
VI. Applications of Aqueous Equilibria.
A recapitulation: types of aqueous equilibria discussed so far:
(a) water dissociation - use $K_w$.
(b) weak monoprotic acids (e.g., HF) - use $K_a$.
(c) weak polyprotic acids (e.g., $H_2CO_3$) - use $K_{a1}$, $K_{a2}$, ...
(d) weak monoprotic bases (e.g., $NH_3$) - use $K_b$.
(e) anions that are conjugate bases of weak acids (e.g., $F^-$) - use $K_b$.
(f) cations that are conjugate acids of weak bases (e.g., $NH_4^+$) - use $K_a$.

For any conjugate acid/base pair, $K_aK_b = K_w$.

A. Neutralization reactions - needed to understand buffers and acid-base titrations.

Two basic ideas: (i) neutralization is the reaction of an acid with a base to form salt plus water, and (ii) the neutralization reaction is quantitative (~100% products) if either the acid or the base is strong (this concept will be useful later).

Ex. strong acid + strong base: nitric acid + potassium hydroxide

Molecular rxn: $HNO_3 + KOH \rightleftharpoons KNO_3 + H_2O$

Net ionic rxn: $H^+ + OH^- \rightleftharpoons H_2O \quad K = 1/K_w = 1.0 \times 10^{-14}$

Since $K >> 1$, the reaction is quantitative.

Ex. weak acid + strong base: hydrofluoric acid + lithium hydroxide

Molecular rxn: $HF + LiOH \rightleftharpoons LiF + H_2O$

Net ionic rxn: $HF + OH^- \rightleftharpoons F^- + H_2O \quad K = ?$

A lesson in manipulation of equilibrium constants: combine acid dissociation of HF with water dissociation (inverted):

\[
\begin{align*}
HF & \rightleftharpoons H^+ + F^- \\
H^+ + OH^- & \rightleftharpoons H_2O \\
\text{Sum: } HF + OH^- & \rightleftharpoons F^- + H_2O
\end{align*}
\]

$K_a = 3.5 \times 10^{-4}$

$K = 1/K_w$

$K = K_a/K_w = 3.5 \times 10^{-4}/1 \times 10^{-14} = 3.5 \times 10^{10}$

Again, since $K >> 1$, the reaction is quantitative.

By the same method, neutralization of a weak base with a strong acid is quantitative:

\[
\begin{align*}
F^- + H^+ & \rightleftharpoons HF \quad K = K_b/K_w = 2.9 \times 10^{-11}/1.0 \times 10^{-14} = 2.9 \times 10^3
\end{align*}
\]

weak base strong acid
In an aqueous equilibria, addition of a common ion from a second electrolyte shifts the equilibrium in the direction needed to reduce the concentration of the common ion.

Ex. \( HF = H^+ + F^- \)  
Add NaF to a solution of HF. The stress is excess \( F^- \). The response is to shift the equilibrium towards reactants. \([H^+]\) decreases (the pH rises), and \([HF]\) rises (percent dissociation decreases).

Ex. \( NH_3 + H_2O = NH_4^+ + OH^- \)  
Add NH\(_4\)Cl to a solution of NH\(_3\). The stress is excess \( NH_4^+ \). The response: \([OH^-]\) decreases (the pH decreases), and \([NH_3]\) increases (percent dissociation decreases).

No calculations are given here since the typical problem is identical to the Type 4 problem in the next section.

C. Buffer solutions - one of the most important topics in aqueous equilibria; implications in all of biochemistry.
A buffer resists changes in pH. Why? See below. Solutions of strong acid \((pH < 2)\) or strong base \((pH > 12)\) are buffers because small amounts of added acid or base do not change the pH by much. For 2 < \(pH < 12\), a buffer is a solution containing significant concentrations of a conjugate weak acid and its conjugate base. Ex. solutions containing HF and NaF, or NH\(_3\) and NH\(_4\)Cl, are buffers. Recognize when you are dealing with a buffer.

Three types of problems are important here: calculation of buffer pH, calculation of pH after adding strong acid or base, and preparation of buffers.

Type 4. Given concentrations of the conjugate acid and base and \(K_a\) for the conjugate acid, calculate the buffer pH. Let acetic acid \((CH_3COOH)\) be HA and acetate \((CH_3COO^-)\) be A\(^-\). A solution contains 0.20 M HA and 0.10 M NaA. \(K_a(HA) = 1.8 \times 10^{-5}\). What is the pH? (note the presence of HA and A\(^-\) in significant conc.)

Solve the slow way: use the acid dissociation equilibria and a table of initial, \(\Delta\), and final conc.

<table>
<thead>
<tr>
<th>HA</th>
<th>=&gt;</th>
<th>H(^+) + A(^-)</th>
<th>(K_a = [H^+][A^-]/[HA])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Init.</td>
<td>0.20 M</td>
<td>0</td>
<td>0.10 M</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>(-x)</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Final</td>
<td>0.20 - x</td>
<td>x</td>
<td>0.10 + x</td>
</tr>
</tbody>
</table>
\[ K_a = 1.8 \times 10^{-5} = \frac{(x)(0.10 + x)}{(0.20 - x)} \quad \text{A quadratic equation} \]

Assume that \( x \) is small compared to both the conjugate acid and the conjugate base (always valid for this course), i.e. \( x << 0.10 \) and \( x << 0.20 \) M. Then:
\[
1.8 \times 10^{-5} = \frac{(x)(0.10)}{(0.20)}; \quad x = \frac{(0.20)(1.8 \times 10^{-5})}{(0.10)} = 3.6 \times 10^{-5} \text{ M} = [H^+] \\
\text{pH} = -\log(3.6 \times 10^{-5}) = 4.44. 
\]

Solve the quick way: the Henderson-Hasselbach equation. \( pK_a = -\log(K_a) \). (derivation given in the text)

\[
\text{pH} = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) 
\]

Note: (i) Always use \( K_a \). If you are given \( K_b \) for the conj. base, convert to \( K_a \).

(ii) Correctly identify which species is the acid and which is the base.

(iii) You can use the ratio of moles or molarity of conjugate base over conjugate acid.

For the above problem, \( pK_a = -\log(1.8 \times 10^{-5}) = 4.74 \), [acid] = [HA] = 0.20 M, [base] = [A\textsuperscript{-}] = 0.10 M, and:
\[
\text{pH} = 4.74 + \log\left(\frac{(0.10)}{(0.20)}\right) = 4.74 + \log(0.50) = 4.74 + (-0.30) = 4.44
\]

Ex. What is the pH of a buffer containing 0.45 M \( \text{NH}_4\text{Cl} \) and 0.15 M \( \text{NH}_3 \)? \( K_a(\text{NH}_3) = 1.8 \times 10^{-5} \).

First, convert \( K_b \) to \( K_a \):
\[
K_a = \frac{K_a}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}
\]

Next, find \( pK_a \):
\[
pK_a = -\log(5.6 \times 10^{-10}) = 9.26
\]

Next, identify the conc. of the conj. acid and base: [acid] = \([\text{NH}_4^+] = 0.45 \text{ M (from NH}_2\text{Cl}]; [base] = [\text{NH}_3] = 0.15 \text{ M.}

Last, use H-H equ. \[
\text{pH} = 9.26 + \log\left(\frac{(0.15)}{(0.45)}\right) = 9.26 + (-0.48) = 8.78
\]

Note special case: if [acid] = [base], then pH = \( pK_a \) (since \( \log(1) = 0 \)). Buffers tend to have pH’s close to the \( pK_a \) of the conj. acid.

Note: the buffer pH depends on the ratio of moles of conj. base to moles of conj. acid. That ratio does not depend on solution volume. Within reasonable limits, buffer pH is not sensitive to dilution.

How do buffers work? The conj. base reacts with any added \( H^+ \), while the conj. base reacts with any added \( \text{OH}^- \). The reactions are quantitative (see section A). The buffering action continues until either the conj. acid or the conj. base is used up.
Type 5. Given a buffer, calculate the pH change after adding strong acid or strong base.

Ex. A buffer is composed of 0.50 M HA and 0.50 M A⁻, where $K_a(\text{HA}) = 1.0 \times 10^{-7}$. (a) What is the pH? (b) What is the pH after 10. mLs of 0.10 M NaOH is added to 100. mL of the buffer?

(a) Original pH = $pK_a = -\log(1.0 \times 10^{-7}) = 7.00$ (since $[\text{HA}] = [\text{A}^-]$)

(b) Use the acid-base neutralization reaction. Here, OH⁻ will neutralize the weak acid HA. Work in moles, not molarity.

<table>
<thead>
<tr>
<th>HA + OH⁻ ⇌ A⁻ + H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Init. 0.050</td>
</tr>
<tr>
<td>Δ -0.0010</td>
</tr>
<tr>
<td>Final 0.049</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th># moles HA</th>
<th>(0.50 M HA)(0.100 L)</th>
<th>0.050 moles</th>
</tr>
</thead>
<tbody>
<tr>
<td># moles A⁻</td>
<td>(0.50 M A⁻)(0.100 L)</td>
<td>0.050 moles</td>
</tr>
<tr>
<td># moles OH⁻</td>
<td>(0.10 M OH⁻)(0.010 L)</td>
<td>0.0010 moles</td>
</tr>
</tbody>
</table>

The neutralization reaction goes quantitatively to products, so # moles of OH⁻ is driven to ~ 0. Use the ΔOH to calculate other Δconc. and calculate final conc. of HA and A⁻. Plug these final conc. into the H-H equ.

$$\text{pH} = pK_a + \log([\text{A}^-]/[\text{HA}]) = 7.00 + \log([\text{A}^-]/[\text{HA}])$$

$$\text{pH} = 7.00 + \log((0.051)/(0.049)) = 7.00 + \log(1.04) = 7.00 + (0.02) = 7.02$$

The buffer changed pH by only 0.02 units. For comparison, the same amount of base added to 100 mLs of pure water would change the pH from 7.00 to about 13.0, a change of 6 units.

Note: if the problem states that acid was added, use the neutralization of the weak base by H⁺:

$$\text{A}^- + \text{H}^+ = \text{HA}$$

Type 5 variation: How many moles of base must be added to change the pH by 1? See the Nakon exercise book for details. Buffer capacity can be defined as the number of moles of strong acid or base required to change the buffer pH by 1 unit.

Type 6: How to prepare a buffer of a specified pH. Ex. Given 1.0 L of a 1.0 M HA solution ($K_a = 1.8 \times 10^{-5}$), how many moles of NaA must be added to prepare a buffer of pH 5.00?

Start with the H-H equ.: $\text{pH} = pK_a + \log([\text{A}^-]/[\text{HA}])$

$$5.00 = 4.74 + \log([\text{A}^-]/[\text{HA}]); \log([\text{A}^-]/[\text{HA}]) = 5.00 - 4.74 = 0.26$$

$$[\text{A}^-]/[\text{HA}] = 10^{0.26} = 1.8$$

It is easier to work in moles: # moles HA = (1.0 M)(1.0 L) = 1.0 moles

$[\text{A}^-]/(1.0 \text{ moles}) = 1.8; [\text{A}^-] = 1.8 \text{ moles} = $ # moles of NaA needed.