Lecture Notes P: Acid-Base Chemistry III

1) Who wants protons more (or who wins in a fight for protons)

Mix HF with NaCN, or mix NaF with HCN

\[
\begin{align*}
\text{HF} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^- & K_a &= 6.6 \times 10^{-4} & \text{p}K_a &= 3.18 \\
\text{HCN} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^- & K_a &= 6.17 \times 10^{-10} & \text{p}K_a &= 9.21
\end{align*}
\]

concept
You have 50 ml of a complex mixture of weak acids that contains some HF and some HCN. Which is larger, [F]/[HF] or [CN]/[HCN]?

(a) [F]/[HF]       (b) [CN]/[HCN]       (c) can’t tell from available information
2) **Once you know the pH, what does a weak acid look like.**

If you know the temperature of Pittsburgh, you can say what it feels like. This is much easier than calculating/predicting the temperature of Pittsburgh.
**Concept**

Some side chains in proteins contain sites that can exchange protons with the surrounding water (i.e. they are weak acids). Consider a protein with the following side chains,

<table>
<thead>
<tr>
<th>Amino Acid</th>
<th>side-chain</th>
<th>Amino Acid</th>
<th>side-chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arginine</td>
<td>$pK_a = 12.48$</td>
<td>Histidine</td>
<td>$pK_a = 6.04$</td>
</tr>
<tr>
<td>Aspartic Acid</td>
<td>$pK_a = 3.90$</td>
<td>Lysine</td>
<td>$pK_a = 10.79$</td>
</tr>
<tr>
<td>Cysteine</td>
<td>$pK_a = 8.33$</td>
<td>Tyrosine</td>
<td>$pK_a = 10.13$</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>$pK_a = 4.07$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Given that the pH of blood is about 7.3, how many of the above side chains would be in their ionic form ($A^-$) in blood?

A) 2  B) 3  C) 4  D) 5

3) **pH indicators**

Consider an indicator that is a weak acid with $K_a = 1.4 \times 10^{-9}$ ($pK_a = 8.8$). The protonated form (HIn) is colorless, and the deprotonated form (In$^-$) is pink. [This is similar to the indicator Phenolphthalein.]

**Who is controlling the pH, and who is being controlled by the pH?**

What is the ratio between the protonated and deprotonated forms ($[HA]/[A^-]$) when the pH is 7.8?

What is the ratio between the protonated and deprotonated forms ($[HA]/[A^-]$) when the pH is 8.8?

What is the ratio between the protonated and deprotonated forms ($[HA]/[A^-]$) when the pH is 9.8?
4) How buffers work.

As the pH changes, the ratio of \([A^-]/[HA]\) changes.

Corollary: To change the pH you have to change the ratio \([A^-]/[HA]\).

So if you have a bunch of \([A^-]\) and [HA] present, and you want the pH to go up, you have to convert most of the HA into \(A^-\).

Consider starting with 100ml of a mixture in which \([A^-] = [HA] = 1M\).

Now add enough OH\(^-\) to convert half the HA into \(A^-\) (50ml of 1M NaOH).

\[
HA + OH^- \leftrightarrow A^- + H_2O \quad K = 1/K_b = K_a/K_w >> 1
\]

If you had added 50ml of 1M NaOH to 100ml of water, the pH would be:

Similarly, if you add enough H\(_3\)O\(^+\) to convert half the \(A^-\) into HA (50 ml of 1M HCl).

\[
A^- + H_3O^+ \leftrightarrow HA + H_2O \quad 1/K_a >> 1
\]

If you had added 50ml of 1M NaOH to 100ml of water, the pH would be: