Discussion Exercise 2: Polyprotic Acids

Answer key

Problem 1: Draw the conjugate acid and the conjugate base of each of these compounds. (Consider the pKa values of the functional groups!)

<table>
<thead>
<tr>
<th>Conj. Acid</th>
<th>Conj. Base</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Conjugate Acid 1" /></td>
<td><img src="image2" alt="Conjugate Base 1" /></td>
</tr>
<tr>
<td><img src="image3" alt="Conjugate Acid 2" /></td>
<td><img src="image4" alt="Conjugate Base 2" /></td>
</tr>
<tr>
<td><img src="image5" alt="Conjugate Acid 3" /></td>
<td><img src="image6" alt="Conjugate Base 3" /></td>
</tr>
</tbody>
</table>

Problem 2: The first pKa of succinic acid is 4.2 and the second pKa of succinic acid is 5.6. How can the same functional group have different pKa values?

After the loss of the first proton, the “new” acid is already negatively charged, making loss of a second proton harder. This is reflected in the higher pKa value.
Problem 3: Phosphoric acid has three pKa values, at approximately 2, 7, and 12. Draw the conjugate acid/base pair for each of these three pKa values.

\[
\begin{align*}
\text{pKa}_1 &= 2 \\
\text{pKa}_2 &= 7 \\
\text{pKa}_3 &= 12
\end{align*}
\]

Problem 4: Draw the following molecules in the correct major ionization state at pH 7. Use Figure 2.11, Table 3.1, and the pKa values given in the problem.

A.  
B.  
C.
Problem 5. Draw the following molecules in their major ionization state(s) at pH 2.3, 6.0, 9.6, and 12.0.

at pH 2.3

at pH 6.0

at pH 9.6

at pH 12
Problem 6. Refer to Figure 2.11. What is the approximate net charge on carbonic acid at pH 3.8? at pH 8.0? at pH 11.5?

At pH 3.8, the pH = pKa, so the molecule is half in its fully protonated, neutral state and half is in the deprotonated, -1 charge state. The net charge is close to -1/2

At pH 8.0, the pH is far higher than the first pKa, so the first proton is fully deprotonated. The pH is 2 units below the second pKa, so the second proton is 99% in its protonated state. The major ionization state is shown below, which has a net charge of close to -1.

At pH 11.0, the pH is far higher than the first pKa, so the first proton is fully deprotonated. The pH is 1 units higher than the second pKa, so the second proton is about 90% in its deprotonate state. The major ionization state is shown below, which has a net charge of close to -2.

Problem 7. What is the isoelectric point for lysine and aspartic acid? (See Table 3.1)

For lysine, the net zero charge species occurs half way between pH 9.6 and 10.8, so the isoelectric point is 10.2
For aspartic acid, the net zero charge species occurs halfway between pH 3.1 and 4.1, so the isoelectric point is 3.6.

![Chemical structures showing pH 3.1, pH 4.1, and pH 9.6]

**Exercises:**

1. Finish doing this thought experiment and filling in the table for points G-J.

<table>
<thead>
<tr>
<th>Point</th>
<th>Added HO⁻</th>
<th>Total Equiv of HO⁻</th>
<th>Molecules of A⁻</th>
<th>Molecules of HA</th>
<th>[A⁻]/[HA]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>8 molecules</td>
<td>1.01</td>
<td>1</td>
<td>99</td>
<td>About 1/100</td>
<td>7.9</td>
</tr>
<tr>
<td>G</td>
<td>41 molecule</td>
<td>1.09</td>
<td>9</td>
<td>91</td>
<td>About 1/10</td>
<td>8.9</td>
</tr>
<tr>
<td>H</td>
<td>41 molecule</td>
<td>1.50</td>
<td>50</td>
<td>50</td>
<td>1/1</td>
<td>9.9</td>
</tr>
<tr>
<td>I</td>
<td>41 molecule</td>
<td>1.91</td>
<td>91</td>
<td>9</td>
<td>About 10/1</td>
<td>10.9</td>
</tr>
<tr>
<td>J</td>
<td>8 molecule</td>
<td>1.99</td>
<td>99</td>
<td>1</td>
<td>About 100/1</td>
<td>11.9</td>
</tr>
</tbody>
</table>
2. Where are the buffer regions for alanine? Explain how the solution acts as a buffer in these pH regions.

The first buffer region is 1.4 to 3.4, which is one pH unit on either side of the first pKa value or 2.4. In this region, there are significant amounts of this conjugate acid/base pair:

```
  \[ \text{H}_3\text{N}^+ - \text{COO}^- \rightleftharpoons \text{H}_3\text{N}^- - \text{COOH} \]
```

The second buffer region is 8.9 to 10.9, which is one pH unit on either side of the second pKa value of 9.9. In this region, there are significant amounts of this conjugate acid/base pair:

```
  \[ \text{H}_3\text{N}^+ - \text{COO}^- \rightleftharpoons \text{H}_2\text{N}^- - \text{COO}^- \]
```

3. Why did we have to start using a different value of pKa half-way through the problem? How do you know which pKa value to use?

After the pH of the solution got significantly above the first pKa value of 2.4, the first proton was completely deprotonated. As the pH got higher, the second acidic proton was the reactive acid. You should use the pKa value that is associated with the proton that is reacting in the reaction of interest.

4. Imagine we had a 1 M triprotic acid with pKa₁ = 3.4, pKa₂ = 8.1, and pKa₃ = 12.9. The solution starts at a high pH so that the acid was completely deprotonated. What is the pH of the solution if:

   A. 0.09 eq. of HCl are added? pH 13.9
   B. 0.5 eq. of HCl are added? pH 12.9
   C. 1.0 eq. of HCl are added? pH \((8.1 + 12.9)/2 = 10.5\)
   D. 2.0 eq. of HCl are added? pH \((3.4 + 8.1)/2 = 5.8\)
   E. 2.5 eq. of HCl are added? pH = 3.4