

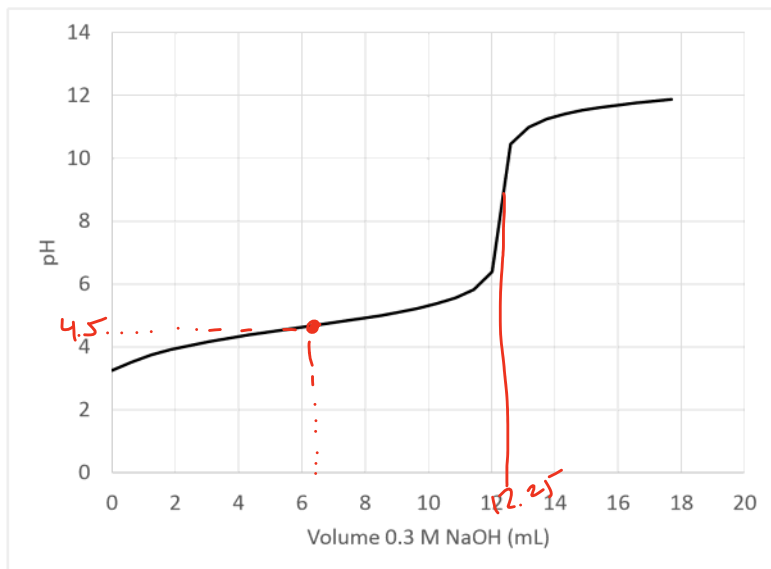
**Problem Set 3****(Due: February 10<sup>th</sup> 5:00 PM)**

- Which of these acids could be used to make a buffer at pH 6.8? You can find a table of pKa values [here](#) or in any general chemistry textbook. Select all that would work.  
formic acid          ammonium          carbonic acid          acetic acid          hydrofluoric acid
- Rank these solutions by increasing pH. You should not need to do any math to answer this question:  
10 mM NaNO<sub>2</sub>          10 mM HNO<sub>2</sub>          10 mM Mg(NO<sub>2</sub>)<sub>2</sub>          10 mM NaNO<sub>3</sub>          10 mM HNO<sub>3</sub>
- Clearly explain why hypochlorous acid is a weaker acid than chlorous acid.
- Consider fluoride and chloride.
  - Which of these ions is a weak base? How do you know?
  - Which would make a more acidic solution? How do you know?
  - The chemistry of these two ions is very similar; however, in solution they undergo different chemical reactions. Think very critically about how each of these ions interact with water and propose a reason that one is a weak base and one is not.
- For each of the following, determine if dissolution in water would make the pH acidic or basic.
  - NaF
  - NH<sub>4</sub>NO<sub>3</sub>
  - NaHSO<sub>4</sub>
  - MgHPO<sub>4</sub>
- Consider phosphoric acid:
  - Draw 3 sequential acid dissociation reactions that this molecule can be involved in.
  - Determine the 2 species at highest concentration at biological pH (7.4).
  - Calculate the concentration of these two chemical species at biological pH if the total concentration is 17 mM.
- The condensation of a fatty acid with glycerol is required to build phospholipids and triacylglycerides.
  - Show the 3 step process for condensation of 16:0 with glycerol.
  - Is the acid or base form of the fatty acid required for this process?
  - The pKa of 16:0 is approximately 4.5. Under biological conditions (pH = 7.4), which form (HA or A<sup>-</sup>) of 16:0 is present in the highest concentration?
  - Calculate the fraction of the fatty acid that is present in the form necessary for the condensation reaction.
  - Think critically about what you have just learned. Does this predict that phospholipid synthesis is likely to happen at biological pH? Explain your answer.
- Calculate the pH after 1mL of 1 M HCl is added to each of the following solutions"
  - 1 L H<sub>2</sub>O at pH 7.0
  - 1 L of a 50 mM carbonic acid buffer at pH 7.0.
- Consider serine:
  - Determine the isoelectric point of serine. You can find a table of pKa values [here](#).
  - Does serine carry a net positive or net negative charge at pH 7.4?

10. Sketch a curve for the titration of NaOH into cysteine. Label the y-axis at the 3 pKa values and the 2 intermediate equivalence points.

11. Consider the titration curve below. Based on what you see:

- What is the pKa of this acid?
- Determine the initial concentration of the acid.
- Calculate the initial pH.



12. You are doing a titration experiment by adding 500 mM NaOH to 300 mL of 18 mM hypochlorous acid.

- What volume of NaOH is needed to reach the  $\frac{1}{2}$  equivalence point?
- What volume of NaOH is needed to reach the equivalence point?

13. Sketch a curve for the titration of 500 mM NaOH into 300 mL of 18 mM hypochlorous acid. Make sure to label the x and y axis for the three important points we talked about in class. Note that this is the same solution as you saw in problem 12.

1. pKas of the acids:

Formic = 3.75

ammonium = 9.25

carbonic acid = 6.35 and 10.33 (hydrogen carbonate)

acetic acid = 4.75

hydrofluoric acid = 3.2.

Weak acids are able to buffer pHs within 1 pH unit of the pKa. In this case, the only acid that has a pKa within 1 of 6.8 is **carbonic acid**.

2. You should be on the lookout for a two main things
  - a. Strong acid/base or Weak acid/base
  - b. Concentration of the acid or base

HNO<sub>3</sub> = strong acid

HNO<sub>2</sub> = weak acid

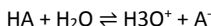
NO<sub>3</sub><sup>-</sup> = conjugate base of a strong acid so NOT a base

NO<sub>2</sub><sup>-</sup> = weak base (conjugate of a weak acid)

Mg(NO<sub>2</sub>)<sub>2</sub> will have a higher [NO<sub>2</sub><sup>-</sup>] than NaNO<sub>2</sub>

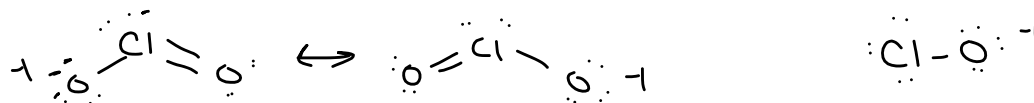
HNO<sub>3</sub> < HNO<sub>2</sub> < NaNO<sub>3</sub> < NaNO<sub>2</sub> < Mg(NO<sub>2</sub>)<sub>2</sub>  
 Acidic                    neutral                    basic

3. These problems are easier to think about from the perspective of base stability. The more stable that the conjugate base is, the more likely it is for the acid (reactant) to be converted to base (product).



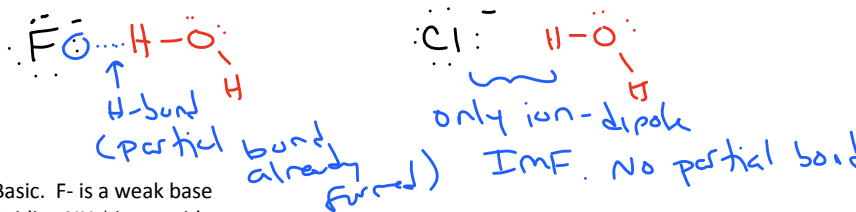
To predict base stability, a major factor is the presence and number of resonance structures. The more resonance structures that you can draw, the more stable the base, therefore more products will form (including more H<sub>3</sub>O<sup>+</sup>).

Chlorite (base form of chlorous acid) has 2 resonance forms.

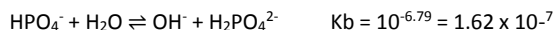


Hypochlorite (base form of hypochlorous acid) has none.

4. F<sup>-</sup> vs. Cl<sup>-</sup>
  - a. F<sup>-</sup> is a weak base because HF is a weak acid. Cl<sup>-</sup> is the conjugate base of HCl, a strong acid, so it is not reactive toward water.
  - b. Chloride. Cl<sup>-</sup> would produce a neutral solution while F<sup>-</sup> would make the solution basic. So, neutral is more acidic than basic.
  - c. We know that fluorine can form H-bonds with water while chlorine cannot. Consequently, F<sup>-</sup> will have a stronger interaction with water (because of the presence of H-bonds). Since F<sup>-</sup> is already H-bonding with water, there is already a shared interaction between F<sup>-</sup> and a proton from water. Since an H<sup>+</sup>---F interaction is always occurring, an H-F covalent bond is more readily formed. Cl<sup>-</sup> does not H-bond, so there will not be a comparable H<sup>+</sup>---Cl interaction.

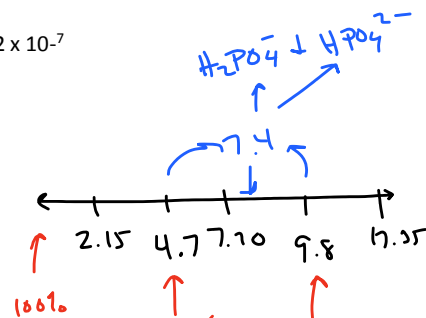
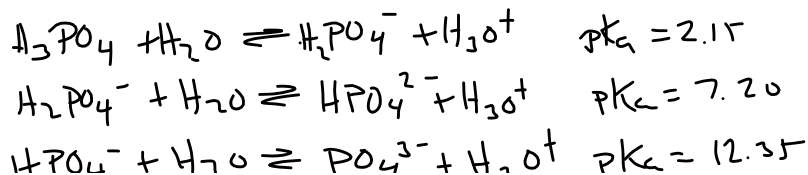


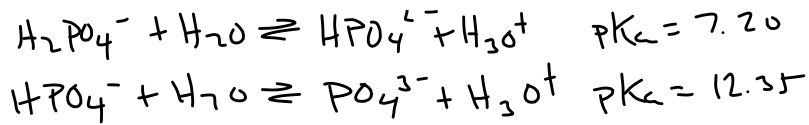
5. pH
  - a. Basic. F<sup>-</sup> is a weak base
  - b. Acidic - NH<sub>4</sub><sup>+</sup> is an acid
  - c. Acidic - HSO<sub>4</sub><sup>-</sup> can theoretically be an acid or a base. However, if it serves as a base (to make OH<sup>-</sup>), H<sub>2</sub>SO<sub>4</sub> is a product. Anytime a strong acid is produced, the reaction does not happen. When the acid hydrolysis reaction happens, SO<sub>4</sub><sup>2-</sup> is formed.
  - d. Basic. HPO<sub>4</sub><sup>2-</sup> is amphoteric. It can undergo an acid or base dissociation reaction. The trick is to figure out which reaction favors products more significantly. These equilibria are shown on the right. The trick to figuring out Kb is to make sure that you start with the correct Ka. In this case, we are focused on the H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> pair, so we need to use the Ka of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>.



K<sub>b</sub> > K<sub>a</sub>, so more OH<sup>-</sup> is produced.

6. Phosphoric acid:





↑ 2.15 4.7 7.10 9.8 11.35  
 100%  $H_2PO_4^-$     100%  $H_2PO_4^-$     100%  $HPO_4^{2-}$

$$7.4 = 7.2 + \log \frac{A^-}{HA}$$

$$0.2 = \log \frac{A^-}{HA}$$

$$\frac{A^-}{HA} = 1.58$$

$$A^- = 1.58 [HA]$$

$$17 \text{ mM} = [HA] + [A^-]$$

$$17 \text{ mM} = [HA] + 1.58 [HA]$$

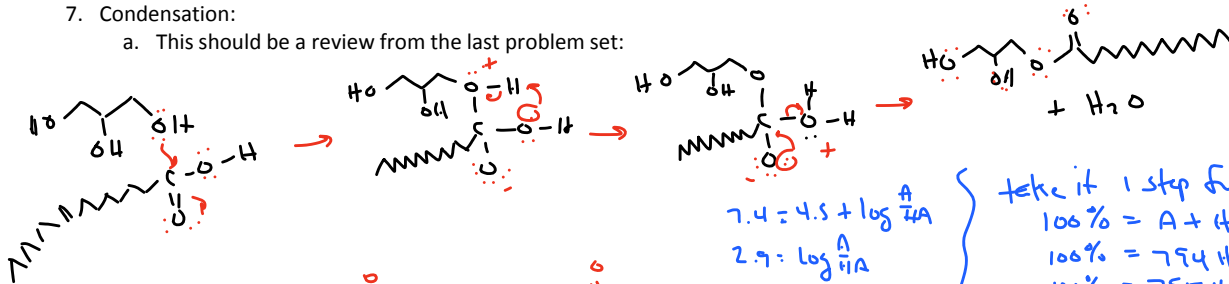
$$17 \text{ mM} = 2.58 [HA]$$

$$[HA] = 6.59 \text{ mM}$$

$$[A^-] = 17 - 6.59 = 10.41 \text{ mM}$$

7. Condensation:

a. This should be a review from the last problem set:



take it 1 step further  
 100% = A + HA  
 100% = 794 HA + HA  
 100% = 795 HA  
 So [A] is 794 times larger than [HA]

$$HA = 0.126\%$$

- b. Acid form is used. ( $C(=O)-O-H$  not  $C(=O)-O^-$ )
- c.  $pH > pK_a$ . More base is present.
- d. Use HH equation to determine the ratio.
- e. If less than 1% of the fatty acid is in the acid form, there will not be very much available to react with glycerol. This is a problem if we want this reaction to happen efficiently.

8. Titration of 1mL of 1 M HCl.

$$0.001 \text{ L} \times \frac{1 \text{ mol}}{1 \text{ L}} = 1 \text{ mmol strong acid, so no } pK_a$$



• after reaction, 1 mmol  $H_3O^+$  is produced

$$\frac{1 \text{ mmol}}{1.001 \text{ L}} = 0.999 \text{ mM} = 9.99 \times 10^{-4} \text{ M}$$

$$pH = 3.00$$

$H_2CO_3$

$$7.0 = 6.35 + \log \frac{A}{HA}$$

$$0.65 = \log \frac{A}{HA}$$

$$10^{0.65} = \frac{A}{HA}$$

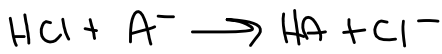
$$A = 4.47 HA$$

$$50 \text{ mM} = HA + 4.47 HA$$

$$50 = 5.47 HA$$

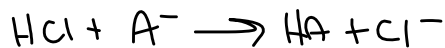
$$[HA] = 9.14 \text{ mM (1L)} = 9.14 \text{ mmol}$$

$$[A^-] = 41.02 \text{ mM (1L)} = 41.02 \text{ mmol}$$



$$I \quad 1 \text{ mmol} \quad 41.02 \quad 9.14$$

$$A^- = 4.47 \text{ HA}$$



|   |        |       |      |
|---|--------|-------|------|
| I | 1 mmol | 41.02 | 8.98 |
| C | -1     | -1    | +1   |
| E | ∅      | 40.02 | 9.98 |

$$[\text{A}^-] = \frac{40.02}{1.001 \text{ L}} = 39.98 \text{ mM}$$

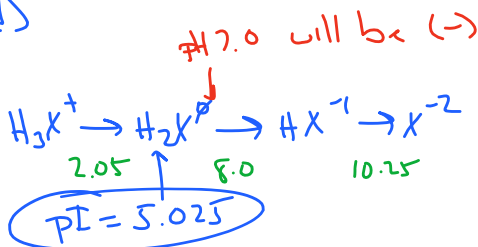
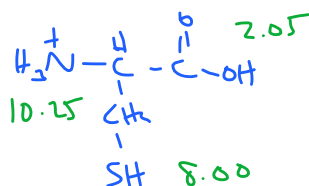
$$[\text{HA}] = \frac{9.98}{1.001 \text{ L}} = 9.97 \text{ mM}$$

$$\text{pH} = 6.35 + \log \frac{39.98}{9.97}$$

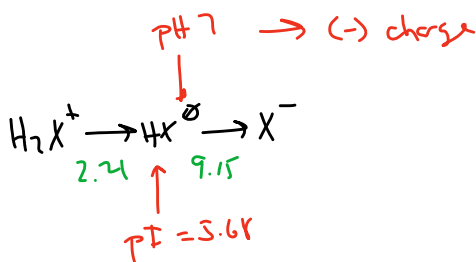
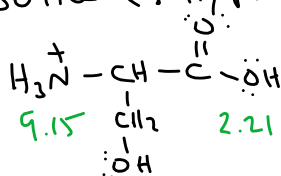
$$\text{pH} = 6.95$$

9. If you downloaded the problem set early, you saw cysteine in this problem. If you downloaded it later, you noticed that I is serine. Both are shown here.

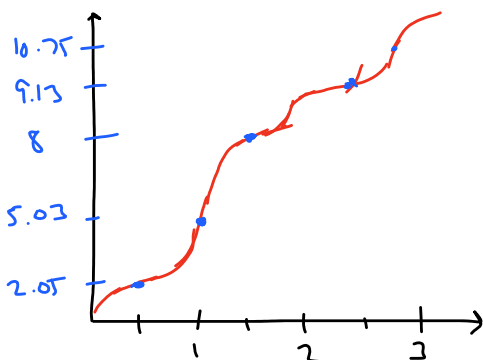
Cysteine (fully protonated)



Serine (fully protonated)



10. Cysteine pKa values: 2.05, 8.00, 10.25. Averages are 5.025 and 9.125



11. pKa labelled on graph above.

- pKa = 4.5. Estimated by pH at 1/2 eq pt.
- Use volume of NaOH at eq. pt. to determine moles of OH<sup>-</sup>. This is equal to moles of the weak acid. Convert this to

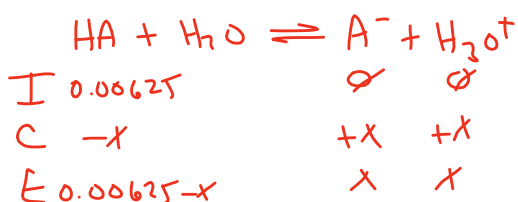
11. pKa labelled on graph above.

- pKa = 4.5. Estimated by pH at 1/2 eq pt.
- Use volume of NaOH at eq. pt. to determine moles of OH<sup>-</sup>. This is equal to moles of the weak acid. Convert this to concentration.

$$V_{\text{NaOH}} = 12.75 \text{ mL} = \frac{0.01275 \text{ L} \cdot 0.3 \text{ mol}}{1 \text{ L}} = 0.00375 \text{ mol NaOH} = \text{mol HA}$$

$$\frac{0.00375 \text{ mol}}{0.6 \text{ L}} = 0.00625 \text{ M} \quad 6.25 \text{ mM}$$

c. ICE to figure out [H<sub>3</sub>O<sup>+</sup>]



$$10^{-4.5} = \frac{x^2}{0.00625-x}$$

$$0 = x^2 + 10^{-4.5}x - 1.97 \times 10^{-7}$$

$$x = 4.28 \times 10^{-4} = [\text{H}_3\text{O}^+]$$

$$\boxed{\text{pH} = 3.37}$$

12. a.  $\frac{0.3 \text{ L} \cdot 18 \text{ mmol HClO}}{1 \text{ L}} = 5.4 \text{ mmol}$

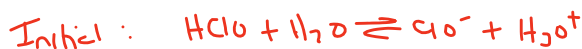
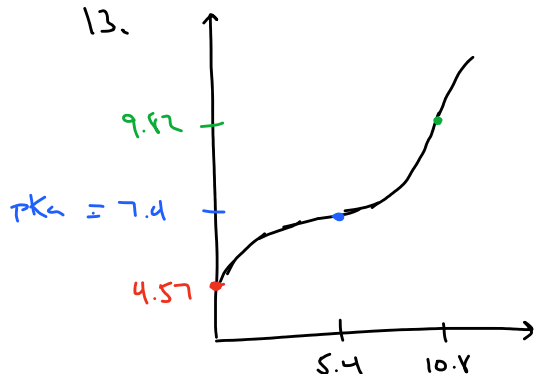
$$\frac{5.4}{2} = 2.7 \text{ mmol NaOH needed for } \frac{1}{2}$$

$$\frac{2.7 \text{ mmol}}{500 \text{ mmol}} = 0.0054 \text{ L}$$

5.4 mL

b.  $5.4 \text{ mL} \times 2 = 10.8 \text{ mL}$

13.



$$10^{-7.4} = \frac{x^2}{0.018-x} = \frac{x^2}{0.018}$$

$$x^2 = 7.17 \times 10^{-10}$$

$$x = 2.68 \times 10^{-5}$$

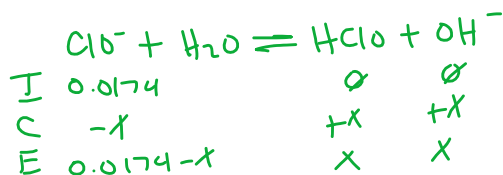
$$3.94 \times 10^{-8} < 0.018 \div 1000$$

Shortest is OK

$$\boxed{\text{pH} = 4.57}$$

Eq. Pt.

$$\frac{0.0054 \text{ mol ClO}^-}{0.3 \text{ L} + 0.0108 \text{ L}} \approx 0.0174 \text{ M}$$



$$K_b = 10^{-6.6} = \frac{x^2}{0.0174 - x} \approx \frac{x^2}{0.0174}$$

(Shortcut  
is ok)

$$x^2 = 4.37 \times 10^{-9}$$

$$x = [\text{OH}^-] = 6.6 \times 10^{-5}$$

$$\text{pOH} = 4.18$$

$$\boxed{\text{pH} = 9.82}$$