Answers to Problem Set 1

1. a). \[ \text{pH} = \text{pK} + \log \left( \frac{\text{Base}}{\text{Acid}} \right) \]; \[ 9.5 = 10.5 + \log \left( \frac{\text{Base}}{\text{Acid}} \right) \]

\[ \log \left( \frac{\text{Base}}{\text{Acid}} \right) = -1 \]; \[ \frac{\text{Base}}{\text{Acid}} = \frac{1}{10} \]; \[ \text{Base} + \text{Acid} = 1 \]

\[ \text{Acid} = 0.91 \]

b). \[ \text{Acid} = 0.24 \]

c). The \( \varepsilon \)-NH\(_2\) group has a pK similar to that of aliphatic amines. The \( \alpha \)-NH\(_2\) group is close to the \( \alpha \)-COO\(^-\) which is electron withdrawing and increases the acidity of the \( \alpha \)-NH\(_2\) group. If the carboxyl group is converted to an ester, which has a strong dipole moment and is more electron withdrawing than the COO\(^-\) group, the pK of the \( \alpha \)-NH\(_2\) group decreases to 7.75.

2. 

\[ \text{pKa}=4.43 \]

\[ \text{pKa}=7.7 \]

\[ \text{pKa}=9.78 \]

\[ \text{pKa}=2.35 \]

a). B

b). B is a dipolar ion.

3. 

\[ \text{pK}=4.43 \]

\[ \text{pK}=7.7 \]

\[ \text{pK}=9.78 \]

\[ \text{pK}=2.35 \]
4. i) (a) due to the limited number of orientations for making H-bonds as compared to Xe dimers.
   ii) (a) the H-bonds are more favorable when isolated in a nonpolar environment due to an entropic effect.
   iii) (b) since the imidazolium group has a + charge, the + dipole at the N-terminus of a helix will lower its pKa while the - dipole at the C-terminus will raise its pKa.

5. a) 1.5 angstroms
    b) 3.5 - 3.7 angstroms
    c) 2-4 aa
    d) protein is 50 angstroms in diameter, so:
       for $\alpha$ helix, need: $50/1.5 = 33$ aa
       for $\beta$ strand, need: $50/3.5 = 14$ aa
       for turn $2\text{ aa}$
       49 aa total

6. The dissociation constant for hemoglobin is: $K_d = (\alpha\beta)^2/(\alpha\beta)^2$
The deoxyhemoglobin dimer is more stable than the oxyhemoglobin dimer by:

   $\Delta(\Delta G^0) = -RT \ln(K_d \text{ oxy})/(K_d \text{ deoxy}) = -RT \ln 6 = -1.35 \times 6 \text{ Kcal/mol}$

   There are six salt linkages; therefore, $\Delta G^0 = -1.35 \text{ Kcal/mol per salt linkage}$.

7. a) Lys, His, Arg and the N-terminus
   b) $\log (Y/1-Y)$
   c) $\log(pO_2)$

   $n$ for both is $\sim 3$

8. a) 2
   b) 0.5
   c) 60