

NAME: _____ **KEY** _____**Problem Set 7 due December 2, 2009**

1. Calculate the pH for each of the following solutions (show your work and sig figs):

a. $[\text{H}]^+ = 3.47 \times 10^{-5} \text{ M}$

$$\text{pH} = -\log(3.47 \times 10^{-5}) = 4.4596 \text{ or } 4.46 \text{ with significant figures}$$

b. $[\text{OH}]^- = 3.47 \times 10^{-5} \text{ M}$

$$\text{pOH} = 4.46$$

$$\text{pH} = 14.00 - 4.46 = 9.54$$

c. A solution made from 1 L of a. and 1 L of b.

This is an acid base neutralization reaction.**Acid + Base = Water****since both solutions have the same molarity and the same volume, the acid and base will neutralize leaving only the $[\text{H}^+]$ from water, so $\text{pH} = 7.00$**

d. A solution made from 100 mL of a. and 900 mL of b.

STRATEGY: Calculate the moles of acid in 100 ml of a, and moles of base in 900 mL of b. Recognize that the moles of acid limit the reaction, so it will be consumed but there will be base left over. The acid is the limiting reactant. Moles of b left over are determined by subtracting the moles acid from the moles of base since we see above they react in a 1:1 mole ratio. The leftover moles of base are in 1000 mL, so this is also the molarity (moles/liter) and pOH and then pH can be determined as above.

Moles acid: = $3.47 \times 10^{-5} \text{ moles/liter} \times 0.100 \text{ L} = 3.47 \times 10^{-6} \text{ moles acid}$

Moles base = $3.47 \times 10^{-5} \text{ moles/liter} \times 0.900 \text{ L} = 31.23 \times 10^{-6} \text{ moles base, Moles}$

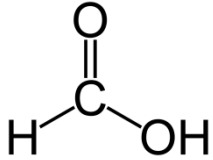
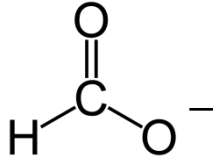
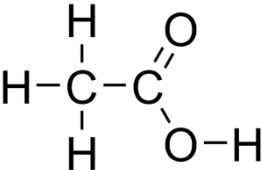
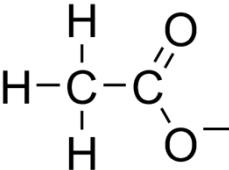
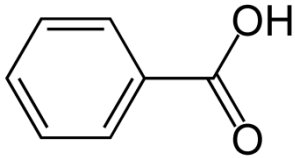
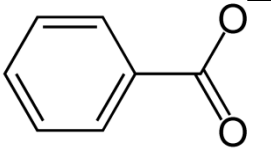
base left over = $31.23 \times 10^{-6} \text{ moles} - 3.27 \times 10^{-6} \text{ moles} = 27.76 \times 10^{-6} \text{ moles base}$

Molarity base = $27.76 \times 10^{-6} \text{ moles/liter} = 2.78 \times 10^{-5} \text{ M}$

$\text{pOH} = 4.56$

$\text{pH} = 14.00 - 4.56 = 9.44$ (note pH did not change very much with addition of 100 ml of acid)

2. Weak acids and bases play a large role in biological processes.
- a. Write down the structures of the following weak acids (and their conjugate bases).

	Acid	Conjugate base	strength
formic acid $K_a = 1.77 \times 10^{-4} M$ $pK_a = -\log K_a = 3.75$			Weakest conjugate base
acetic acid $K_a = 1.77 \times 10^{-5}$ $pK_a = -\log K_a = 4.75$			Strongest conjugate base
benzoic acid $K_a = 6.3 \times 10^{-5} M$ $pK_a = -\log K_a = 4.2$			Medium strength conjugate base

- b. Calculate the pKas for each of the acids above.

See above

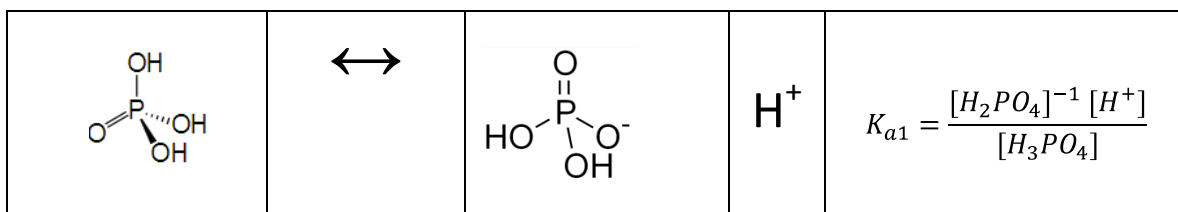
- c. Arrange the weak acids in order of increasing strength of their conjugate bases

Increasing strength of conjugate base:

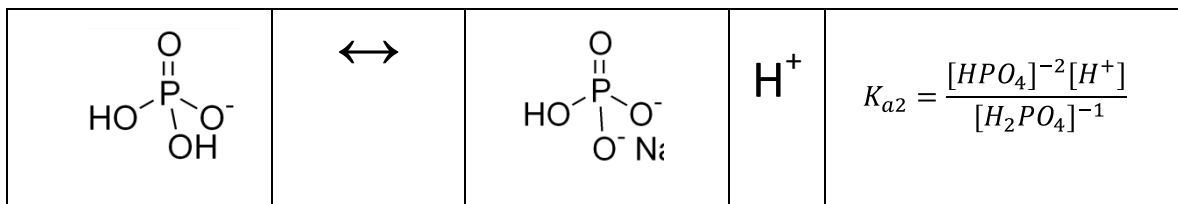
formic acid (**formate**) < benzoic acid (**benzoate**) < acetic acid (**acetate**)

3. Phosphoric Acid and its conjugate bases are important in intracellular pH buffering. With three titratable protons, phosphoric acid has the chemical structure H_3PO_4 . Write down the acid dissociation reactions and the equilibrium expressions associated with each pK_a listed below.

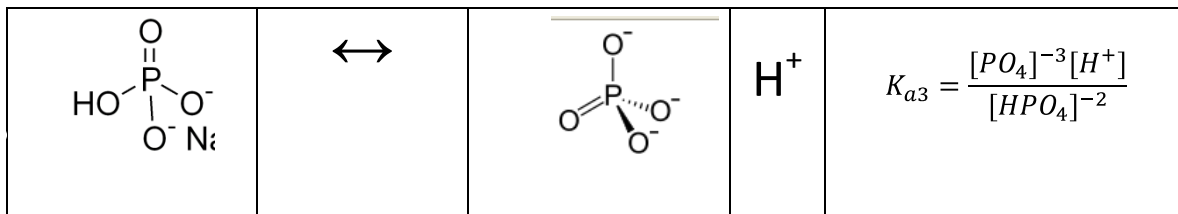
$$pK_{a1} = 2.75$$



$$pK_{a2} = 7.20$$



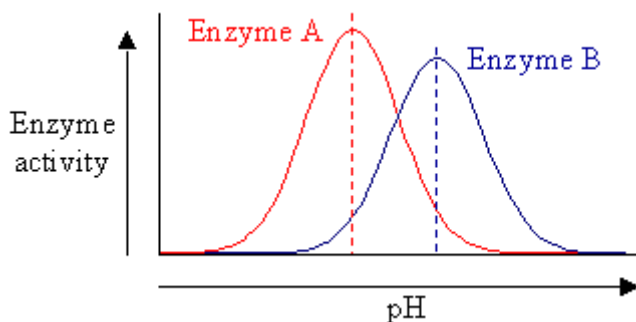
$$pK_{a3} = 12.35$$



- b. Which of the equilibrium reactions above is most relevant to acid/base reactions that occur within the cytoplasm? Why?

pKa2 is most relevant because it happens about pH 7 which is physiological pH

4. Shown below is the activity versus pH profile for two enzymes.



a. Why does the activity of each enzyme increase as the pH rises?

The increase in the activity of the enzyme as pH rises must be due to the de-protonation of a side group in the active site. For each enzyme, there is a peak in activity, after which the activity decreases.

b. Why does the activity of each enzyme decrease as the pH rises?

The decrease in the activity of the enzyme must be due to the denaturation of the enzyme, loss of three dimensional structure.

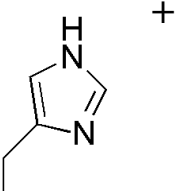
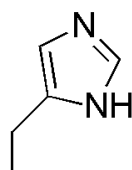
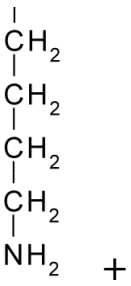
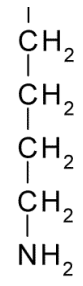
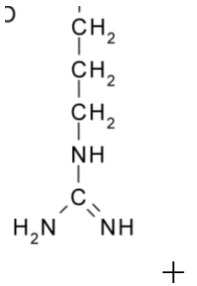
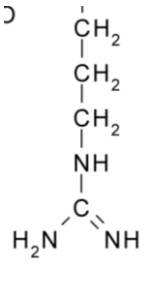
c. Which enzyme would most likely be active in the stomach (and not the gut), and which would be active in the gut (and not the stomach) and why.

Enzyme A must be active in the stomach, enzyme B in the gut, because the activity of A peaks at a lower pH. The stomach, with a pH of 1-3 presents just such a low pH to activate enzyme A. The gut, with a pH closer to 7, presents a more alkaline pH to activate enzyme B.

d. Draw the structure of the acid and conjugate base ONLY for the side groups of the amino acids Asp (pKa 3.75) and Glu (pKa 4.75). Include charges ONLY for the side group in each form.

	Acid group	Conjugate base
Aspartic Acid pKa 3.75	$\begin{array}{c} \text{CH}_2 \\ \\ \text{C} \\ / \quad \backslash \\ \text{HO} \quad \text{O} \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \\ \text{C} \\ / \quad \backslash \\ \text{O} \quad \text{O} \end{array}$
Glutamic Acid side group pKa 4.75	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{C} \\ / \quad \backslash \\ \text{HO} \quad \text{O} \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{C} \\ / \quad \backslash \\ \text{O} \quad \text{O} \end{array}$

- e. Draw the structures of the conjugate acid and base ONLY for the side groups of the amino acids His (pKa 7.5), Lys (pKa 11.5), and Arg (pKa 13.0). Include charges ONLY for the side group in each form.

	Conjugate Acid	Base
Histidine pKa 7.5		
Lysine pKa 11.5		
Arginine 13.0		

- f. If the peak in the activation activity for Enzyme A is 5, which is the most likely amino acid side group responsible for the increase in activity and why.

Glutamic acid because it has a pKa of 4.75, which is very close to peak of activity in enzyme A

- g. If the peak in the activation activity for Enzyme B occurs at pH 7, which is the most likely amino acid side group responsible for the increase in activity and why.

Histidine, because it has a pKa of 7.5, which is very close to the peak of activity in enzyme B