CH 302 – Unit 3 Review 2

BUFFERS, TITRATIONS, PROTONATION STATES, INDICATORS

Acid and Base Question Types (Simplified)

- Strong acid, strong base questions
  - Simple relationships converting $[H_3O^+]$ and $[OH^-]$ to pH, pOH
- Weak acid, weak base questions
  - Approximations or quadratic formula (if necessary) with your general formula:
  - $HA \rightleftharpoons H^+ + A^-$ OR $B \rightleftharpoons BH^+ + OH^-$
  - Solve for $[H^+]$ using K_a Solve for $[OH^-]$ using K_b
- Buffer questions
  - Mixtures of a weak acid and its salt (conjugate base) ; weak base and its salt (conjugate acid)
  - Solve for pH, pOH using Henderson-Hasselbalch equation
- **TODAY: Neutralization reactions and titration experiments**
  - By adding a titrant to an analyte solution, you can neutralize your original species. Depending where you are in the neutralization experiment, you will make different calculations based on the three scenarios above, for a total of 4 calculations: all original solution, buffer, all conjugate solution (full neutralization), overshoot.

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 $CH_3COOH(aq)$ to $NaCH_3COO(aq)$. 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!)
- **Buffer zone:** +/- one pH unit of the pKa (where there is an ideal 1:1 ratio of $HA:A^-$)
- **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 anaylte)
- **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

Common Ion Effect

Real mechanism of a buffer

- **The common ion effect:** the overall solubility of a weak electrolyte decreases when one of its ions are already in solution. Think of the pH value of acetic acid under two different conditions:

$NaCH_3COO \rightarrow Na^+ + CH_3COO^-$

	$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$		
R			
I	0.1M	0	0
C	−x	+x	+x
E	0.1M − x	x	x

$pH = 2.87$

	$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$		
R			
I	0.1	0	0.1
C	−x	+x	+x
E	0.1 − x	x	0.1 + x

$$K_a = \frac{(x)(0.1+x)}{0.1-x}$$

$x = 0.00134\ldots$

$x = 0.000818$

$pH = pK_a = 4.74$

Sapling Question

$3.56 = 3.74 + \log \frac{40}{60}$

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

Suppose there is 1.00 L of an aqueous buffer containing 60.0 mmol of formic acid ($pK_a = 3.74$) and 40.0 mmol of formate.

Calculate the pH of this buffer.

pH = 3.56

What volume of 4.00 M NaOH would be required to increase the pH to 4.93?

volume: mL

$$4.93 = 3.74 + \log\left(\frac{40 + x}{60 - x}\right)$$

$$10^{4.93-3.74} = \frac{40+x}{60-x}$$

→ mmol NaOH

mmol NaOH → mol × $\frac{L}{4\,mol}$ = L NaOH

Sapling Question

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

You need to prepare 100.0 mL of a pH 4.00 buffer solution using 0.100 M benzoic acid ($pK_a = 4.20$) and 0.220 M sodium benzoate.

How many milliliters of each solution should be mixed to prepare this buffer?

benzoic acid: _____ mL

sodium benzoate: _____ mL

$$pH = pKa + \log\frac{A^-}{HA}$$

$$4.00 = 4.20 + \log \frac{A^-}{HA}$$

$$-0.20 = \log \frac{A^-}{HA} = 0.63$$

$$10^{-0.20} = \frac{A^-}{HA} = 0.63$$

$$C_{A^-} = 0.220\ M$$

$$C_{HA} = 0.100\ M$$

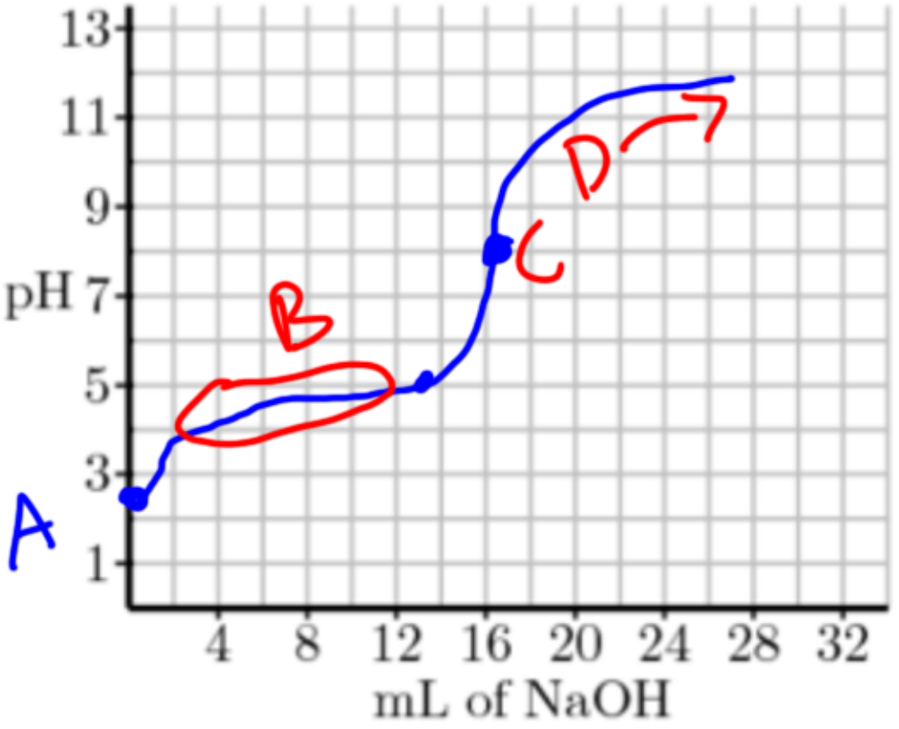
$$0.63 = \frac{\text{mmol } A^-}{\text{mmol } HA} = \frac{C_{A^-} V_{A^-}}{C_{HA} V_{HA}} = \frac{(0.220\ M)(V_{A^-})}{(0.100\ M)(100\text{mL} - V_{A^-})}$$

$$V_{total} = 100\text{mL} = V_{A^-} + V_{HA}$$

$$V_{A^-} = 100\text{mL} - V_{HA}$$

$$V_{HA} = 100\text{mL} - V_{A^-}$$

NaOH (titrant) to Weak Acid (analyte)



A Type I, $[H^+] = \sqrt{K_a \cdot C_A}$

B Type II, Buffer Problem
RICE Table: Moles

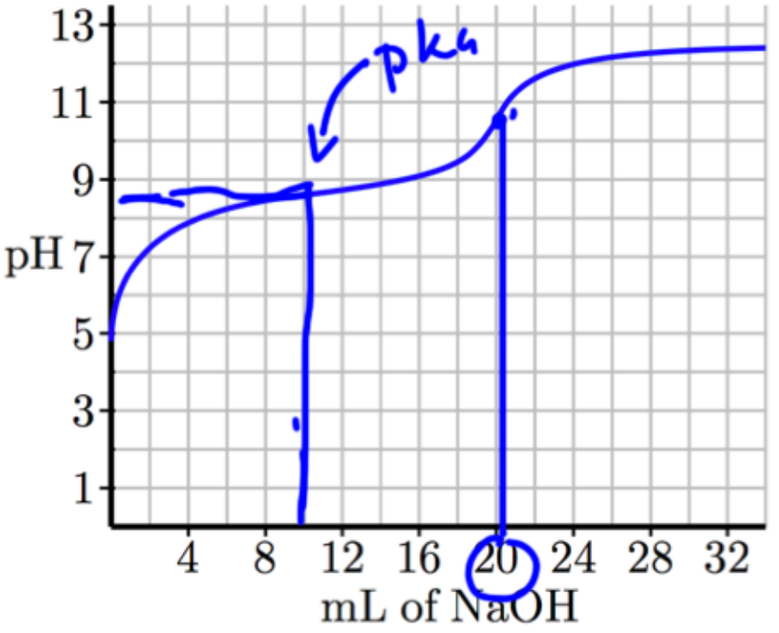
C Type I, $[OH^-] = \sqrt{K_B \cdot C_B}$
* Type II RICE table (moles)

D Type I, Type II RICE
$pOH = -\log [NaOH]$
↓
excess

excess
↓
diluted

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 values do they give you?

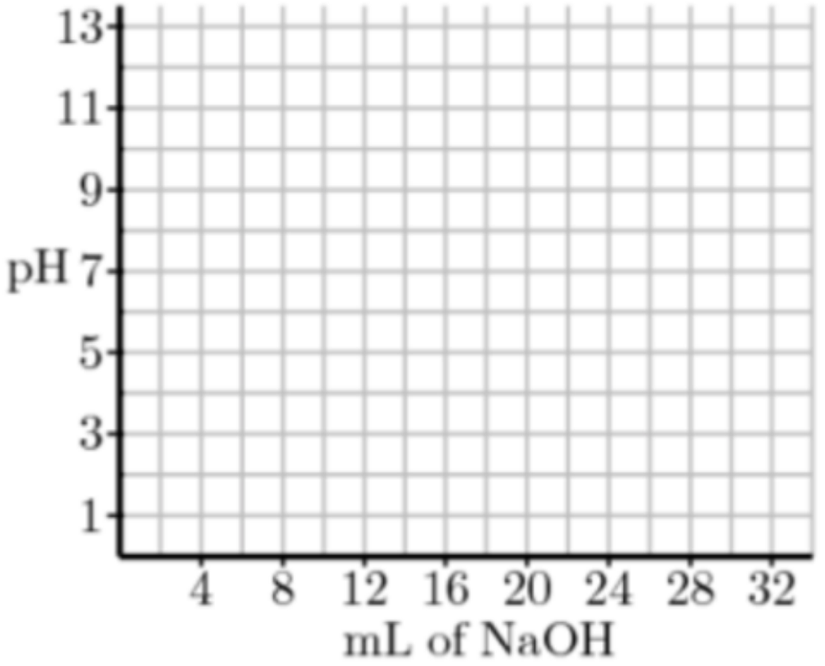


① EQ pt 20mL, pH = 10.6
L pt to [HA] initial
moles NaOH = moles HA

② ½ pt : ½ volume of eq pt.
10mL, pH = 8.5
moles HA = moles A⁻ pH = pKa

On Your Own

Plot the points on the titration curve using the table of data. Identify the equivalence point and the half equivalence point on both the graph and the table. Label the 4 zones for calculations (A, B, C, D) and how you would make each calculation.



Total Volume NaOH added	Total # moles OH^- added to solution	# moles after Neutralization mmol			Measured pH
		CH_3COOH	CH_3COO^-	OH^-	
0 mL	0.0 mmol	0.8	0	0	3.437
2 mL	0.2 mmol	0.6	0.2	0	4.295
3 mL	0.3 mmol	0.5	0.3	0	4.542
4 mL	0.4 mmol	0.4	0.4	0	4.761
5 mL	0.5 mmol	0.3	0.5	0	4.981
6 mL	0.6 mmol	0.2	0.6	0	5.236
7 mL	0.7 mmol	0.1	0.7	0	5.603
8 mL	0.8 mmol	0.0	0.8	0	8.312
9 mL	0.9 mmol	0.0	0.8	0.1	10.96
10 mL	1.0 mmol	0.0	0.8	0.2	11.257

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 < pKa

- A molecule is deprotonated when the acidic proton is OFF the molecule
  - Think A^- or B in a titration experiment

pH > pKa

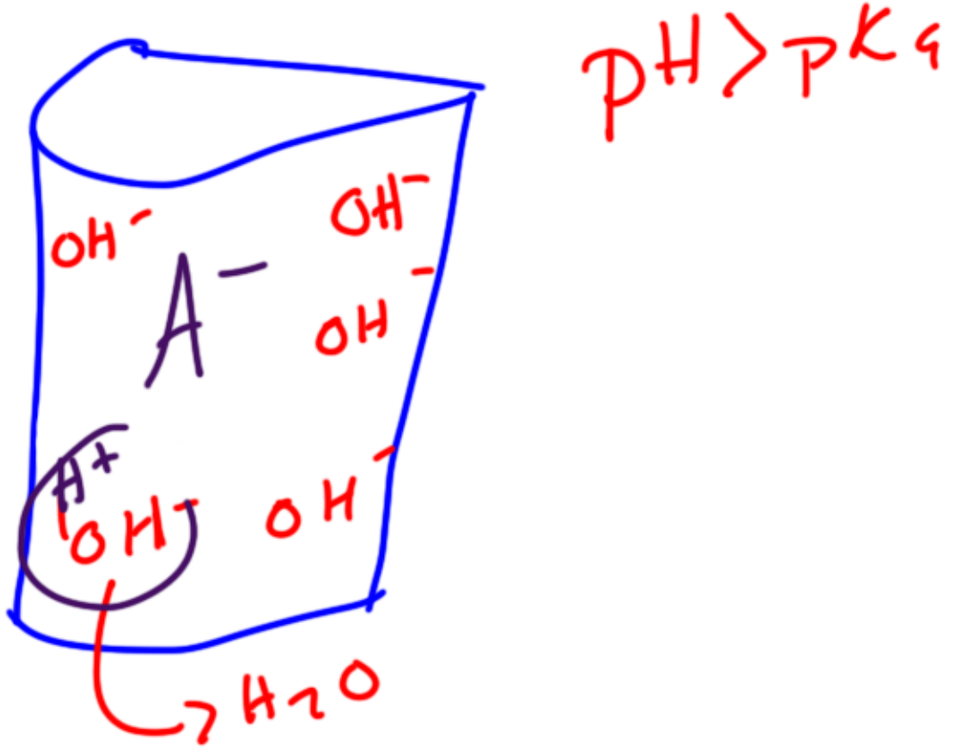
- As you might expect, a buffer contains a mix of the protonated and deprotonated states
- Whether a molecule is protonated or deprotonated depends on the relationship between the pH of solution and the pK_a of the molecule.

Conceptualizing Protonation States

- Begin with your fundamental definitions of acids and bases
- When the water is more acidic than your molecule (pH < pKa), the water is more proton donating (acidic) and the molecule is more proton accepting (basic)

Conceptualizing Protonation States

- When the water is more basic than your molecule (pH > pKa), the water is more proton accepting and the molecule is more proton donating



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

We can take this one small step forward to calculate the fraction of species:

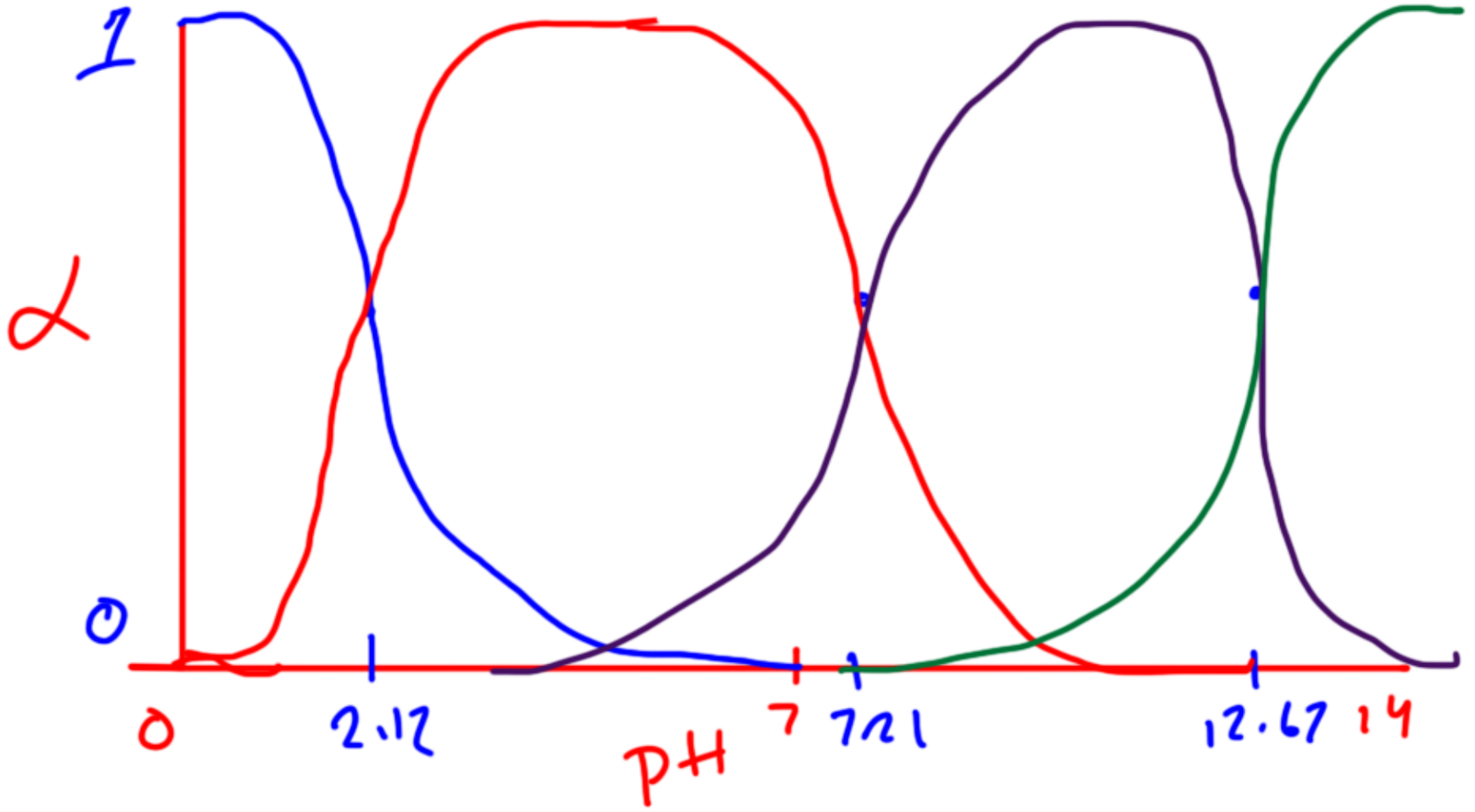
$$f_{HA} = \frac{[HA]}{[HA] + [A^-]} = \frac{mol\ HA}{mol\ HA + mol\ A^-}$$

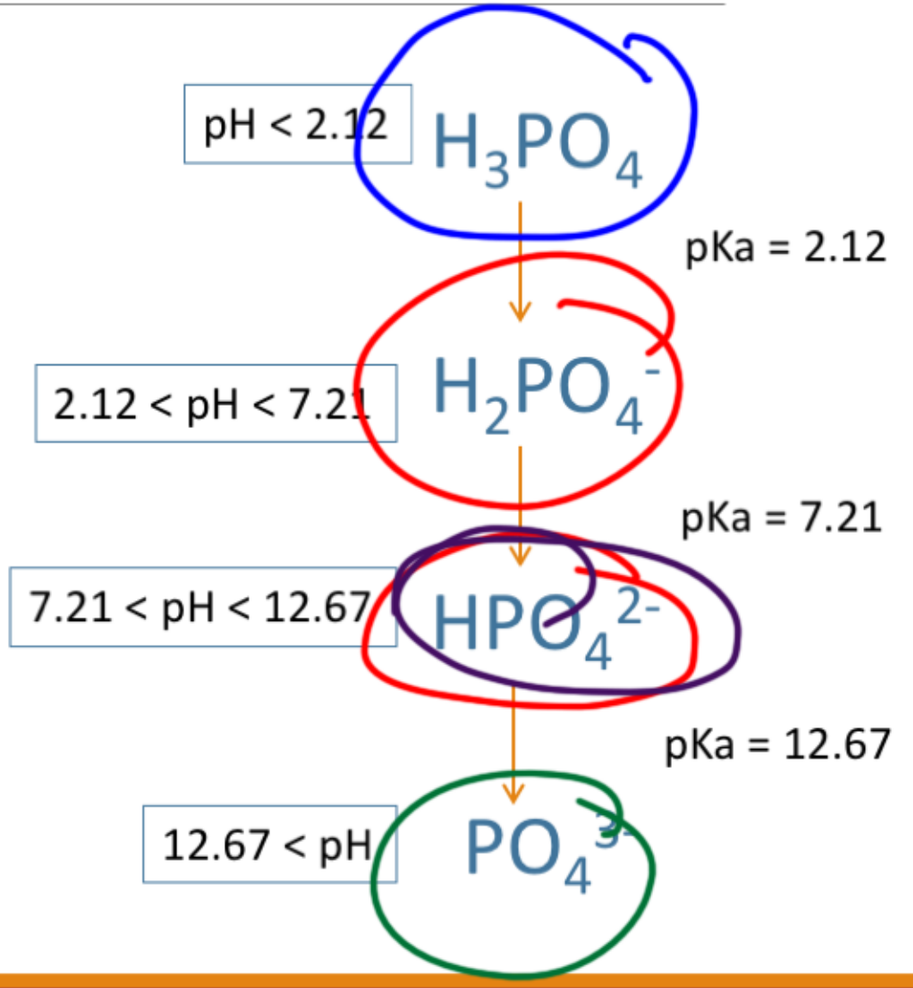
$$f_{A^-} = \frac{[A^-]}{[A^-] + [HA]} = \frac{mol\ A^-}{mol\ A^- + mol\ HA}$$

or just...

$$f_{A^-} = 1 - f_{HA}$$

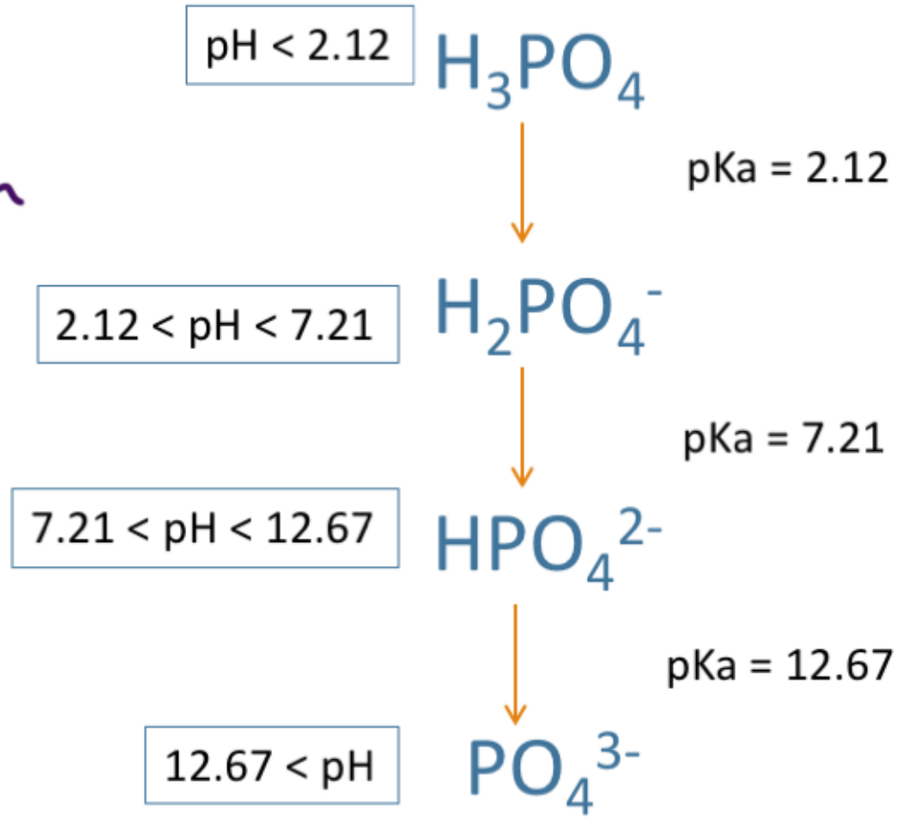
Polyprotic Fundamentals: H_3PO_4





Fraction of Species: H_3PO_4

Draw the titration curve and compare to a diagram



Question

$pK_{a1} \rightarrow H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$

$pK_{a2} \rightarrow HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$

What is the dominant for of sulfurous acid (H_2SO_3) at the following pH values:

$pK_{a1} = 1.82$ $pK_{a2} = 7.00$

pH = 4 HSO_3^-

pH = 9 SO_3^{2-}

pH = 7 → HSO_3^- & SO_3^{2-}

H_2SO_3

HSO_3^-

SO_3^{2-}

Which of the following would be the best buffer for pH = 2?

a. H_2SO_3 and SO_3^{2-}

b. H_2SO_3 and HSO_3^-

c. HSO_3^- and SO_3^{2-}

→ 1.82

0.82 – 2.82

Question

Now consider a different molecule, phenolphthalein. This molecule has only one acidic proton with a pK_a = 8.2. When phenolphthalein is protonated, it is clear. When it is deprotonated, it is pink. What is the color at the following pH values?

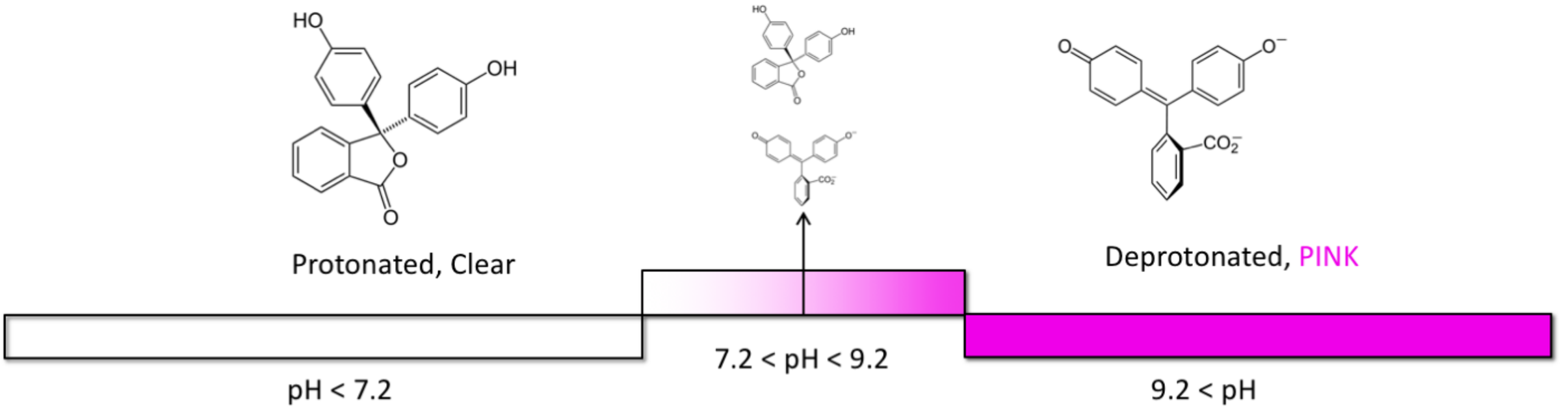
pH = 4 pH < pKa pink

pH = 12 pH > pKa clear

pH = 8.2 pH = pKa clear – pink

Dominant Species: Indicators

- The purpose of an indicator is to change color in a particular pH range (color change occurs *about* at +/- 1 pH unit from the pKa). The protonated and deprotonated forms of the molecule will have different colors. **Therefore, the color of solution will represent the dominant species in solution.**
- Consider phenolphthalein, pKa = 8.2:



Dominant Species: Indicators

- Apply this to fraction of species for phenolphthalein (pKa = 8.2):