

Exam 1

Monday, February 13, 2017 12:16 PM

This exam is scheduled for 75 minutes and I anticipate it to take the full time allotted. You are free to leave if you finish. In multiple part problems, points awarded will not be penalized for incorrect answer on previous parts, so simply **move on if you get stuck on one part**. If you need to, make up an answer for the previous part. Always neatly show work for partial credit.

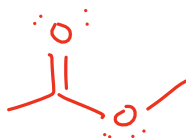
When you draw Lewis structures, ALWAYS include lone pairs and redraw them to show the correct molecular geometry! Show all formal charge.

1. For each of the following, sketch a complete Lewis structure that contains the indicated functional group. Make sure to include all lone pairs and label any formal charge.

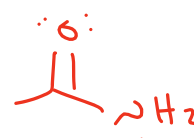
Ketone



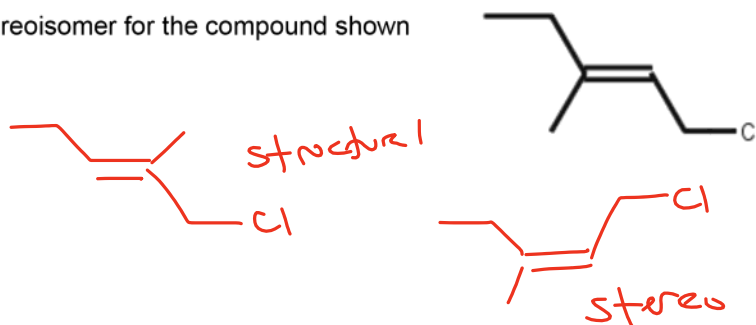
Ester



Amide



2. Draw one structural **and** one stereoisomer for the compound shown here.

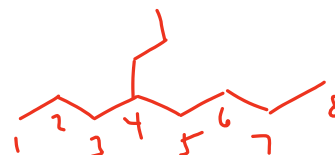


3. Draw the correct structure for each of the following:

2-heptene

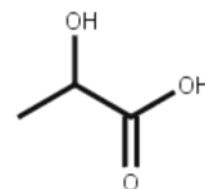
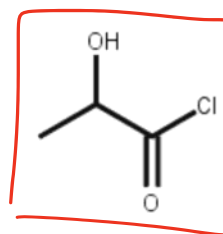


4-propyloctane



4. Which of these compounds do you expect to have a larger log P value at neutral pH? To receive credit, you must provide clear rationale for your choice.

$$P = \frac{[X]_{oct}}{[X]_{H_2O}}$$



- more H-bonds
 - COO⁻ @ pH 7
 both make it more soluble
 in H₂O (↑ [X]_{H₂O})

5. What is the difference between a saturated and unsaturated fatty acid?

no double bonds at least one double bond

6. Rank the following fatty acids by their tendency to **increase** membrane fluidity.

18:3n-3

①

16:0

④

18:0

③

16:1n-7

②

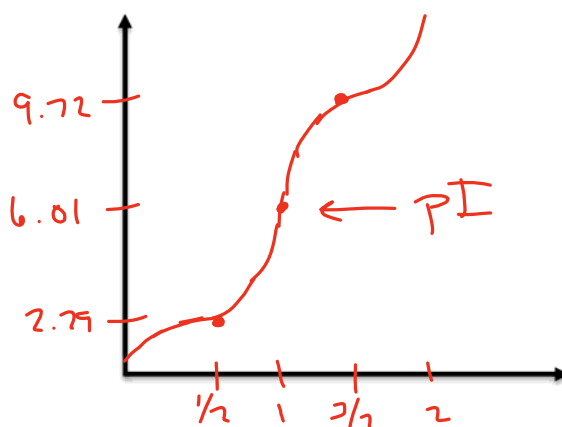
7. Consider the diprotic amino acid valine (pKa 2.29 and 9.72).

a. Using the HX formalism that we learned in class, show two sequential acid dissociation reactions. Include the correct charge on all chemical species.



b. Which two forms of valine are present at highest concentration at pH 4? $\text{H}_2\text{X}^+ \downarrow \text{HX}$

c. Sketch a titration curve for valine. Make sure to label the pH at the $\frac{1}{2}$, 1, and $\frac{3}{2}$ equivalence points. Label the isoelectric point on your curve.



d. Which functional group of valine has the more acidic pKa? For full credit, you must clearly explain why using chemical logic.

carboxylic acid

base form has resonance forms, so it is stable.

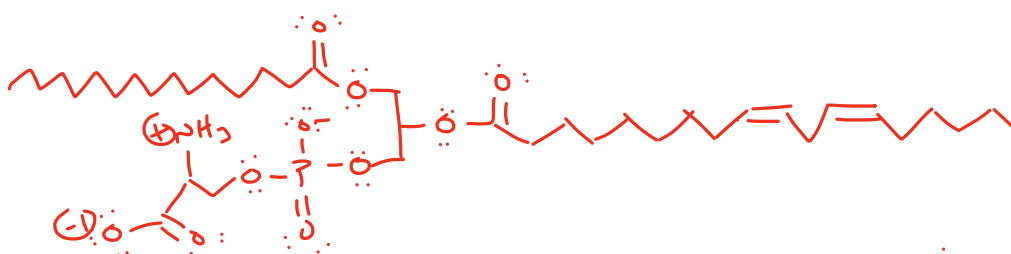
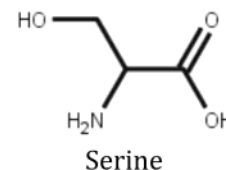


amine does not

8. Why do lipid bilayers form? A full credit answer will include a clear analysis of thermodynamics.

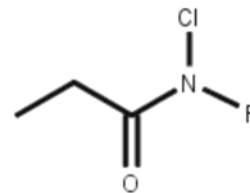
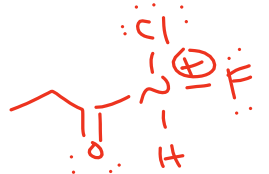
This really boils down to entropy. The hydrophobic tail has a cage of H₂O around it when dissolved in H₂O. This cage gets shed when the tails aggregate. This displacement of H₂O provides a huge entropic driving force that overcomes the endothermic penalty.

9. Draw phosphatidylserine (as it would look at pH 7.0) that is made with 16:0 and 18:2n-6.



10. Show a three-step reaction process (mechanism) for the hydrolysis one of the susceptible bonds in the molecule you drew in problem 9. You can abbreviate unnecessary parts of the molecule as R.

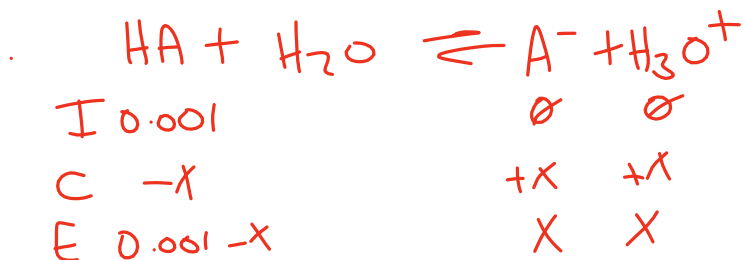
11. The compound shown has a pKa of 8.1.
a. The base form is shown. Draw the acid form.



- b. Clearly explain why the compound is not susceptible to hydrolysis at neutral pH.

The N that is adjacent to the electrophile is protonated @ this pH. It makes the electrophile much less δ^+

12. Calculate the pH of a 1 mM solution of benzoic acid (pKa = 4.20).



$\text{pH} = 3.65$

$$10^{-4.2} = \frac{x^2}{0.001 - x}$$

$$10^{-7.2} - 10^{-4.2} x = x^2$$

$$0 = x^2 + 10^{-4.2} x - 10^{-7.2}$$

$$x = 2.22 \times 10^{-4}$$

13. Consider the titration of 0.5 M NaOH into 250 mL of a weak acid. From the information below, determine each of the following. Use the following page to show your work. You may use the mathematical shortcut to avoid the quadratic equations.

Useful information:

- It takes exactly 10 mL to reach the equivalence point.
- The buffer range is 4.7 – 6.7

pKa 5.7

Initial [Acid] 20 mM

Initial pH 3.7

pH @ Eq. Pt. 8.99

pH after 4 mL of NaOH has been added 5.52

[HA]
 mol HA : $\frac{0.01 \text{ L} \times 0.5 \text{ mol/L}}{0.25 \text{ L}} = \frac{0.005 \text{ mol}}{0.25 \text{ L}} = 0.02 \text{ M}$
 20 mM

Initial pH

$$10^{-5.7} = \frac{x^2}{0.02}$$

$$x^2 = 3.99 \times 10^{-8}$$

$$x = [\text{H}_3\text{O}^+] = 2 \times 10^{-4}$$

$$\text{pH} = 3.7$$

Eq. Pt. 250 ml + 10 ml
 260 ml

$$[\text{A}^-] = \frac{0.005 \text{ mol}}{0.26 \text{ L}} = 0.0192 \text{ M}$$

$$K_b = 10^{-8.3} = \frac{x^2}{0.019}$$

$$x^2 = 9.5 \times 10^{-11}$$

$$x = [\text{OH}^-] = 9.76 \times 10^{-6}$$

$$\text{pH} = 8.99$$

$$4 \text{ mL NaOH} = \frac{0.004 \times 0.5 \text{ mol/L}}{0.25 \text{ L}} = 0.008 \text{ mol}$$



I	0.005	0.008	∅
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C	-0.002	-0.002	+0.002
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E	0.003	∅	0.002
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$$\text{pH} = 5.7 + \log \frac{0.002}{0.003}$$

$$\text{pH} = 5.52$$