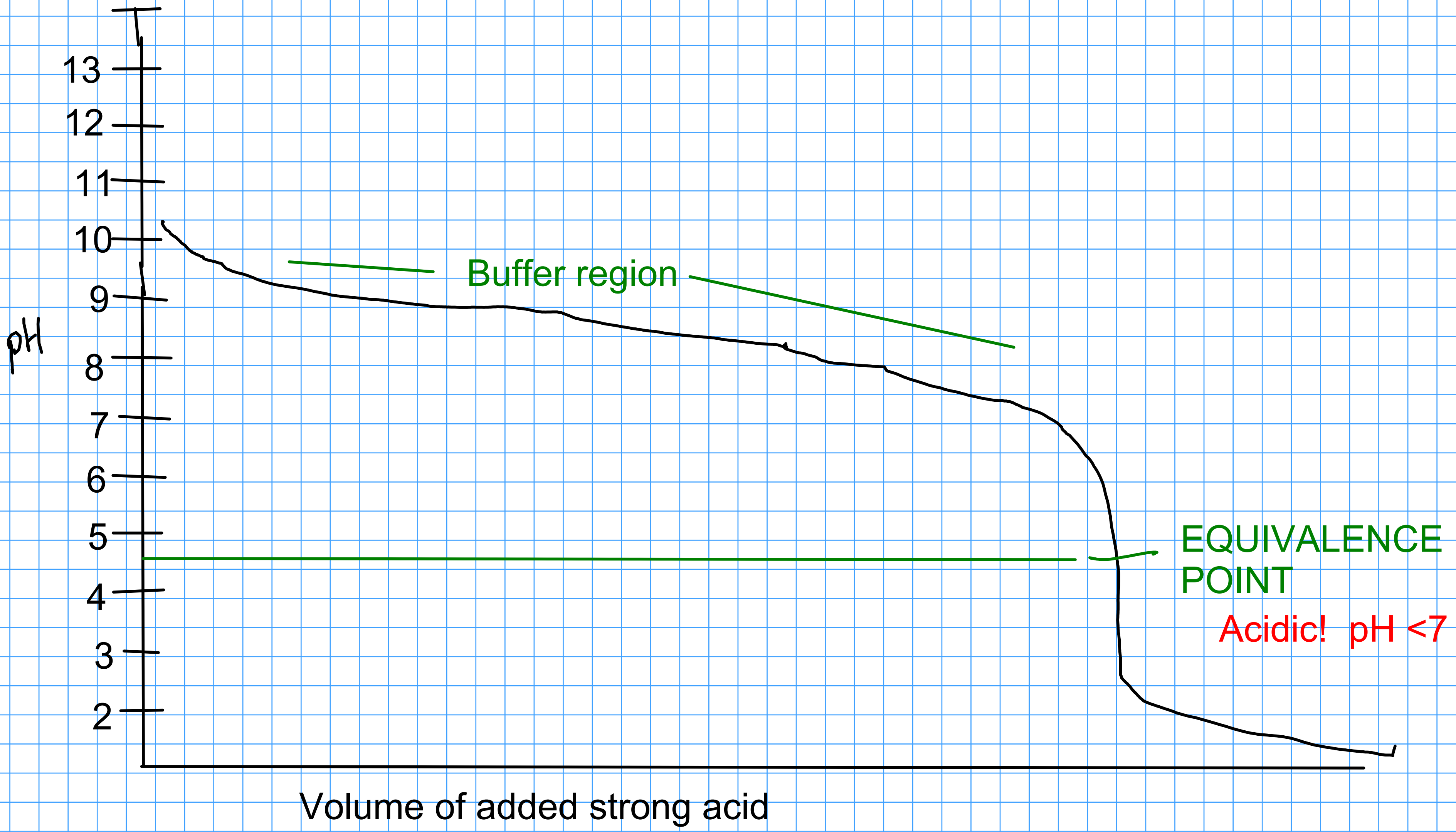
AFTER THE EQUIVALENCE POINT

... 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.



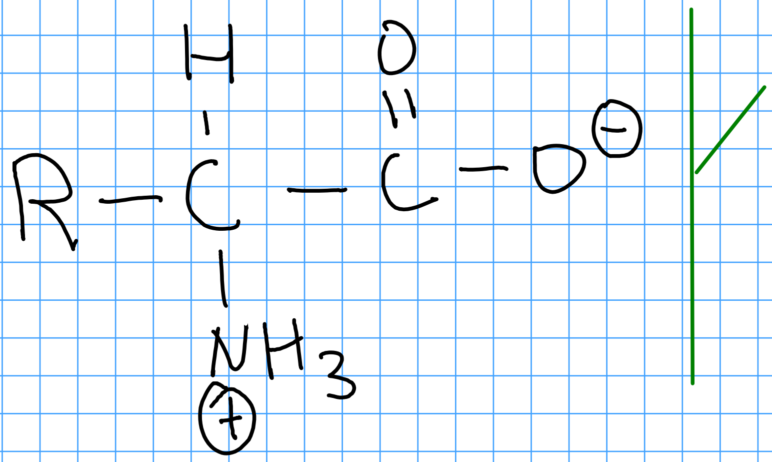
$B + HA \rightarrow BH^+ + A^-$

weak base

acidic salt

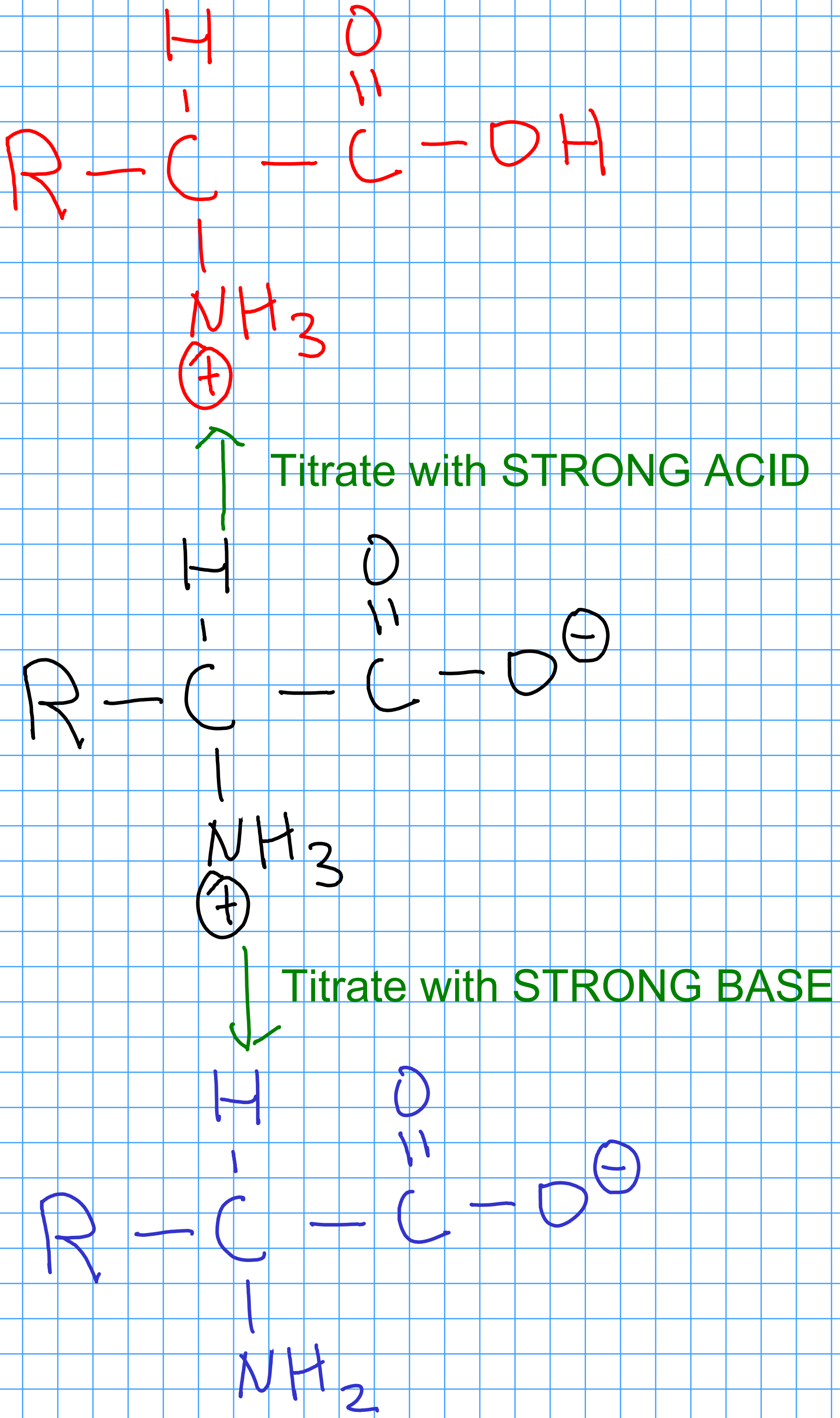
AMINO ACIDS

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



ZWITERION form - has both a positive and negative charge

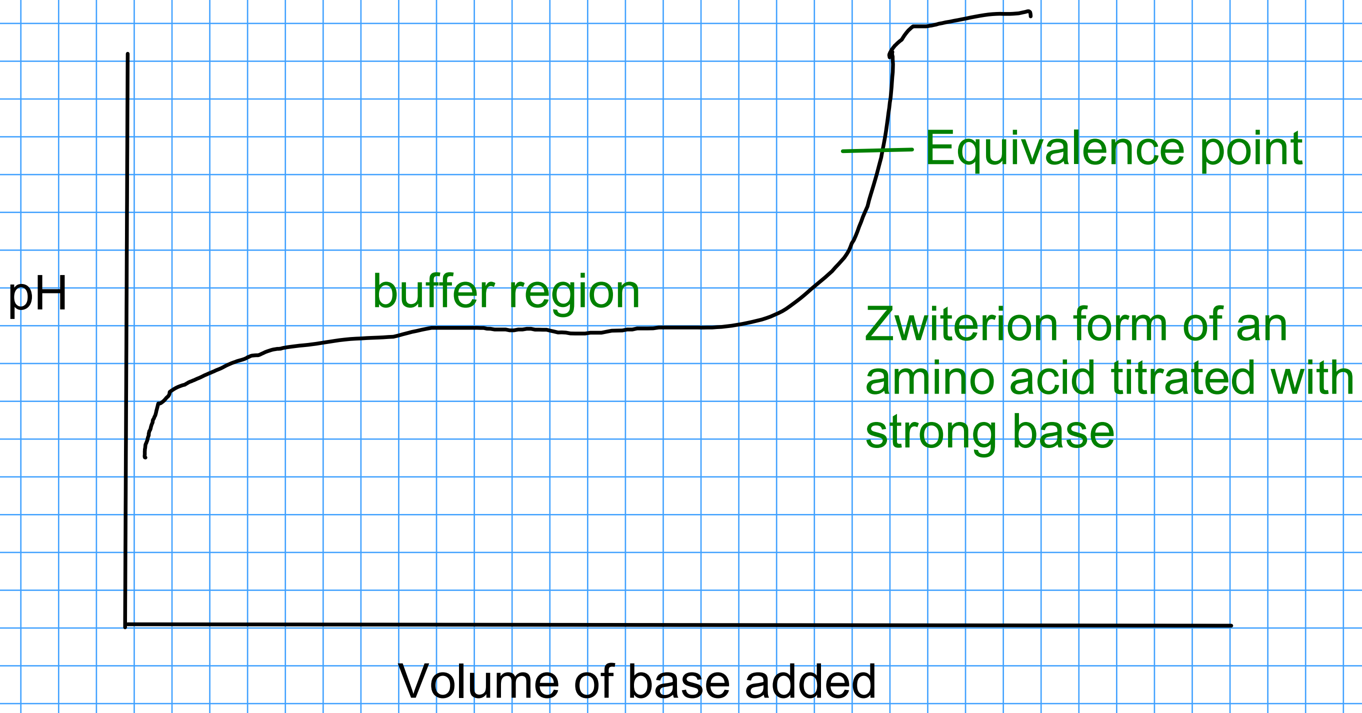
... titration? How do we titrate this? With a strong acid OR a strong base.



Titrate with STRONG ACID

Titrate with STRONG BASE

Sample titration curve for an amino acid titrated with strong base

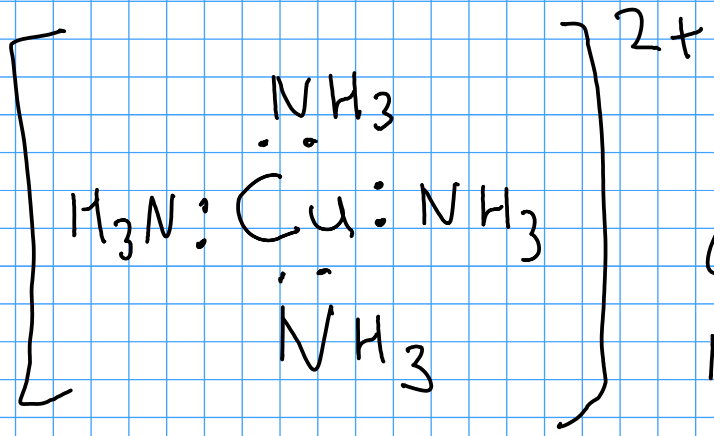


Looks similar to the titration of a regular weal acid with strong base!

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



$$\left[H_3N:\overset{\overset{NH_3}{\cdot\cdot}}{\underset{\underset{NH_3}{\cdot\cdot}}{Cu}}:NH_3 \right]^{2+}$$

Cu^{2+} metal center

NH_3 ligands

DEEP BLUE color in solution

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

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

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

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.

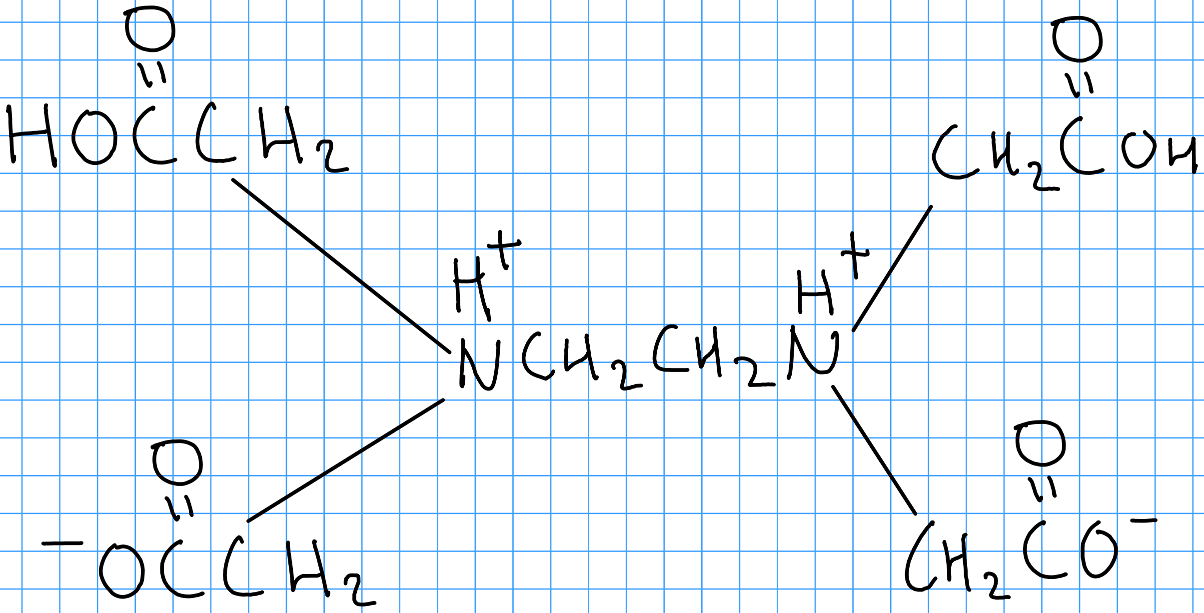
CHELATING AGENTS

- 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

$$H_4Y \rightleftharpoons H_3Y^- + H^+$$

$$H_3Y^- \rightleftharpoons H_2Y^{2-} + H^+$$

$$\boxed{H_2Y^{2-}} \rightleftharpoons HY^{3-} + H^+$$

$$HY^{3-} \rightleftharpoons \boxed{Y^{4-}} + H^+$$

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!

$$\text{Black T - Metal complex} \xrightarrow[\text{EDTA binds more tightly to the metal than Black T does!}]{\text{EDTA replaces Black T in the complex at the end of the titration}} \text{Black T (free)}$$

RED

BLUE

PRECIPITATION TITRATION

- A titration where analyte and titrant react to form a precipitate (insoluble compound), which is detected by some means other than weighing the precipitate.

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

- You may use the same reaction for both a gravimetric procedure and a precipitation titration. Why titrate? The main issue is time.

- Use an indicator that reacts with the silver ion (or the chloride ion), and when precipitation is complete, the indicator will change color (since there would now be either free silver ion or NO free chloride ion in solution)

- What factors affect precipitation titrations?

① - ACIDITY OF SOLUTION (pH)

② - Formation of complexes ex: Ag^+ complexes with NH_3

$Ag(NH_3)_2^+$ ... soluble

③ - Side reactions - other things that form precipitates with the titrant

pH AND PRECIPITATION

- Some precipitates are formed from the anoins of weak acids. These precipitates are affected by pH due the equilibrium of the anion and its acid.

$$MA(s) \rightleftharpoons M^+(aq) + \boxed{A^-}(aq)$$

Some
MA solid dissolves

$$\boxed{A^-} + H^+ \rightleftharpoons HA$$

Acid dissociation equilibrium ALSO involves part of the precipitate

So, the presence of acid will INCREASE the solubility of this weakly BASIC precipitate. The removal of A by the acid will cause more MA to dissolve in response. Le Chateleir's principle!

We can actually solve the equilbrium equations for the amount of MA that dissociates if we know how much of the acid is present, but it's often easier to control pH instead!

COMPLEXES AND PRECIPITATION

- Reactions involving metal ions in a precipitate can also influence the solubility of that precipitate. Many metal ions can form COMPLEXES with Lewis bases. These Lewis bases can thus interfere with the formation of precipitate!

$$MA(s) \rightleftharpoons \boxed{M^+}(aq) + A^-(aq)$$

MA dissolves to some extent

$$\boxed{M^+} + L \rightleftharpoons ML^+(aq)$$

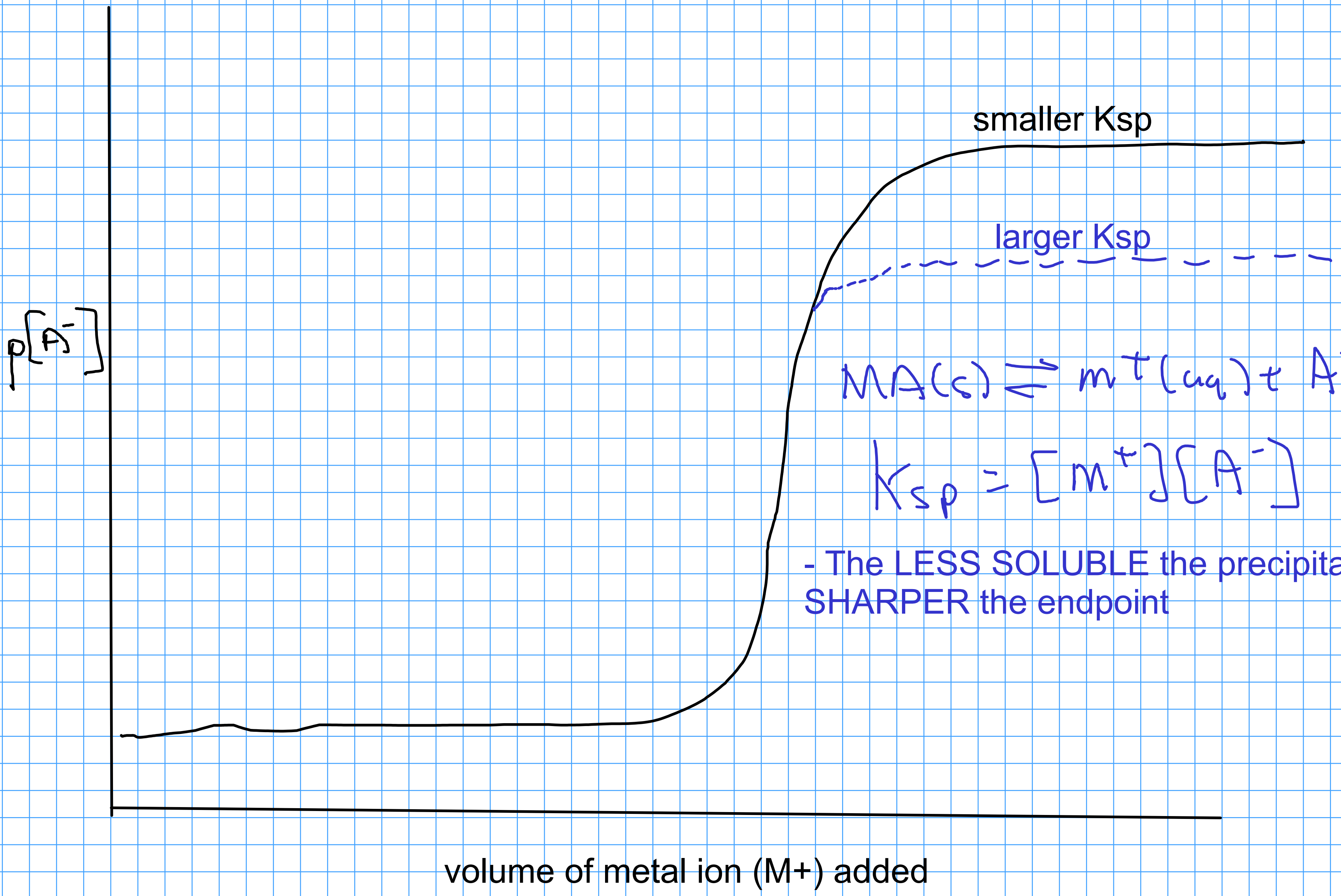
ligand (Lewis base)

soluble complex

Complex formation (Lewis acid/base reaction with the metal ion)

As with the presence of the acid, the presence of a complexing agent (ligand) will INCREASE the solubility of the precipitate by decreasing the concentration of free metal ion.

You can calculate the effect of the presence of complexing agent on the solubility, but it's often easier to avoid the problem in the first place by carefully choosing things like buffer composition.



$MA(s) \rightleftharpoons M^+(aq) + A^-(aq)$

$K_{sp} = [M^+][A^-]$

- The LESS SOLUBLE the precipitate, the SHARPER the endpoint

$M^+ + A^- \rightleftharpoons MA(s)$

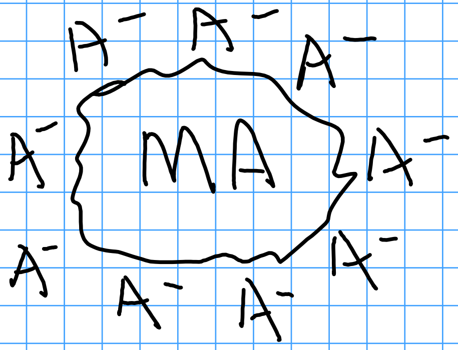
INDICATORS for precipitation titrations

Indicators that react with the titrant (metal ion M+)

- Another anion that precipitates with the metal ion to form a brightly colored precipitate. You need an anion that forms a more soluble (less stable) precipitate that the analyte

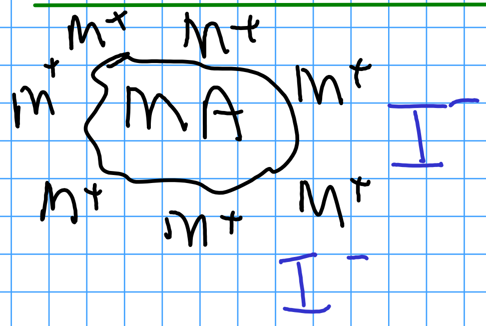
- A ligand that forms a colored complex with the metal ion after all the analyte has reacted. Again, this complex should be sufficiently UNSTABLE so that it doesn't form until after the analyte has precipitated.

Indicators that ADSORB (stick) to the precipitate



Initially, where there's lots of A- around, the forming precipitate tends to attract these A- ions, which cover the particles. The INDICATOR is ALSO an anion, I- ... it's repelled from all the A- ions that are stuck to the precipitate

I^-

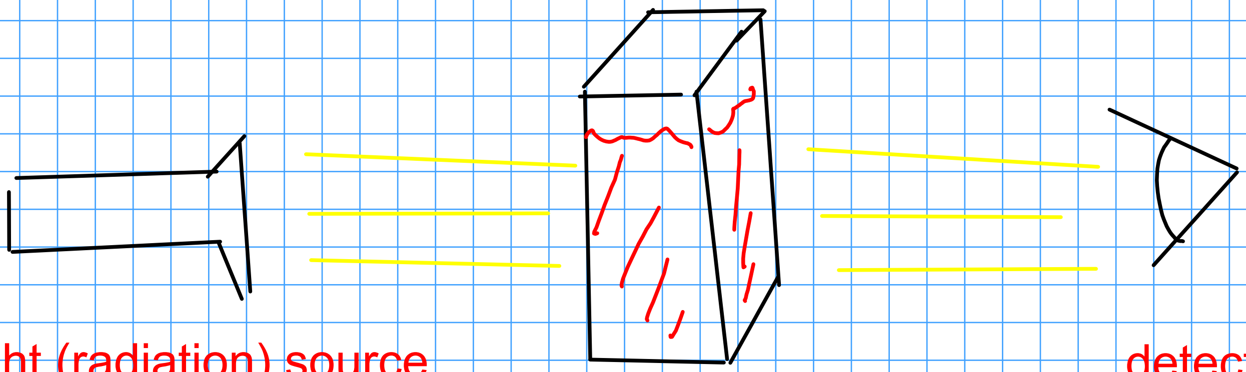


After the equivalence point, the precipitate particles are surrounded by metal ions, which do NOT repel the indicator. The indicator can now adsorb to the precipitate, resulting in a color change

SPECTROSCOPY

- SPECTROSCOPY - analysis of a sample by way of interaction with electromagnetic radiation

- SPECTROMETRY - quantitative determination of a sample by way of interaction with electromagnetic radiation



light (radiation) source
flashlight

sample
red Kool-Aid

detector
eye

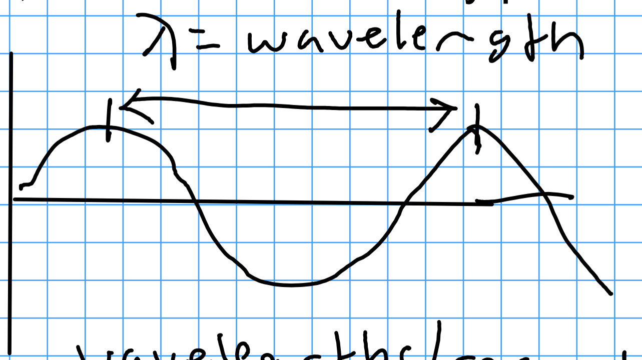
So what happens?

White light interacts with the Kool-Aid and you get a different color and intensity of light out of the other side (and into the eye)

- How does light interact with the Kool-Aid (or any other matter)

Light / EM radiation is composed of particles we call "photons", which are essentially packets of energy

$$E = \underbrace{h}_{\text{PLANCK'S CONSTANT}}\underbrace{\nu}_{\text{FREQUENCY}}$$



wavelengths/second = frequency = ν

Different colors of light have different energy content. This energy can interact with atoms and molecules.

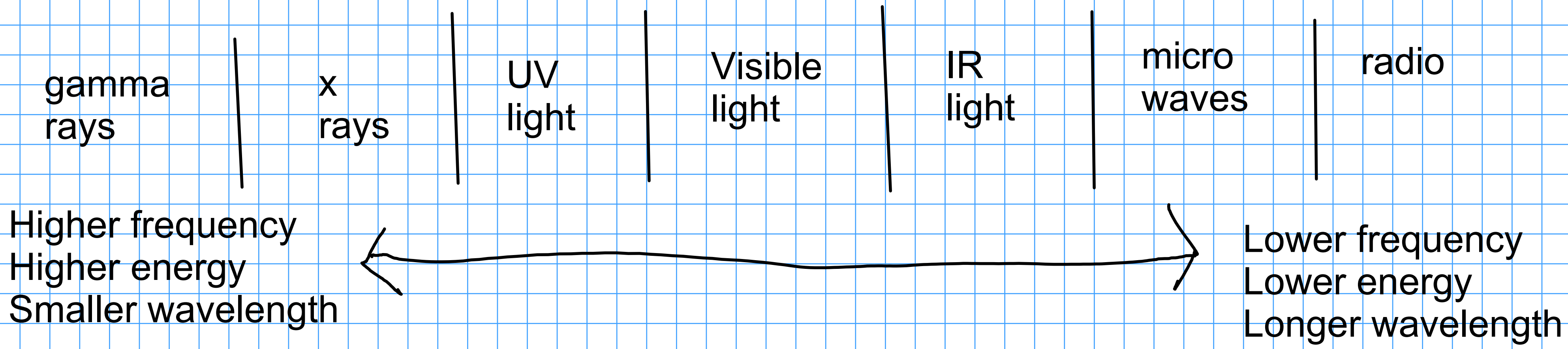
EM Spectrum

gamma rays	x rays	UV light	Visible light	IR light	micro waves	radio

Higher frequency
Higher energy
Smaller wavelength

↔

Lower frequency
Lower energy
Longer wavelength



gamma rays	x rays	UV light	Visible light	IR light	micro waves	radio

Higher frequency
Higher energy
Smaller wavelength

Lower frequency
Lower energy
Longer wavelength

X-rays: Cause ionization

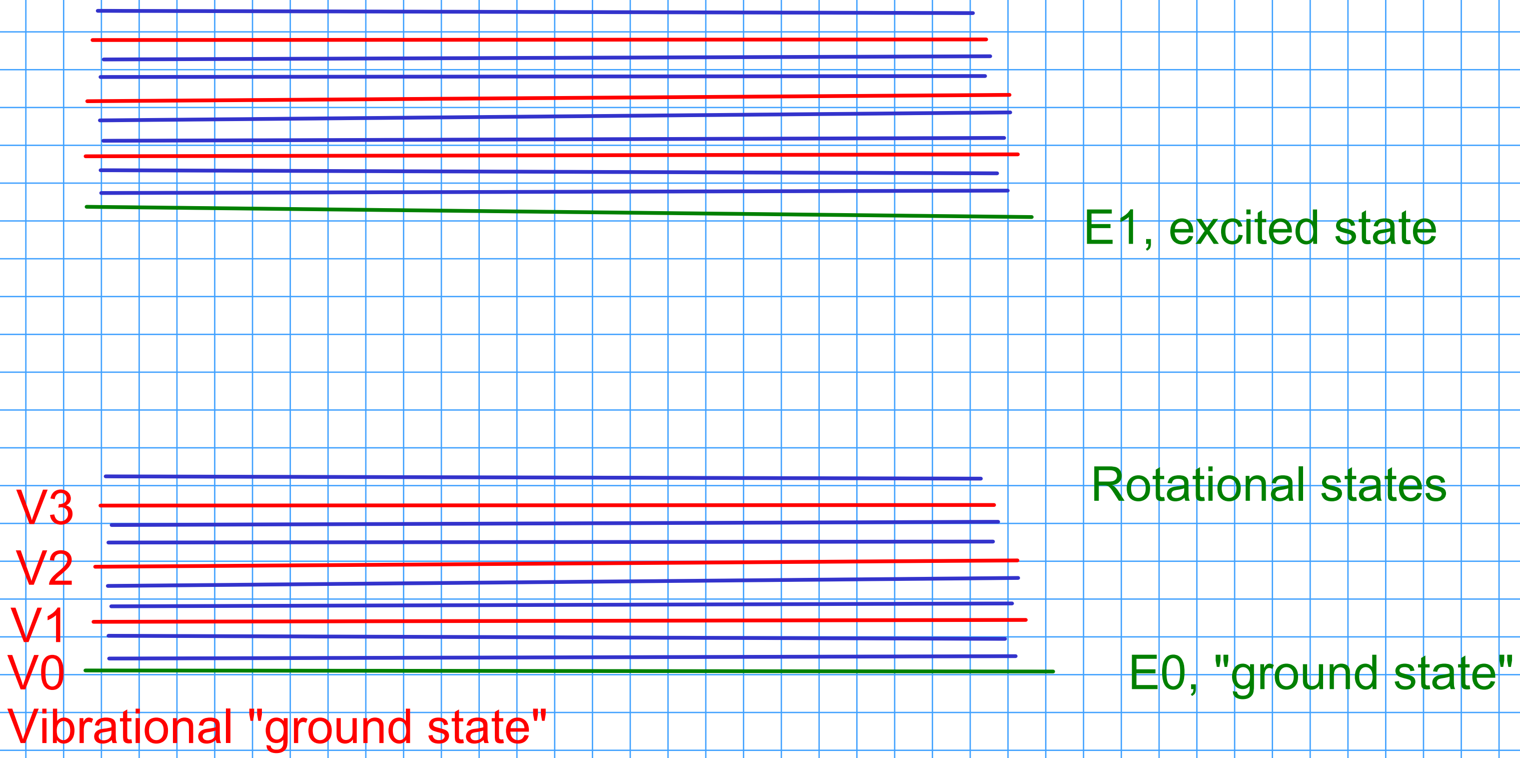
UV: Causes "electronic transitions" - electrons changing energy levels

Visible: Causes "electronic transitions" -electrons changing energy levels

IR: Causes molecular VIBRATION

Microwaves: Cause molecular ROTATIONS

Most ANALYTICAL (quantitative) spectrometry is of the UV/Visible (UV/VIS)



Electronic transitions - highest energy requirement. Involve UV/VIS light

Vibrational transitions - lower energy requirement. Involve IR light

Rotational transitions - lowest enegy requirement. Involve microwaves

How do we use these transitions to our benefit?

iNSTRUMENTATION

SOURCE → MONOCHROMETER → SAMPLE → DETECTOR → READOUT

Sources:

- depends on the type of radiation needed

VISIBLE: Tungsten filament incandescent bulb

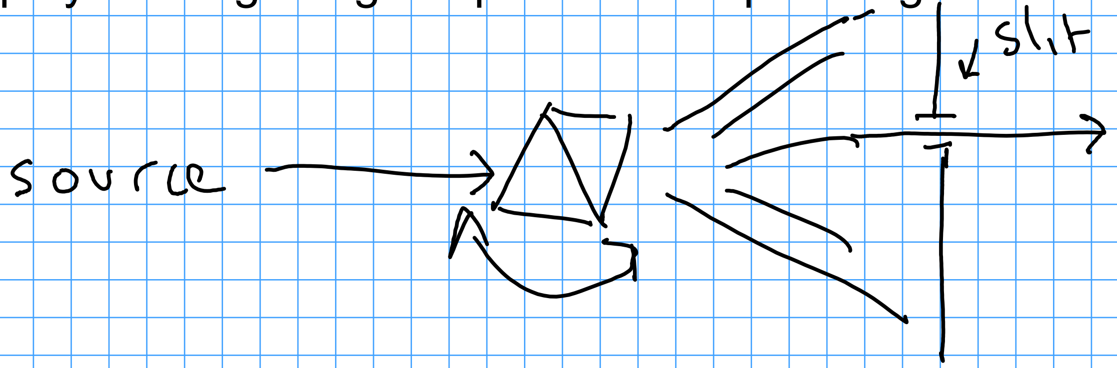
UV: Hydrogen or deuterium lamp

IR: "Globar". Essentially, a heated filament.

Monochrometer

-device that allows only radiation of a certain frequency to pass

- employ either gratings or prisms to disperse light over a slit, which blocks most of the dispersed light



Adjust the frequency of light by rotating prism or grating.

Samples:

- generally held in CELLS (usually samples are in liquid form)

- CELLS must be transparent to the kind of radiation used for the analysis

- Different techniques require different materials

  VIS: Glass or quartz
  UV: Quartz (but not glass)
  IR salt plates (various configurations) - NaCl, KBr