Class 7.3
Aqueous Equilibrium

CHEM 102H
T. Hughbanks

Mixed Solutions

- Most (not all) of Chapter 10 of your text deals with how various solutions of a single acid or base affect the pH.
- Now we deal mixtures of acids, bases, and salts.
- A key concept to keep in mind involves conjugate acids and bases.

Acid plus Salt w/conjugate Base

Example: what is the pH of a solution that is 0.1M in HF in HF and 0.05 M NaF?
For hydrofluoric acid, $pK_a = 3.46$.

$$\text{HF}(aq) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$$

<table>
<thead>
<tr>
<th>Initial</th>
<th>Final</th>
<th>Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M</td>
<td>0</td>
<td>0.05 M</td>
</tr>
<tr>
<td>0.1 - x</td>
<td>x</td>
<td>0.05 + x</td>
</tr>
</tbody>
</table>

Ans. $x = 6.79 \times 10^{-4}$ (exact) $6.93 \times 10^{-4}$ (approx)
Conclusions from last example

- HF is an acid that is only moderately weak, but in the presence of added F\(^-\) the net dissociation of HF is strongly suppressed.
- The 2% error in the approximate answer will only get smaller for this kind of situation with weaker acids.

The buffer effect

When appreciable amounts of both HA and A\(^-\) are present, pH will be near pK\(_a\) of the acid.

Henderson-Hasselbalch Eqn.

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \Rightarrow [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}
\]

take "-log" of both sides of the right-hand eqn,

\[
pH = pK_a - \log \frac{[\text{HA}]}{[\text{A}^-]} = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]}
\]

When appreciable amounts of both HA and A\(^-\) are present, [HA] = [HA]\(_{\text{initial}}\), [A\(^-\)] = [A\(^-\)]\(_{\text{initial}}\)

\[
pH = pK_a + \log \frac{[\text{A}^-]_{\text{initial}}}{[\text{HA}]_{\text{initial}}}
\]
**Henderson-Hasselbalch Eqn.**

- Remember where the eqn. comes from or how it must work, otherwise you’re likely to get the logarithm mixed up!
- Alternatively, just get used to playing with the equilibrium const. expression, and don’t try to memorize “H-H” eqn. at all.

---

**Base buffers**

- Work in a manner analogous to the acid case, e.g., what is the pH of a solution that is 0.15M in NH₃ and 0.10 M NH₄Cl? For NH₃, pK_b = 4.74.

\[
\text{NH}_3(aq) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^- (aq)
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>Equil.</th>
<th>Ans.</th>
</tr>
</thead>
</table>
| 0.15 M  | 0.10 M | x = [OH⁻] = \(2.73 \times 10^{-5}\)  
(approx = exact to 3 digits) |

---

**Buffer effect, “H-H” for bases**

\[
\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+(aq) + \text{OH}^-(aq)
\]

\[
p\text{OH} = p\text{K}_b + \log \frac{[\text{BH}^+]_{\text{initial}}}{[\text{B}]_{\text{initial}}}
\]

Alternatively, use the acid equation and the pK_a of the conjugate acid: pK_a = 14 - pK_b.
How a buffer works

pH changes relatively slowly over a fairly wide range of concentration ratios $[HA]/[A^-]$.

How to prepare a buffer

1. Find an acid (or conjugate acid) with a $pK_a$ within ~ 0.5 of the desired pH.
2. Adjust $HA$ to $A^-$ ratio.

Example: How do we prepare a buffer for pH = 5?

Buffer Capacity

Compare two cases:
1. Add 50 ml of 0.1M HCl to 50 ml of pure H$_2$O. Find final pH.
2. Add 50 ml of 0.1M HCl to 50 ml of a buffer solution that is 0.2 M in CH$_3$COOH and 0.2 M in Na[CH$_3$COO]. Find initial and final pH.
Titrations

- As you have seen in the lab, acid (base) concentrations in samples are determined by controlled addition of known quantities of base (acid) in “neutralization” reactions.
- ... and as you have also seen, the first step in a titration involves the preparation of a standard solution to perform the titration.

---

**Strong acid / Strong Base**

Example: Add 0.25 M NaOH to 10 mL 0.375 M HNO₃ solution.

---

**Strong acid/ Weak base**

Example: Add 0.20 M HCl to 10 mL 0.35 M (CH₃)₃N solution

(CH₃)₃N: pKᵦ = 9.81