

## BIOC 141: Problem Set 2

1. Weak acids (a.k.a buffers) play an absolutely crucial role in biochemistry.
  - a. What is an acid? How does a weak acid differ from a strong acid? Is water a weak acid?

There are several common categories of acids, which describe acids:

**Bronsted-Lowry: a compound that can be a proton donor** <----- often we mean this one

Lewis: an electron acceptor

Arrhenius: when added to water, increases the  $[H^+]$  of water.

A strong acid is one that more or less totally dissociates in solution (equilibrium favors protons dissociating from the compound and becoming free protons in solution). Water is a weak acid with a  $pK_a$  of 15.7, and can also function as a base [accepting protons], making it an amphoteric species.

- b. Sketch the titration curves (equivalents  $OH^-$  on the x-axis, pH on the y-axis) for two weak acids, one with  $pK_a = 5$ , the other with  $pK_a = 9$ . Are the shapes of the two titration curves different?

The two curves are quite similar, with the major change being that they are shifted vertically relative to each other. The  $pK_a = 9$  weak acid has its buffer region centered at pH 9, the  $pK_a = 5$  acid has its buffer region centered at pH = 5.

- c. Sketch the titration curve for a strong acid. Does the shape of the curve differ from those in (b)? Why or why not?

The main distinction between a strong acid and a weak acid is that the strong acid almost totally dissociates; there's virtually no buffering capacity (in the form of protonated strong acid) in solution to neutralize  $OH^-$  being added.

Thus, there is no buffer region in the titration curve (we don't draw an inflection point at 1/2 equivalent of hydroxide.)

2. An enzyme-catalyzed reaction was carried out in a 0.2 M Tris buffer, pH 7.8. As a result of the reaction, 0.03 mole/liter of  $H^+$  was produced.

- a. What was the ratio of  $Tris^0$  (the conjugate base form of the buffer) to  $Tris^+$  (the weak acid form of the buffer) at the start of the reaction (i.e., before the 0.03 mole/liter of  $H^+$  was produced)? The  $pK_a$  of Tris is 8.1.

Originally, it was an equilibrium satisfying the HH equation:

$$pH = pK_a + \log([Tris^0]/[Tris^+])$$

$$7.8 = 8.1 + \log([Tris^0]/[Tris^+])$$

$$10^{-0.3} = [Tris^0]/[Tris^+]$$

$$[Tris^0] = 0.501187[Tris^+]$$

**Initial ratio  $Tris^0 : Tris^+$ : 501 parts  $Tris^0$  : 1000 parts  $Tris^+$**

- b. What were the concentrations of  $Tris^+$  and  $Tris^0$  at the start of the reaction?

Initial ratio  $Tris^0 : Tris^+$ : 501 parts  $Tris^0$  : 1000 parts  $Tris^+$   
and that there were 0.2M Tris (meaning  $[Tris^+] + [Tris^0] = 0.2M$ )

$$[Tris^+] * (501 \text{ part } Tris^0 / 1000 \text{ part } Tris^+) + [Tris^0] = 0.2M$$

$$1.501 [Tris^0] = 0.2 \text{ M}$$

$$[Tris^0] = 0.1332 \text{ M}, \text{ so } [Tris^+] = 0.2M - [Tris^0] = 0.0668 \text{ M}$$

$$\begin{aligned} \text{----> } [Tris^0] &= 0.1332 \text{ M} \\ \text{----> } [Tris^+] &= 0.0668 \text{ M} \end{aligned}$$

- c. What were the concentrations of  $Tris^+$  and  $Tris^0$  at the end of the reaction?

We produced 0.03M  $H^+$ , which will protonate  $Tris^0$

This gives us  $[Tris^0] = 0.1332M - 0.03M = 0.1032 \text{ M}$  and  $[Tris^+] = 0.0668M + 0.03M = 0.0968 \text{ M}$

**Final  $[Tris^0] = 0.1032 \text{ M}$   
Final  $[Tris^+] = 0.0968 \text{ M}$**

- d. What is the pH at the end of the reaction?

by the HH equation:

$$pH = pK_a + \log([Tris^0]/[Tris^+])$$

$$pH = 8.1 + \log(0.1032M/0.0968M) = 8.1 + 0.028$$

**final pH = 8.128 which we'll round to pH 8.1**

- e. What would the final pH have been had the reaction occurred in an unbuffered solution with an initial pH of 7.8?

Without the buffer, we would have added 0.03M  $H^+$  to the initial  $[H^+]$  concentration directly:

$$\text{initial } [H^+] = 10^{-pH} = 10^{-7.8} = 1.585 * 10^{-8} \text{ M}$$

$$\text{final } [H^+] = \text{initial } [H^+] + 0.03M = \text{about } 0.03M$$

$$\text{final pH} = -\log(\text{final } [H^+]) = -\log(0.03M) = 1.523$$

**final pH = 1.5**

3. For each of the following amino acids, calculate the ratio of charged side chain to uncharged side chain in the bloodstream (pH 7.4). Use the pKa values in Table 2.2. ... I have values in Table 2.1, not 2.2.

a. **Glu** - pKa 4.1 - carboxylic acid [deprotonated is charged] - guesstimate is  $10^3$  deprot: 1 prot  
 $\text{pH} = \text{pKa} + \log(\text{RCOO}^-/\text{RCOOH})$  1995 part  $\text{RCOO}^-$  : 1 part  $\text{RCOOH}$   
 $7.4 - 4.1 = \log(\text{RCOO}^-/\text{RCOOH})$   
 $10^{3.3} = \text{RCOO}^-/\text{RCOOH}$   
 $[\text{RCOO}^-] = [\text{RCOOH}] * 10^{3.3}$

**So charged side chain:uncharged side chain = 1995:1**

b. **Cys** pKa 8.3 - thiol [deprotonated is charged] - guesstimate 1 deprot : 10 prot

$\text{pH} = \text{pKa} + \log(\text{RS}^-/\text{RSH})$   
 $7.4 - 8.3 = \log(\text{RS}^-/\text{RSH})$   
 $10^{-0.9} = [\text{RS}^-]/[\text{RSH}]$   
 $[\text{RS}^-] = 0.1259[\text{RSH}]$

1 parts  $\text{RS}^-$ : 7.94 parts  $\text{RSH}$

**So charged side chain:uncharged side chain = 1:7.94**

c. **Arg** pKa 12.5 - amino - protonated is charged] - guesstimate 1 deprot :  $10^5$  prot

$\text{pH} = \text{pKa} + \log(\text{RNH}_2/\text{RNH}_3^+)$   
 $7.4 - 12.5 = \log(\text{RNH}_2/\text{RNH}_3^+)$   
 $10^{-5.1} = [\text{RNH}_2]/[\text{RNH}_3^+]$   
 $[\text{RNH}_2] = 7.943 * 10^{-6} * [\text{RNH}_3^+]$

1 part  $\text{RNH}_2$  : 126,000 parts  $\text{RNH}_3^+$

**So charged side chain:uncharged side chain = 126,000 : 1**

d. **His** pKa 6.0 - amino [protonated is charged] - guesstimate 10 deprot : 1 prot

$\text{pH} = \text{pKa} + \log(\text{RRN}/\text{RRNH}^+)$   
 $7.4 - 6.0 = \log(\text{RRN}/\text{RRNH}^+)$   
 $10^{1.4} = [\text{RRN}]/[\text{RRNH}^+]$   
 $[\text{RRN}] = 25.12 * [\text{RRNH}^+]$

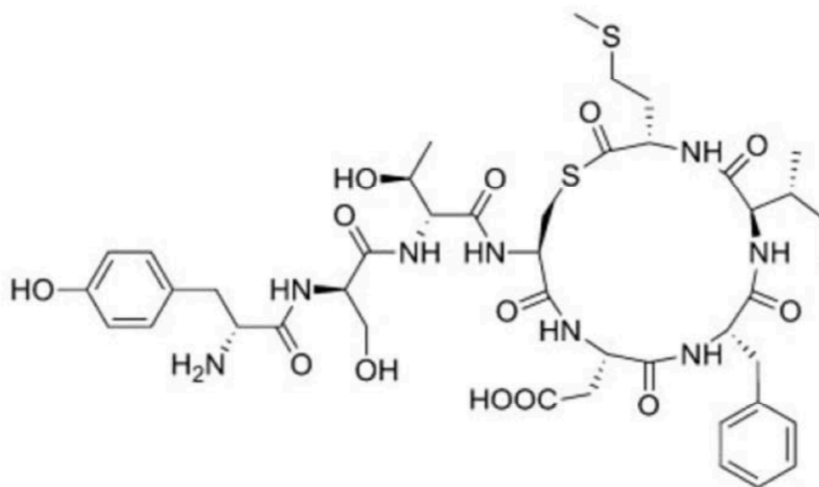
1 part  $\text{RRNH}^+$  : 25.1 parts  $\text{RRN}$

**So charged side chain:uncharged signed chain = 1:25.1**

e. **Leu** alkane sidechain. pKa too high to bother thinking about at blood pH. (Guessing around 45)

Is essentially 100% uncharged side chain. ( $1:10^{40}$ )

4. Consider the following oligopeptide:



- Box each amino acid and identify it by its one-letter abbreviation
- Determine the net charge of the oligopeptide at pH values of 2, 7, and 12