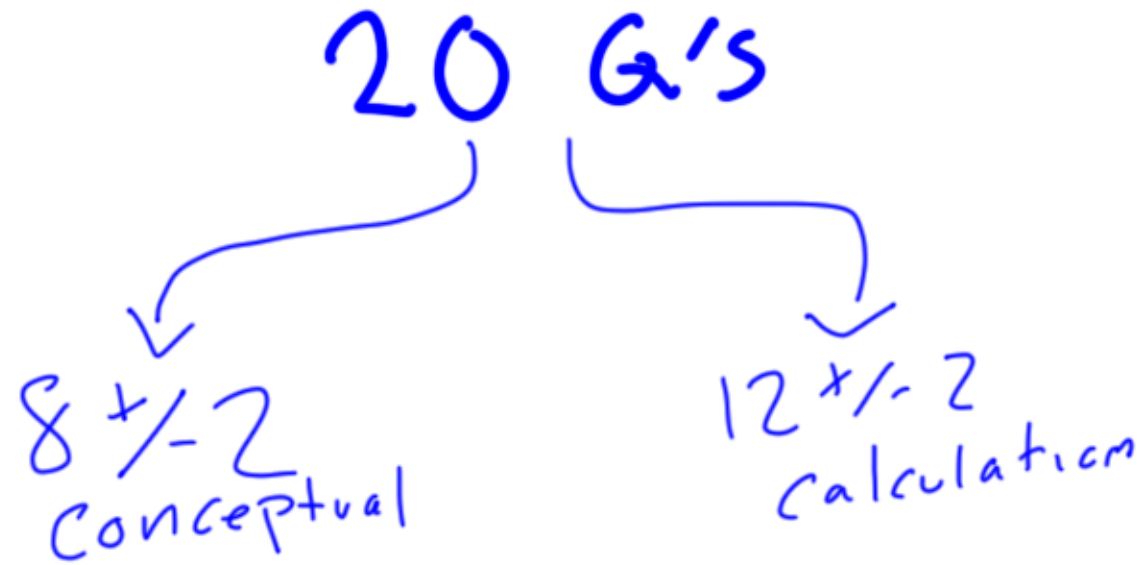


Dr. McCord's Exam 3 Page: <https://goo.gl/KR17Fu> <---- has some helpful equations, shortcuts, and all the learning outcomes

CH 302 – Unit 3 Exam 3

ACID BASE EQUILIBRIA, KSP

Exam 3 Breakdown



13 acid/base
+/- 1

7 KSP

+/- 1

Don't Study: Selective ppt.
Non-approximations

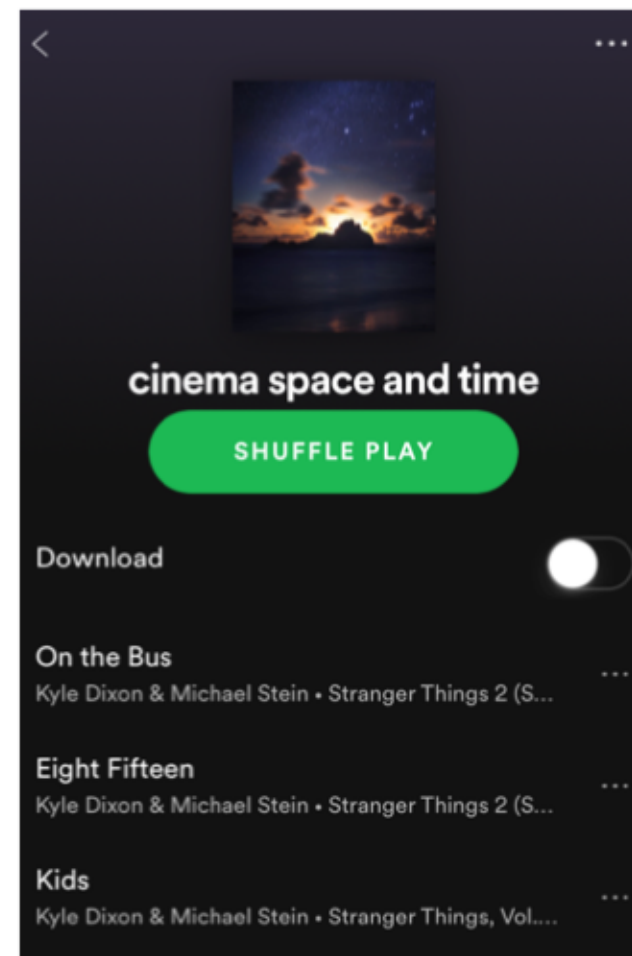
Fish Tank

Reminders:
strong acids + bases
P.T. Sheet +
KSPs, K_a 's / b 's
Indicators

Succeeding on Exam 3

Extra practice resources:

1. Work/ re-work all Canvas extra practice and McCord Buffer/Titration problems
2. Gchem has A LOT of worksheets on acid/bases for buffers through polyprotics; there is one good worksheet on Ksp
3. Sapling actually has a lot of good problems. Here are the essentials:
 - HW05: 1, 3, 4, 10, 11, 13, 14, 16, 17, 18, 20
 - HW06: 2, 4, 5, 6, 7, 8, 9, 11, 14, 15 (you can ignore 16, 17)
4. Lecture Notes / Doodles: spend plenty of time to fully understand ALL lecture examples (especially REEF questions)



Acids & Bases Pt. II

NEUTRALIZATION REACTIONS, BUFFERS, TITRATIONS, POLYPROTICS

Buffer and Titration Terms

- ✓ **Buffer:** a solution that consists of a weak acid and its salt (conjugate base) or a weak base and its salt (conjugate acid). The solution will resist large changes in pH.
- ✓ **The common ion effect:** the overall solubility of a weak electrolyte decreases when one of its ions are already in solution. Think adding $\text{CH}_3\text{COOH}(\text{aq})$ to $\text{NaCH}_3\text{COO}(\text{aq})$. Both the CH_3COOH and NaCH_3COO share the common ion of acetate; therefore, the degree to which CH_3COOH dissociates goes down (pH goes up!). **Remember, this is the actual mechanism of a buffer.**
dissociation
- **Buffer zone:** +/- one pH unit of the pKa (pKa is where there is an ideal 1:1 ratio of $\text{HA}:\text{A}^-$)
- **Buffer capacity:** the amount (either in grams, moles, or volume) of titrant needed to shift the pH out of the buffer zone from the pKa
- **Titration:** the precise addition of titrant to analyte to measure the pH change of the analyte solution; used to characterize the analyte solution (identify the concentration or even identity of the analyte)
- **Titrant:** the strong acid or base with a known concentration added to the analyte
- **Analyte:** the solution to which the titration is added; typically an unknown concentration

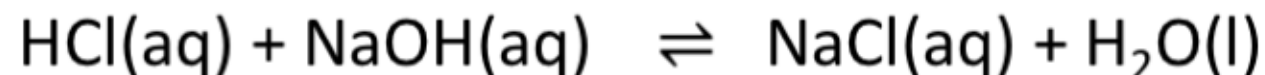
Neutralization Reactions: Salts

- The product of a neutralization reaction is a salt. In acid/base chemistry, your salt can be neutral, acidic, or basic depending on the reaction.

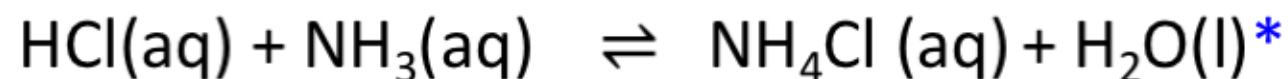
- GENERIC REACTION (very helpful):



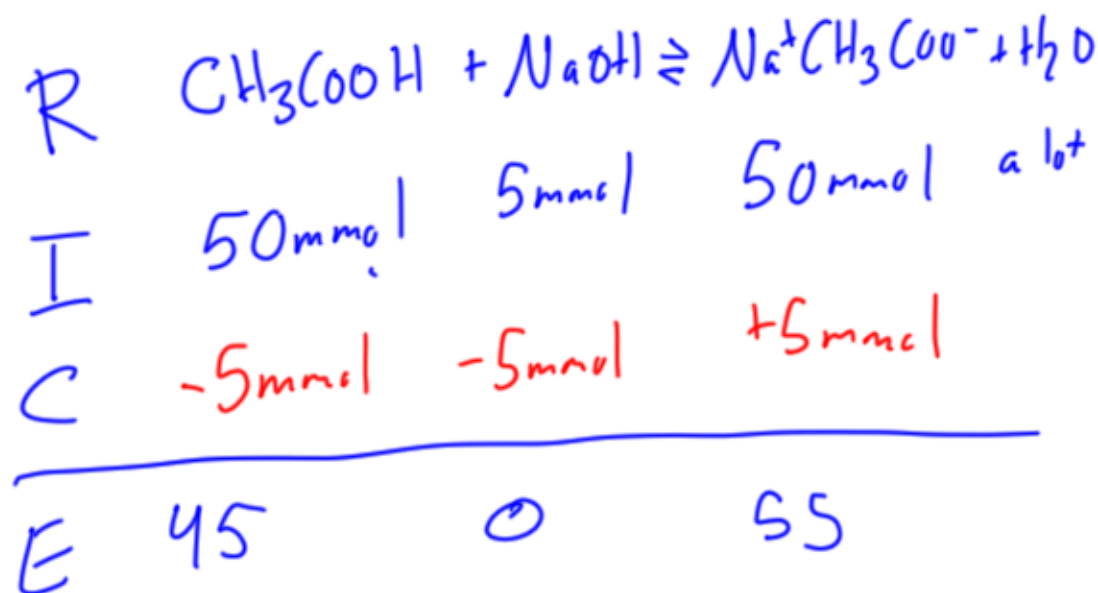
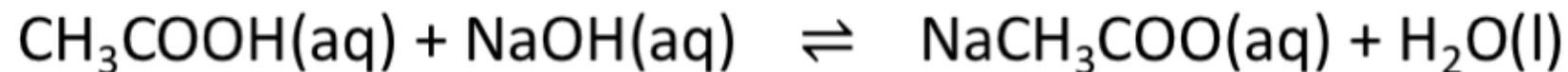
- Strong Acid, Strong Base: results in a neutral salt



- Strong Acid to weak base: results in an acidic salt



- Strong base to weak acid: results in a basic salt



Buffers: Conceptual, Calculation

$$\frac{\text{mol } A^-}{\text{mol } HA}$$

- The purpose of a buffer is to resist changes in pH.

Here's the idea:

- If you add 0.1 mole of NaOH to pure water, you are adding 0.1 mole of OH^- . This results in a pretty big change in pH
- If you add 0.1 mole of NaOH to a solution of acetic acid and sodium acetate, you are just creating 0.1 mole more of sodium acetate. **This barely increases the pH**

$$\text{pH} = \text{pK}_a + \log\left(\frac{A^-}{HA}\right)$$

~~$$\text{pOH} = \text{pK}_b + \log\left(\frac{BH^+}{B}\right)$$~~

- By definition, a buffer is made of:
 - A weak acid and its salt (conjugate base)
 - A weak base and its salt (conjugate acid)

By definition, a buffer is effective when:

- The pH is within about +/- 1 of the pK_a or pK_b
- This favorable ratio of the weak acid : salt (or weak base : salt) is known as the "Buffer Zone"

By definition, a buffer is made by:

- Mixing a weak acid and a strong base
 - Mixing a weak base and a strong acid
- (in an acceptable ratio)

2 : 1

What is a buffer and what is not:

- A buffer only functions in the "Buffer Zone," which is +/- 1 pH point of the pK_a (for a weak acid buffer) or pK_b (generally the standard for a weak base buffer).
- Based on this definition, a buffer must be composed of a weak acid + strong base; weak base + strong acid.

Ideal Buffer $HA : A^-$

Example Question: Which of the following will form an ideal buffer at ~~neutral~~ $pH = 6.37$?

- a. 0.1 M, 100 mL NaOH + 0.1 M, 100 mL Carbonic Acid, $pK_{a1} = 6.37 \Rightarrow 100\% A^-$
- b. 0.05 M, 100 mL NaOH + 0.1 M, 100 mL Hydrofluoric Acid, $pK_a = 3.20$ WRONG PH
- c. 0.05 M, 100 mL NaOH + 0.1 M, 100 mL Carbonic Acid, $pK_{a1} = 6.37$
- d. 0.06 M, 100 mL NaOH + 0.1 M, 100 mL Carbonic Acid, $pK_{a1} = 6.37$

Adjusting the pH

- When in doubt, use a RICE table for the neutralization reaction! But here's what is happening mathematically... Consider a solution that consists of 50 mmol HA and 50 mmol A⁻ (it is at half eq point):

- When you add "x" moles of strong acid:

$$\text{pH} = \text{pK}_a + \log \left(\frac{50 \text{ mmol A}^- - x}{50 \text{ mol HA} + x} \right)$$

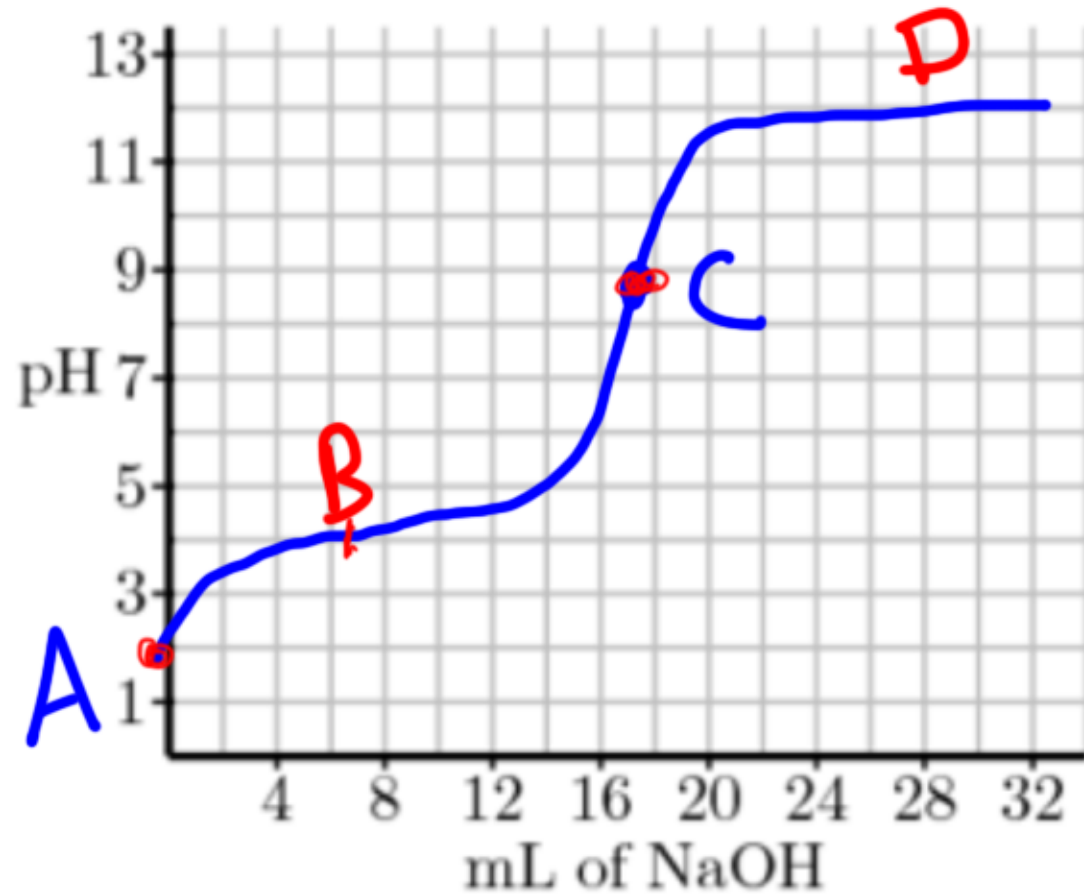
- When you add "y" moles of a strong base:

$$\text{pH} = \text{pK}_a + \log \left(\frac{50 \text{ mmol A}^- + y}{50 \text{ mmol HA} - y} \right)$$

- When you add "x" moles of strong acid AND "y" moles of a strong base:

$$\text{pH} = \text{pK}_a + \log \left(\frac{50 + y - x}{50 + x - y} \right)$$

Titration of Buffered Solutions



A) Before you have started:

Calculate pH using the approximation formula or using $K_a = \frac{[H^+][A^-]}{[HA]}$.

B) Within the buffer zone:

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

Also: when $pK_a = pH$ (middle of the buffer zone)

C) At the equivalence point:

You only have the salt of your weak acid in solution. Use $K_w = K_a K_b$, then solve for $[OH^-]$, pOH , then convert to pH

D) After the equivalence point:

Find the pH using the excess base in solution

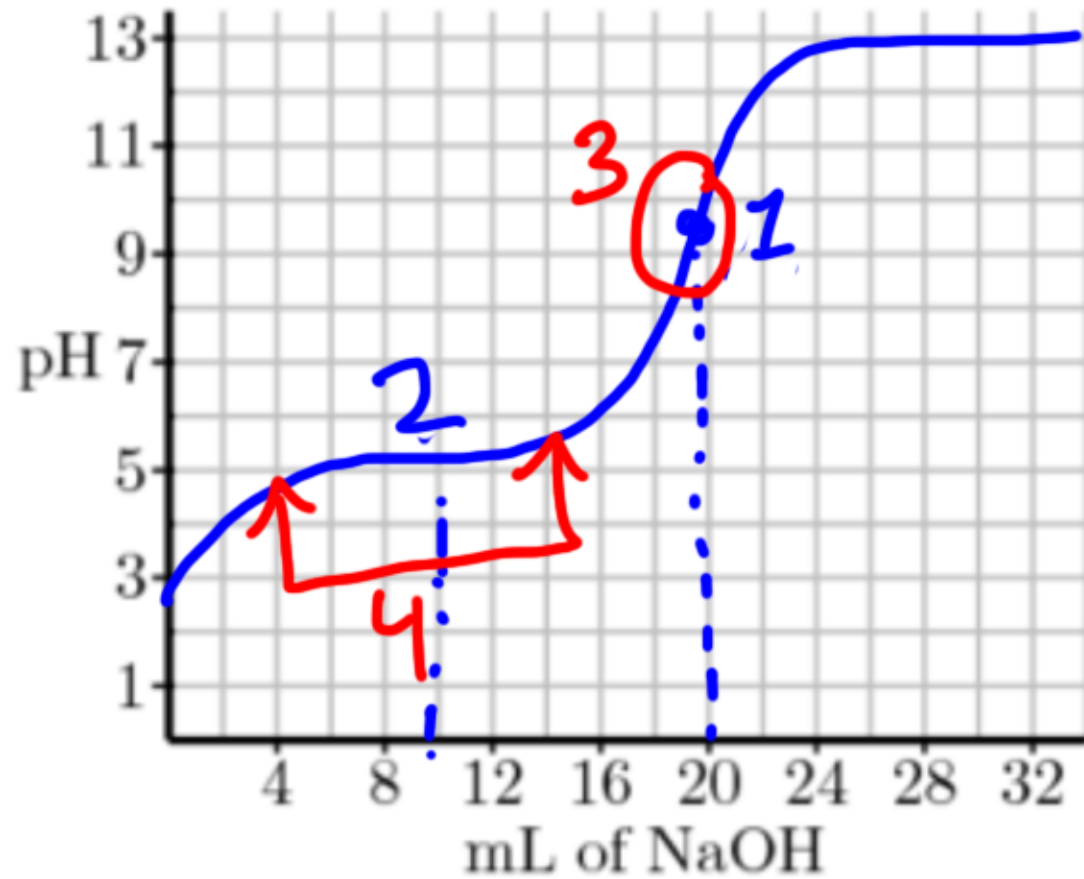
$$pOH = -\log ([\text{excess base}])$$

$$pH = 14 - pOH$$

Points to know:

- Equivalence point
- End Point
- Half-equivalence point
- Buffer Zone

Titration Curve: Points to Know



1) Equivalence Point

Full neutralization:
moles titrant = moles analyte
Ex: 100% conjugate base (A^-)

2) Half-Equivalence Point

$pH = pK_a$
moles HA = moles A^-
Ex: HALF neutralized (1:1, HA: A^-)
Ideal Buffer

3) End Point

Where you indicator changes color
OBSERVATIONAL depiction of equivalent point

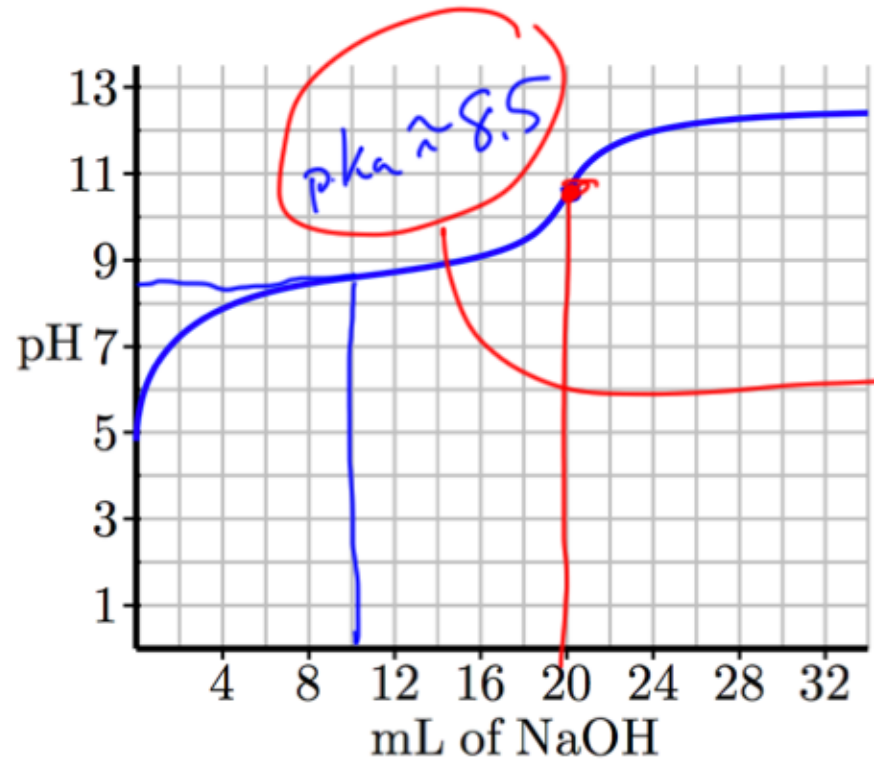
4) Buffer Zone

± 1 pH unit of the pK_a

Know
the
difference

The Titration Curve

Analyze the following graph involving 0.065 M NaOH titrating a 100 mL weak acid. What are the key points and what is the significance of each?



mols NaOH = mols HA
initial concentration
 $[HA] = \frac{\text{mols HA}}{0.100L}$

1st \Rightarrow eq pt, 20 mL NaOH
pH = 10.5

pKa \rightarrow Ka \rightarrow identify analyte

Titrations: Indicators

The role of an indicator in a titration experiment is to change color at the equivalence point of the analyte.

What does this mean:

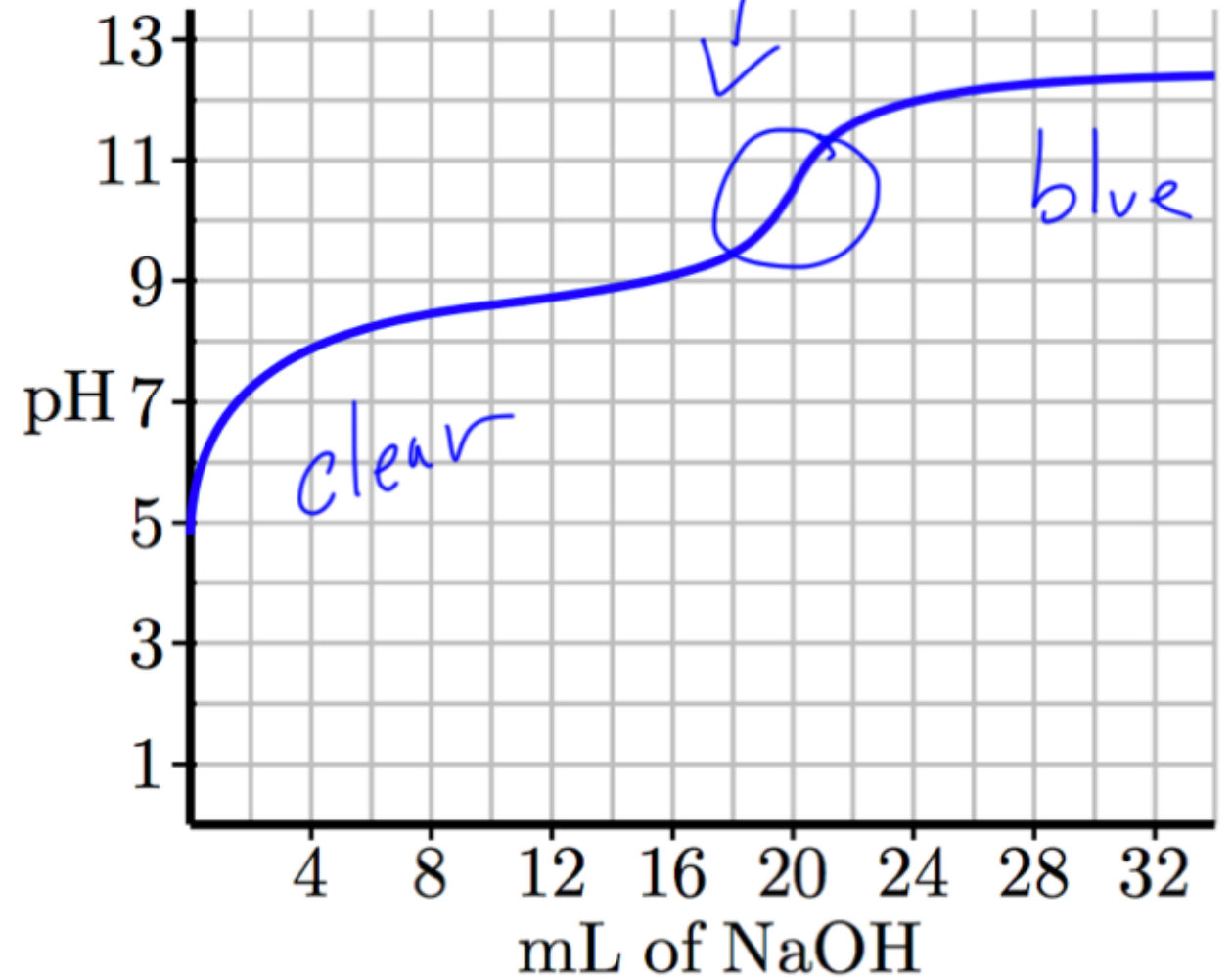
The pH of the equivalence point for the analyte should be close to the pKa of the indicator.

The color change range (buffer zone) of the indicator includes the pH of the equivalence point for the analyte.

Consider the same titration curve with the thymolphthalein indicator:

pKa = 9.9

Color change region = 9.4-10.6



Complete Neutralizations

It is important to remember that a titration is just a controlled neutralization reaction

- Full neutralizations take you all the way to the **equivalence point** (remember the question on Exam 2), and are still very important for this exam.
- **The easiest way to quantify complete neutralizations is with the equation below:**

$$C_1V_1 = C_2V_2$$

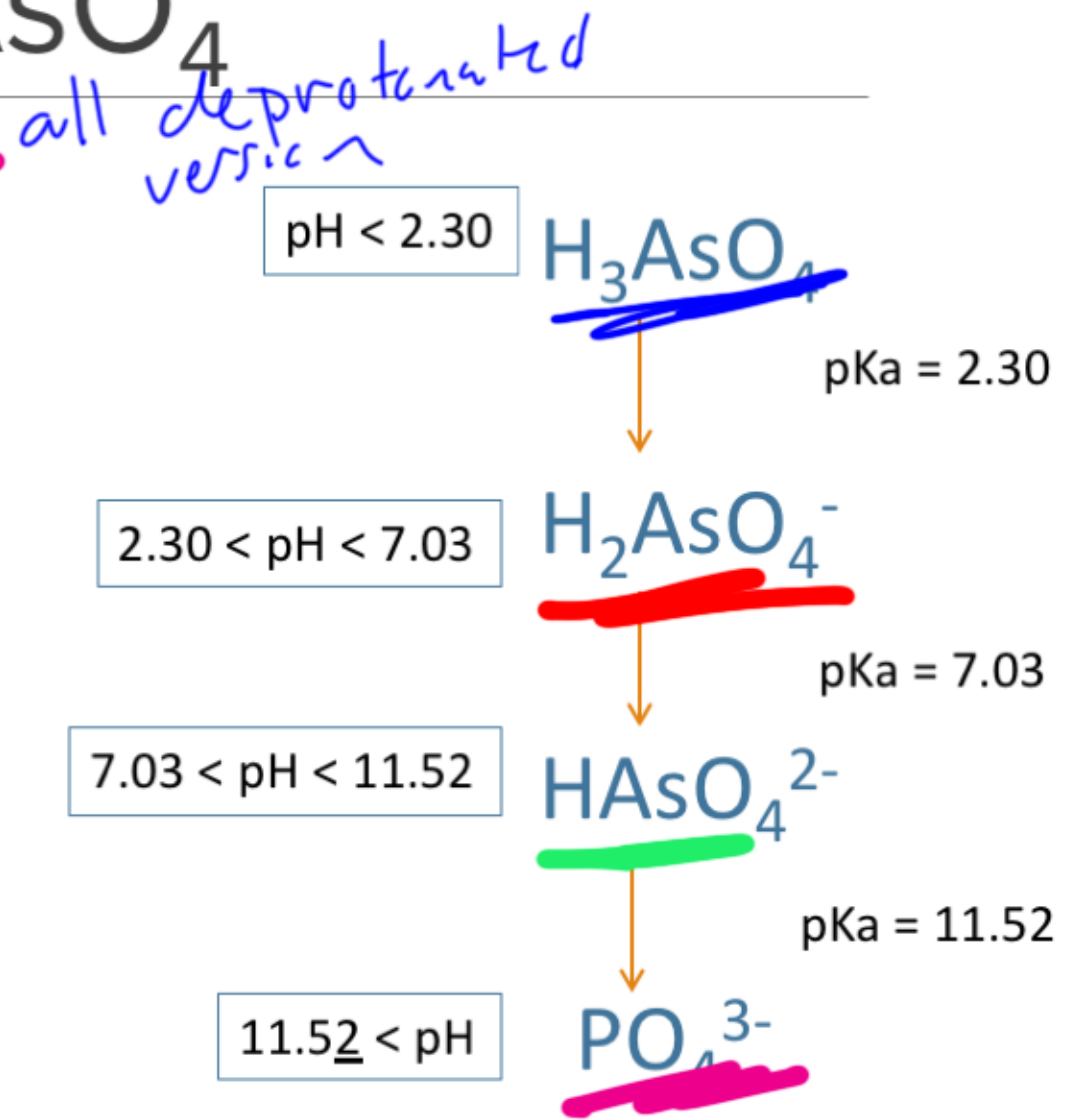
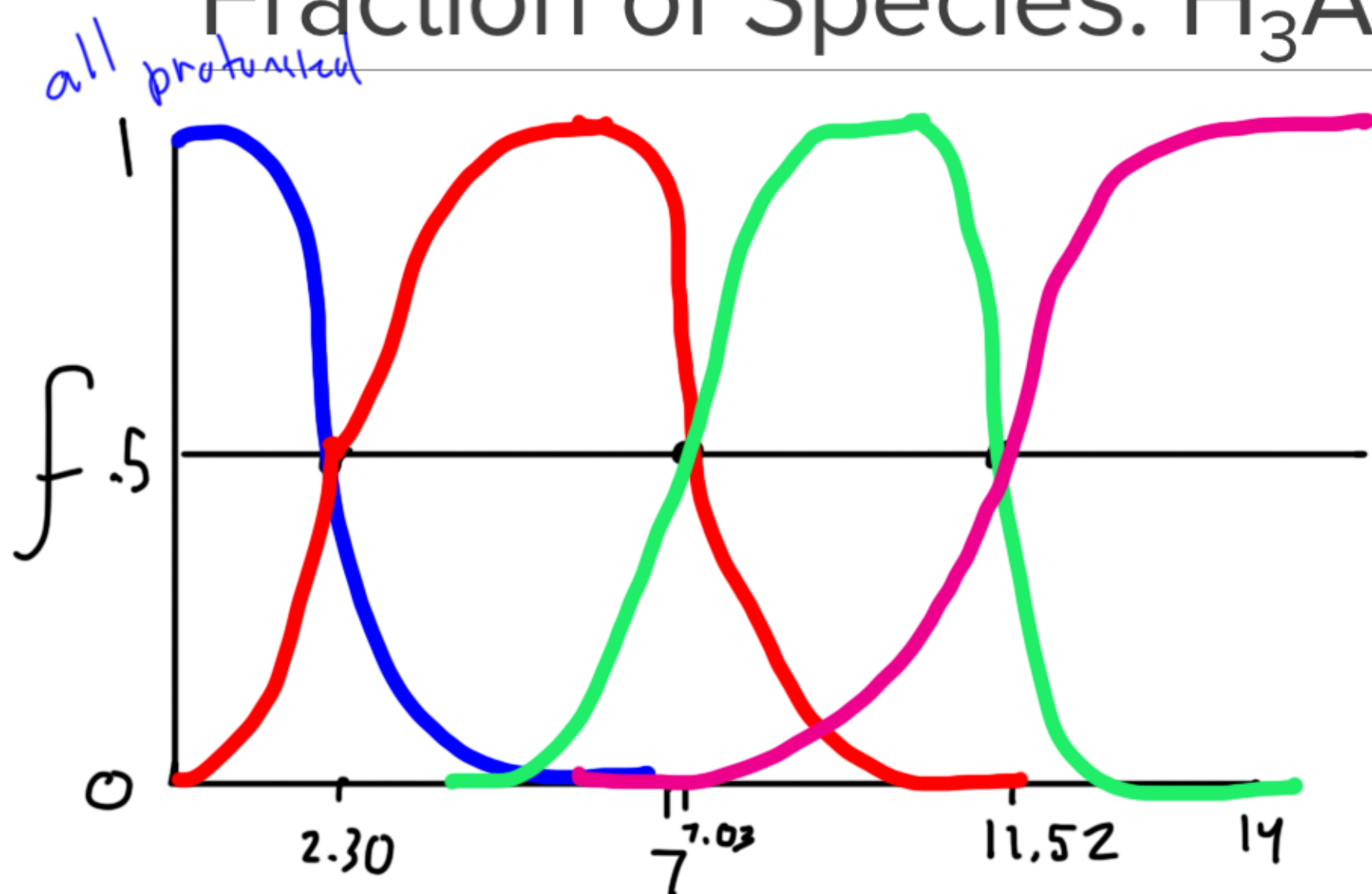
Protonated vs. Deprotonated States

- A molecule is **protonated** when the acidic proton is **ON** the molecule
 - Think HA or BH⁺ in a titration experiment $pH < pK_a$
- A molecule is **deprotonated** when the acidic proton is **OFF** the molecule
 - Think A⁻ or B in a titration experiment $pH > pK_a$
- As you might expect, a buffer contains a mix of the **protonated** and **deprotonated** states
- Whether a molecule is protonated or deprotonated depends on the relationship between the **pH of solution** and the **pK_a of the molecule**.

Conceptualizing Protonation States

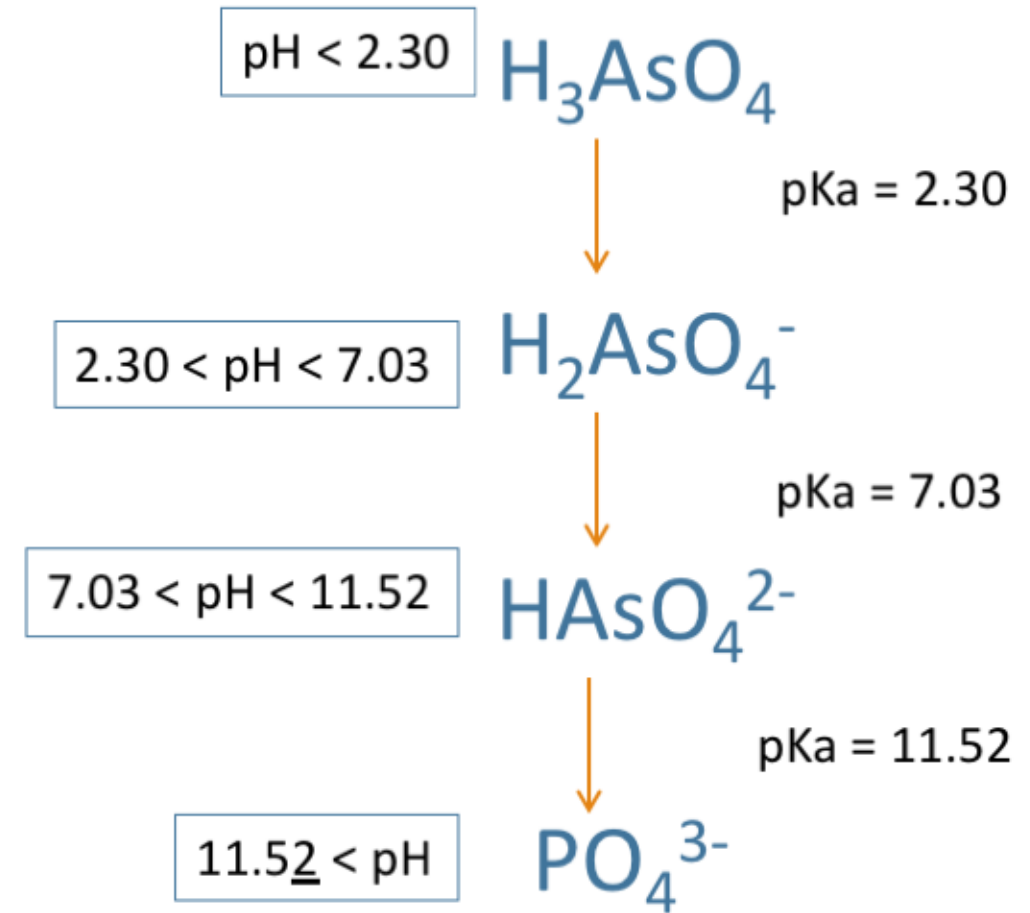
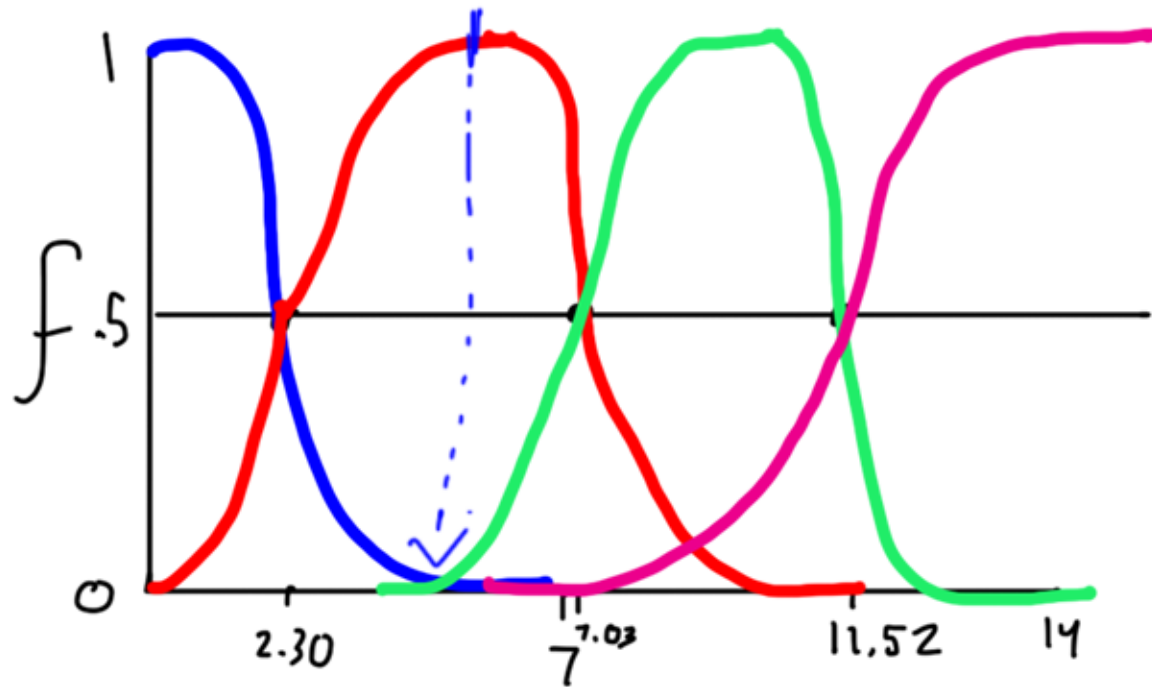
- For weak acids, especially for organic compounds and polyprotic acids, you can determine the “protonation-state” of your molecule at any given pH.
- A few simple rules go a long way with answering these types of questions:
 1. **Think about your molecule.** Your pK_a represents the pH where you have equal protonated and deprotonated states ($[HA]=[A^-]$).
 2. **Think about your environment.** The pH compared to the pK_a will tell you whether your molecule is protonated or deprotonated.
 3. If $pH < pK_a$; you have too many hydrogen ions in solution for it to be favorable for a hydrogen ion on your molecule to “pop off”
 - **Think about it: when the environment is more acidic, it is more “proton-donating,”**
 4. If $pH > pK_a$; the environment around your molecule is thirsty for hydrogen ions, so it is favorable for a hydrogen ion on your molecule to pop off
 - **Think about it: when the environment is more basic, it is more “proton-accepting.”**

Fraction of Species: H_3AsO_4





Fraction of Species: H_3AsO_4

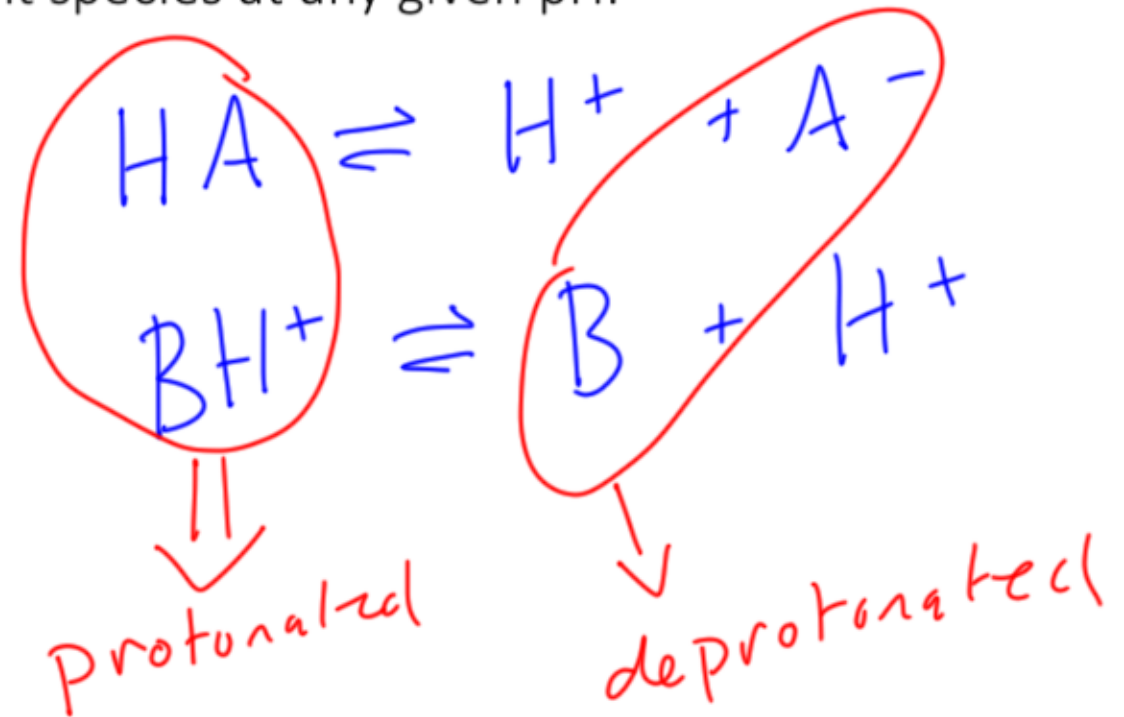
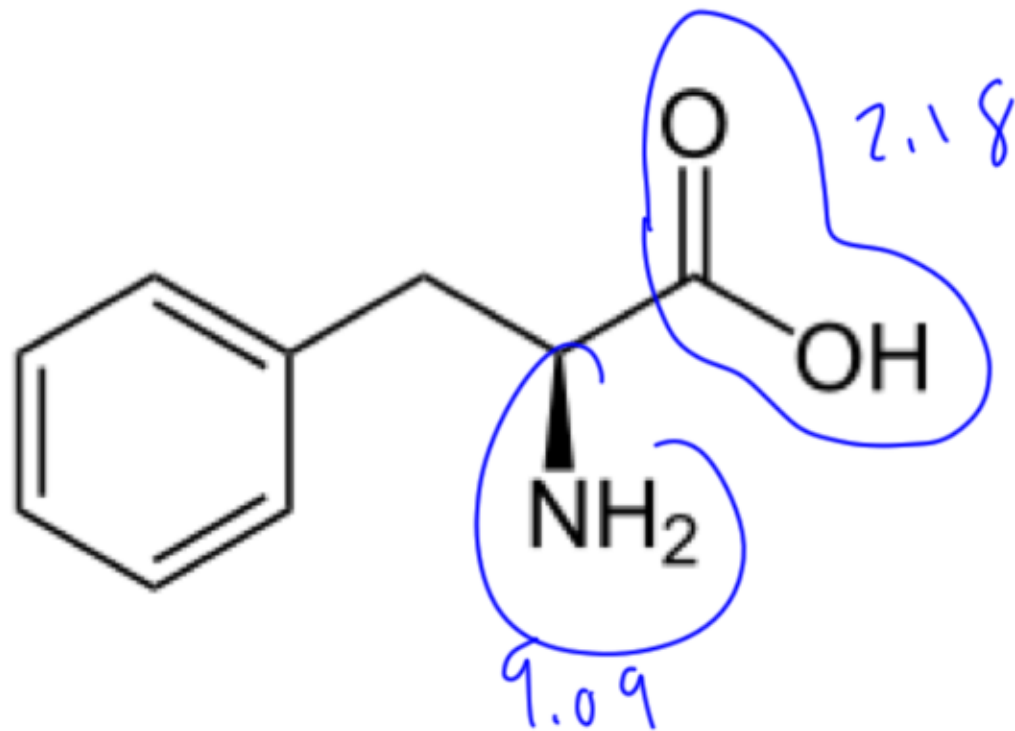


The pH of any "intermediate species" is given by the formula:

$$\text{pH} = \frac{\text{pKa}_1 + \text{pKa}_2}{2}$$

Big-ass Molecule

Consider the molecule below, which is the big-ass molecule phenylalanine. This molecule has two functional groups that participate in acid/base chemistry with pKa's of 2.18 and 9.09. Just like any polyprotic molecule, you can determine the dominant species at any given pH.



Solubility Equilibria, K_{sp}

K_{sp} IS A UNIQUE FORM OF EQUILIBRIUM THAT QUANTIFIES THE DISSOLUTION OF A SOLID SALT INTO ITS AQUEOUS PRODUCTS.

WE MOSTLY FOCUS ON SPARINGLY SOLUBLE SALTS

K_{sp} , Q_{sp} , and Saturation - Definitions

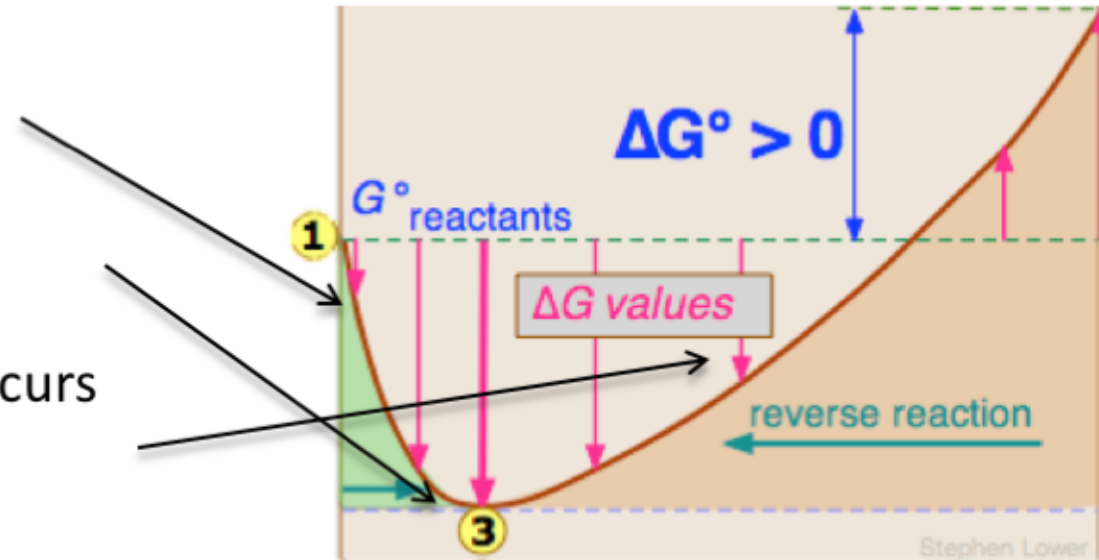
- **Solubility Product (K_{sp}):** K_{sp} is a constant that represents the product of all ion concentrations at equilibrium **specific to a given salt**. **This is the K of the salt dissolution reaction.**
- **Molar Solubility:** Solved from K_{sp} , molar solubility represents the maximum amount of solute that can dissolve for a reaction in terms of Molarity (M). This term is represented by the “x” in K_{sp} calculations. **This is your best measurement of the solubility of a salt.**
- **Common Ion Effect:** When an ion is already present in solution, the molar solubility of a salt containing that ion significantly decreases.
- **Reaction Quotient Solubility Product (Q_{sp}):** Q_{sp} is a variable that is calculated by the product of all ion concentrations typically **at a point away from equilibrium**. Solved in the same way as K_{sp} , Q_{sp} uses experimental values rather than equilibrium values.
- **Saturation:** when the maximum amount of ions are present in solution ($K_{sp} = Q_{sp}$)
 - Saturation is an equilibrium position where $Q = K$.
 - Dissolution: when $Q_{sp} < K_{sp}$ and your reaction moves forward (solid becomes ions)
 - Precipitation: when $Q_{sp} > K_{sp}$ and your reaction moves backward (ions become solid)

← NOT equilibrium

Saturation: Q_{sp} vs. K_{sp}

- K_{sp} represents the ion product of a saturated solution in terms of molar solubility (x). You can think of it as a measurement of the maximum saturation capacity of a solution.
- Q_{sp} represents the ion product of the actual concentrations of ions at any given time. You can control these concentrations experimentally. **You can think of Q_{sp} like a starting point**
- **Remember:** K_{sp} is a fixed value ; Q_{sp} is defined by the your actual concentrations in your experiment. **Therefore, your value of Q_{sp} in relationship to K_{sp} will describe what happens:**

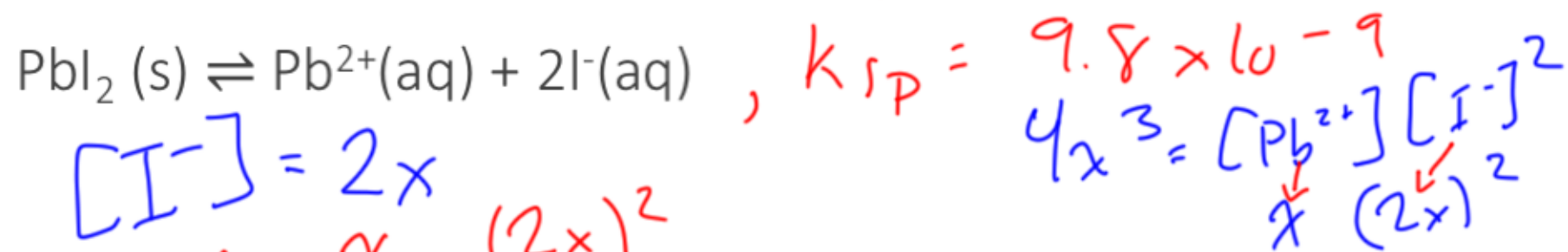
1. $Q_{sp} < K_{sp}$ (**unsaturated**) ; more solid can dissolve if added to the solution
2. $Q_{sp} = K_{sp}$ (**saturated**) ; your reaction is at equilibrium
3. $Q_{sp} > K_{sp}$ (**over saturated**) ; precipitation occurs until $Q_{sp} = K_{sp}$



Solubility and Stoichiometry

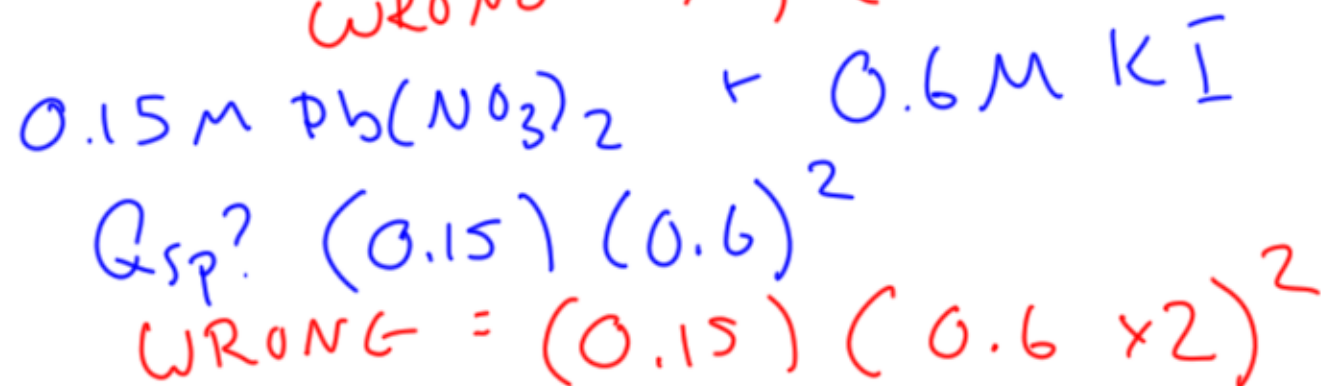
The most important conceptual focus of solubility always tends to revolve around stoichiometry. When do you use coefficients (ex: when is the answer $2x$ and when is it $[I^-]$ without multiplying)? What is the role of exponents?

Remember: the mass action expression is the concentrations raised to the power of their coefficients:



$$[\text{I}^{-}] = 2x$$

WRONG = $x, (2x)^2$



Common ion
Qsp ppt
Qs

K_{sp} Question Types

There are three main scenarios of solubility equilibria:

1. You add a chunk of a sparingly soluble salt to deionized water and calculate the molar solubility from the K_{sp} and stoichiometry (or vice versa).

- $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(2x)^2 = 4x^3$
- x is your molar solubility; x and $2x$ are your ion concentrations here (NOT x and $(2x)^2$)

2. You add a chunk of a sparingly soluble salt to a solution with a common ion already in solution

- $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(0.05M - 2x)^2 = 4x^3$
- x is still your molar solubility, but much lower than in the previous example
- Hint: the math is always easier when you ignore the variable subtracted from the given concentration (the $2x$ in this example)

3. You mix two aqueous solutions to perform a double displacement precipitation reaction

- $Q_{sp} = [Pb^{2+}][I^-]^2$
- If $Q > K$, a precipitate forms
- You can use stoichiometry to determine how much precipitate forms (For small K_{sp} values, you can assume 100% precipitation to solve for the mass of ppt)

K_{sp} to Molar Solubility

1:1	x^2
1:2	$4x^3$
1:3	$27x^4$
2:3	$108x^5$

What is the molar solubility of Li_3PO_4 ? The K_{sp} of Li_3PO_4 is 3.2×10^{-9} .

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

$$K_{sp} = (3x)^3 x = 27x^4$$

K_{sp} is the "Solubility Product," which is a constant unique to a particular compound that represents the product of ion concentrations that are present at equilibrium

$$\sqrt[4]{\frac{K_{sp}}{27}} = x$$

$$x = 3.3 \cdot 10^{-3} \text{ M}$$

x represents the "Molar Solubility," which is a direct measurement of solubility. Molar solubility is the concentration of a solute that dissolves in molarity (M) for a reaction.

K_{sp} and the common ion effect

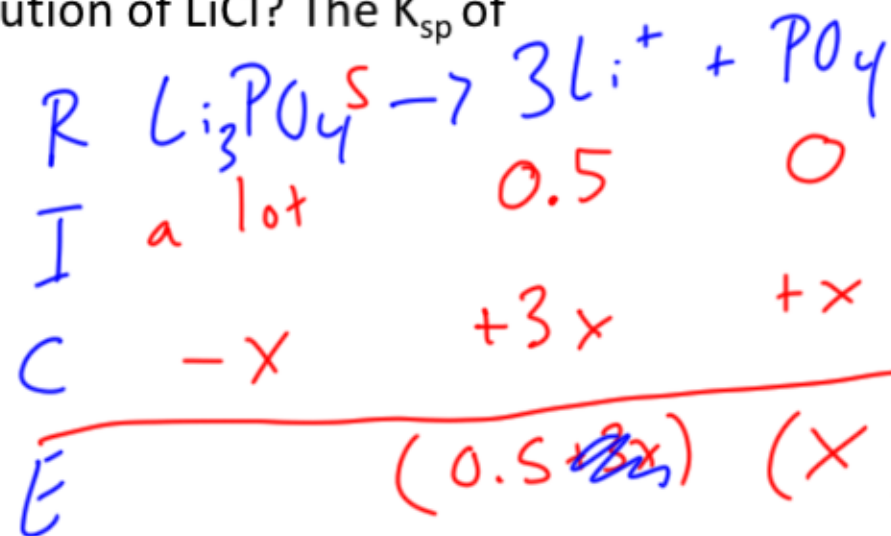
What is the apparent molar solubility of Li_3PO_4 when added to a 0.5M solution of LiCl ? The K_{sp} of Li_3PO_4 is 3.2×10^{-9} .

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

$$K_{sp} = (0.5)^3 x$$

$$x = \frac{K_{sp}}{(0.5)^3} = \frac{K_{sp}}{.125}$$

$$x = 2.56 \cdot 10^{-8} \text{ M}$$



K_{sp} remains constant (because it is a constant). Therefore, you should predict that the presence of a common ion decreases the overall "apparent" molar solubility of your compound.

Notice how the molar solubility here is much less than that of the last problem we solved.

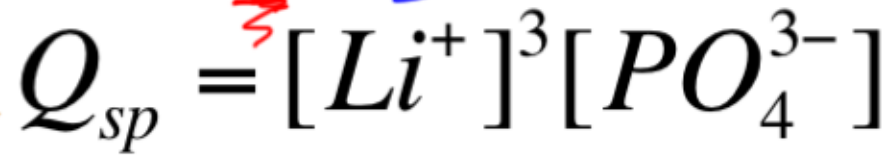
K_{sp} vs. Q_{sp}

$$C_2 = \left(\frac{0.2 M \times 0.135 L}{0.135 + 0.250 L} \right) = 0.07$$

$$C_1 V_1 = C_2 V_2 \quad C_2 = \left(\frac{0.1 M \times 0.250 L}{0.135 + 0.250 L} \right) = 0.065$$

What happens when you mix 135mL 0.2M lithium nitrate and 250mL 0.1M potassium phosphate? The K_{sp} of Li_3PO_4 is 3.2×10^{-9} .

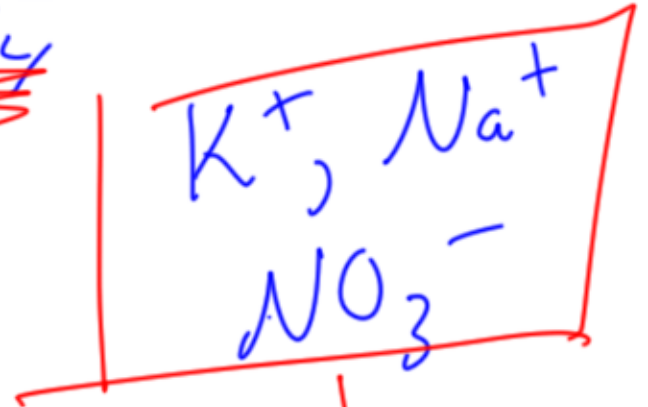
Here you are given "starting point" concentrations of lithium and phosphate ions. Therefore, your ion product will be Q_{sp} .



$$Q_{sp} = (0.07 M)^3 (0.065 M) = 2.2 \cdot 10^{-5}$$

$$Q_{sp} > K_{sp}$$

You have oversaturated your solution. The reaction will run backwards until equilibrium is reached, resulting in a solid Li_3PO_4 precipitate.



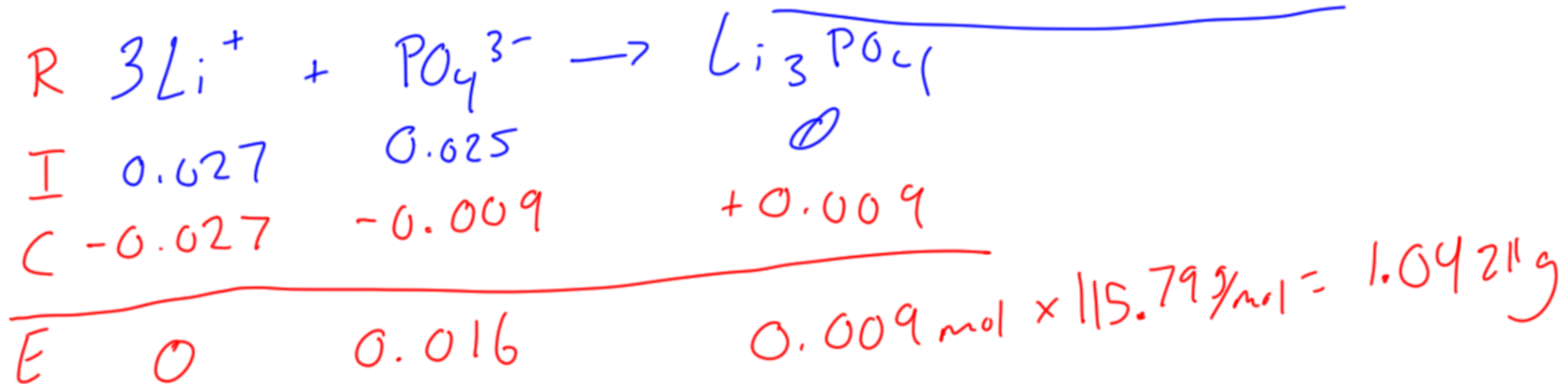
totally soluble

Precipitation Stoichiometry

Take the last example into account: 0.027 mol 0.025 mol

What happens when you mix 135 mL 0.2 M lithium nitrate and 250 mL 0.1 M potassium phosphate? The K_{sp} of Li_3PO_4 is 3.2×10^{-9} .

What is the mass of the resulting precipitate? **The trick: assume 100% solubility.**



K_{sp} Solubility Comparison

Which of the following salts is more soluble?



or



K_{sp} Solubility Comparison

Which of the following salts is more soluble?



$$K_{sp} = (3x)^3 x = 27x^4$$

$$\sqrt[4]{\frac{K_{sp}}{27}} = x$$

$$x = 3.3 \cdot 10^{-3} M$$

or



$$K_{sp} = (x)(2x)^2 = 4x^3$$

$$\sqrt[3]{\frac{K_{sp}}{4}} = x$$

$$x = 1.2 \cdot 10^{-4} M$$