Ch. 8: Monoprotic Acid-Base Equilibria

Outline:

- 8-1 Strong Acids and Bases
- 8-2 Weak Acids and Bases
- 8-3 Weak-Acid Equilibria
- 8-4 Weak-Base Equilibria
- 8-5 Buffers

**Strong Acids and Bases**

HBr is a strong acid, so the following reaction goes to completion:

\[ \text{HBr} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Br}^- \]

If the concentration of HBr is 0.10 M, then \([\text{H}_3\text{O}^+] = 0.10 \text{ M}\), and the pH can be calculated as:

\[ \text{pH} = \log(\text{[H}^+\text{]}) = -\log(0.10) = 1.00 \]

However, if activity coefficients are taken into account, the ionic strength of 0.10 M HBr is \(\mu = 0.10 \text{ M}\), for which the activity coefficient of H\(^+\) is 0.83. Then:

\[ \text{pH} = -\log A_{\text{H}^+} = -\log([\text{H}^+]\gamma_{\text{H}^+}) = -\log((0.10)(0.83)) = 1.08 \]

Generally, we will neglect activity coefficients, unless there is a specific point to be made regarding inert species or related phenomena.

For 0.10 M KOH (strong base, complete dissociation), \([\text{OH}^-] = 0.10 \text{ M}\). Thus,

\[ [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} \text{ M}; \text{ hence, } \text{pH} = -\log([\text{H}^+]) = 13.00 \]

Useful relation: \(\text{pH} + \text{pOH} = -\log K_w = 14.00 \text{ at } 25 \text{ °C}\)
Dilemma and Cure

What is the pH of $1.0 \times 10^{-8}$ M KOH?

$$[H^+] = K_w / (1.0 \times 10^{-8}) = 1.0 \times 10^{-6} \text{ M}; \text{ so, pH} = 6.00$$

**Dilemma:** We know that a strong base cannot produce an acidic solution; so, something is wrong with using this relation.

**Cure:** To deal with this case, we use the systematic treatment of equilibrium (Chapter 7). We must consider the autoprotolysis of water, and production of $\text{OH}^-$.

**Step 1:** Write out the pertinent reactions.

$$\text{H}_2\text{O} \rightleftharpoons H^+ + \text{OH}^-$$

**Step 2:** Charge balance. Solution species are $K^+$, $H^+$ and $\text{OH}^-$, so

$$[H^+] + [K^+] = [\text{OH}^-]$$

**Step 3:** Mass balance. All $K^+$ comes from KOH, so $[K^+] = 1.0 \times 10^{-8}$ M.

**Step 4:** Equilibrium constant. $K_w = [H^+][\text{OH}^-] = 1.0 \times 10^{-14}$

**Step 5:** Count. There are 3 equations, and three unknowns, $[K^+]$, $[H^+]$ and $[\text{OH}^-]$. 
Step 6: Since we are looking for pH, we set $x = [H^+]$ and

$$[OH^-] = [H^+] + [K^+] = x + 1.0 \times 10^{-8}$$

Insert $[OH^-] = 1.0 \times 10^{-8} + x$ into the $K_w$ equilibrium equation, and solve the problem:

$$[H^+][OH^-] = K_w$$

$$(x)(1.0 \times 10^{-8} + x) = 1.0 \times 10^{-14}$$

$$x^2 + (1.0 \times 10^{-8})x - (1.0 \times 10^{-14}) = 0$$

$$x = \frac{-1.0 \times 10^{-8} \pm \sqrt{(1.0 \times 10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$= 9.6 \times 10^{-8} \text{ M} \quad \text{or} \quad -1.1 \times 10^{-7} \text{ M}$$

The negative solution from the quadratic equation is rejected, and therefore

$$[H^+] = 9.6 \times 10^{-8} \text{ M}, \quad \text{with pH} = -\log[H^+] = 7.02$$

This result makes a lot of sense, since we know that a dilute solution of a strong base should be only slightly basic (i.e., slightly above 7.00).
1. When the concentration is “high” ($\geq 10^{-6}$ M), pH is calculated by just considering the added $H^+$ or $OH^-$. That is, the pH of $10^{-5.00}$ M KOH is 9.00.

2. When the concentration is “low” ($\leq 10^{-8}$ M), the pH is 7.00. We have not added enough acid or base to change the pH of the water itself.

3. At intermediate concentrations of $10^{-6}$ to $10^{-8}$ M, the effects of water ionization and the added acid or base are comparable. Only in this region is a systematic equilibrium calculation necessary.

Region 1 is the only practical case. Unless you were to protect $10^{-7}$ M KOH from the air, the pH would be governed by dissolved $CO_2$, not KOH.
A Misconception

The misconception that dissociation of water always produces $10^{-7}$ M $\text{H}^+$ and $10^{-7}$ M $\text{OH}^-$ is true only in pure water with no added acid or base. In $10^{-4}$ M HBr, for example, the pH is 4. The concentration of $\text{OH}^-$ is $[\text{OH}^-] = K_w/[\text{H}^+] = 10^{-10}$ M. But the only source of $[\text{OH}^-]$ is dissociation of water. If water produces $10^{-10}$ M $\text{OH}^-$, it must also produce $10^{-10}$ M $\text{H}^+$ because it makes one $\text{H}^+$ for every $\text{OH}^-$. In $10^{-4}$ M HBr solution, water dissociation produces only $10^{-10}$ M $\text{OH}^-$ and $10^{-10}$ M $\text{H}^+$.
Weak Acids and Bases

Recall that a weak acid is an acid that does not completely dissociate (i.e., the reaction below does not go to completion). The acid dissociation constant, $K_a$ is given below:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Similarly, the reaction for a weak base does not go to completion, and the reaction is used to define the base hydrolysis constant, $K_b$:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

The three $pK'$s are the negative logs of the equilibrium constants:

$$pK_w = -\log[K_w]; \quad pK_a = -\log[K_a]; \quad pK_b = -\log[K_b]$$

As $K$ increases, $pK$ decreases, and vice versa.
Weak Acids and Bases, 2

Comparing formic and benzoic acids: formic acid is a stronger acid, with a larger $K_a$ and smaller $pK_a$, than benzoic acid.

Recall that the acid HA and its corresponding base, $A^-$, are said to be a *conjugate acid-base pair*, and similarly, B and BH$^+$ are a conjugate pair. The important relation between $K_a$ and $K_b$ for a conjugate acid-base pair is

$$K_a \cdot K_b = K_w$$

The conjugate base of a weak acid is a weak base, and the conjugate acid of a weak base is a weak acid. e.g., if HA has $pK_a = 4$ ($K_a = 10^{-4}$), then the weak conjugate base has $pK_b = 10$ ($K_b = 10^{-10}$). If HA becomes a weaker acid, $A^-$ becomes a stronger base (but never a strong base). If HA is strong (e.g., HCl), then the conjugate base, Cl$^-$, is so weak, that it is not even a base in water!
Acid Dissociation Constant

Acid dissociation constants are listed in Appendix G of the 8th edition of Harris, with all compounds shown in their fully protonated forms.

**e.g.**, Diethylamine is shown as \((\text{CH}_3\text{CH}_2)\text{2NH}_2^+\), which is the diethylammonium ion. The value of \(K_a (1.0 \times 10^{-11})\) given is actually \(K_a\) for the diethylammonium ion. Therefore, \(K_b\) for diethylamine is \(1.0 \times 10^{-3}\).

For polyprotic species, several values of \(K_a\) are given

<table>
<thead>
<tr>
<th>(pK_a)</th>
<th>(K_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4 (POH)</td>
<td>0.04</td>
</tr>
<tr>
<td>3.51 (OH)</td>
<td>(3.1 \times 10^{-4})</td>
</tr>
<tr>
<td>6.04 (POH)</td>
<td>(9.1 \times 10^{-7})</td>
</tr>
<tr>
<td>8.25 (NH)</td>
<td>(5.6 \times 10^{-9})</td>
</tr>
</tbody>
</table>

where \(pK_1\) (1.4) is for dissociation of one of the phosphate protons, and \(pK_2\) (3.51) is for the hydroxyl proton. The third most acidic proton is the other phosphate proton, for which \(pK_3 = 6.04\), and the NH+ group is the least acidic (\(pK_4 = 8.25\)).
Acid Dissociation Constant, 2

If a structure in Appendix G has a charge other than 0, it is not the structure that belongs with the name. Names refer to neutral molecules. The neutral molecule pyridoxal phosphate is not the species drawn below, which has a +1 charge. The neutral molecule pyridoxal phosphate is

![Pyridoxal Phosphate Structure](image)

We took away a POH proton, not the NH$^+$ proton, because POH is the most acidic group in the molecule ($pK_a = 1.4$).

As another example, consider the piperazine:

![Piperazine Structures](image)

Appendix G gives $pK_a$ for ionic strengths of 0 and 0.1 M, when available. We will use $pK_a$ for $\mu = 0$ unless there is no value listed or we need $\mu = 0.1$ M for a specific purpose. For pyridoxal phosphate, we used values for $\mu = 0.1$ M because none are listed for $\mu = 0$. 
Weak-Acid Equilibria

Compare the ionizations of ortho- and para-hydroxybenzoic acids:

Why is the ortho isomer 30 times more acidic than the para isomer? Any effect that increases the stability of the product of a reaction drives the reaction forward. In the ortho isomer, the product of the acid dissociation reaction forms a strong, internal hydrogen bond.

By stabilizing the product, the internal hydrogen bond is thought to make o-hydroxybenzoic acid more acidic than p-hydroxybenzoic acid.
Weak-Acid Equilibria, 2

A typical problem is to find the pH of a solution of weak acid HA. We know [HA] (formal concentration, \( F \)) and the value of \( K_a \). The systematic treatment of equilibrium yields:

\[
\text{Reactions: } \quad \text{HA} \overset{K_a}{\rightleftharpoons} \text{H}^+ + \text{A}^- \quad \text{H}_2\text{O} \overset{K_w}{\rightleftharpoons} \text{H}^+ + \text{OH}^- \\
\text{Charge balance: } \quad [\text{H}^+] = [\text{A}^-] + [\text{OH}^-] \\
\text{Mass balance: } \quad F = [\text{A}^-] + [\text{HA}] \\
\text{Equilibrium expressions: } \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad K_w = [\text{H}^+][\text{OH}^-]
\]

So, there are four equations and four unknowns ([A\text{\textsuperscript{-}}, [HA], [H\text{\textsuperscript{+}}], [OH\text{\textsuperscript{-}}]). Unfortunately, this is not easy (read: tedious) to solve, since a cubic equation results from this set of simultaneous equations. However, simplifying approximations are useful:

For most weak acids, [H\text{\textsuperscript{+}}] from HA will be much greater than [H\text{\textsuperscript{+}}] from H\text{\textsubscript{2}}O. When HA dissociates, it produces A\text{\textsuperscript{-}}. When H\text{\textsubscript{2}}O dissociates, it produces OH\text{\textsuperscript{-}}. If dissociation of HA is much greater than that of H\text{\textsubscript{2}}O, then [A\text{\textsuperscript{-}}] >> [OH\text{\textsuperscript{-}}], and the CB equation becomes:

\[
[\text{H}^+] \approx [\text{A}^-]
\]

Now the solution reduces to a simpler quadratic equation (written example - consider 0.0500 M o-hydroxybenzoic acid).
Fraction of Dissociation

The fraction of dissociation, $\alpha$, is defined as the fraction of the acid in the form $A^-$:

$$\alpha = \frac{[A^-]}{[A^-] + [HA]} = \frac{x}{x + (F - x)} = \frac{x}{F}$$

For 0.0500 M $o$-hydroxybenzoic acid,

$$\alpha = \frac{6.8 \times 10^{-3} \text{ M}}{0.0500 \text{ M}} = 0.14$$

i.e., the acid is 14% dissociated at a formal concentration of 0.0500 M.

Weak electrolytes (compounds that are only partially dissociated) dissociate more as they are diluted. $o$-hydroxybenzoic acid is more dissociated than $p$-hydroxybenzoic acid at the same formal concentration because the ortho isomer is a stronger acid.
Weak Acid Problems

To find the pH of a weak acid, immediately set \([H^+] = [A^-] = x\), and set up:

\[
\alpha = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{(F - x)} = K_a
\]

where \(F\) is the formal concentration of HA. The approximation \([H^+] = [A^-]\) is poor only if the acid is too dilute or too weak, neither of which constitutes a practical problem.

e.g., Weak-acid problem: find the pH of 0.050 M trimethylammonium chloride (i.e., \((CH_3)_3NH^+\)). This ion is a weak acid, with a conjugate base of trimethylamine. The \(Cl^-\) ions have no acidic or basic properties, and are ignored. Appendix G lists the trimethylammonium ion with a \(pK_a\) of 9.799 at ionic strength \(\mu = 0\).

*(written example)*

![Diagram of trimethylammonium chloride](image_url)
Weak Base Equilibria

Treatment of weak bases is almost identical to that of weak acids.

\[
B + H_2O \leftrightharpoons BH^+ + OH^- \quad K_b = \frac{[BH][OH^-]}{[B]}
\]

Assume that nearly all \( OH^- \) comes from the reaction of \( B + H_2O \), and little comes from dissociation of \( H_2O \). Setting \([OH^-] = x\), we must also set \([BH^+] = x\), because one \( BH^+ \) is produced for each \( OH^- \). If the formal concentration of base \( F = [B] + [BH+] \), then

\[
[B] = F - [BH^+] = F - x
\]

Then the equilibrium expression for \( K_b \) is given as

\[
\frac{[BH^+][OH^-]}{[B]} = \frac{x^2}{F - x} = K_b
\]

This is exactly like the weak acid problem, excepting that \( x = [OH^-] \).
Weak Base Problem

Consider the commonly occurring weak base, cocaine.

\[
\text{Cocaine} + \text{H}_2\text{O} \rightleftharpoons \text{Cocaine}^+ + \text{OH}^- \quad K_b = 2.6 \times 10^{-6}
\]

If the formal concentration is 0.0372 M, what is the pH? (written example)

This should not be confused with “free base” cocaine, which is often heard about on classic rock stations around North America.
Conjugates Revisited

Earlier, we considered \( o- \) and \( p- \) hydroxybenzoic acids, designated HA. Now consider their conjugate bases. For example, the salt sodium \( o- \) hydroxybenzoate dissolves to give \( \text{Na}^+ \) (which has no acid-base chemistry) and \( o- \) hydroxybenzoate, which is a weak base. The acid-base chemistry is the reaction of \( o- \) hydroxybenzoate with water:

\[
\begin{align*}
\text{Ar-CO}_2^- + \text{H}_2\text{O} & \rightleftharpoons \text{Ar-CO}_2\text{H} + \text{OH}^- \\
\text{A}^- (o-\text{hydroxybenzoate}) & \quad F - x \\
\text{HA} & \quad x 
\end{align*}
\]

From \( K_a \) for each isomer, we calculate \( K_b \) for the conjugate base.

<table>
<thead>
<tr>
<th>Isomer of hydroxybenzoic acid</th>
<th>( K_a )</th>
<th>( K_b = K_w/K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho</td>
<td>( 1.07 \times 10^{-3} )</td>
<td>( 9.3 \times 10^{-12} )</td>
</tr>
<tr>
<td>para</td>
<td>( 2.9 \times 10^{-5} )</td>
<td>( 3.5 \times 10^{-10} )</td>
</tr>
</tbody>
</table>

Using each value of \( K_b \) and letting \( F = 0.050 \, 0 \, \text{M} \), we find

- pH of 0.050 \, 0 \, \text{M} \, o-\text{hydroxybenzoate} = \textbf{7.83}
- pH of 0.050 \, 0 \, \text{M} \, p-\text{hydroxybenzoate} = \textbf{8.62}

These are reasonable pH values for solutions of weak bases. Furthermore, as expected, the conjugate base of the stronger acid is the weaker base. (Written problem)
Buffers

A buffered solution resists changes in pH when acids or bases are added or when dilution occurs. There must be comparable amounts of the conjugate acid and base (within a factor of ~10) to exert significant buffering.

Characteristics of buffers:

• A buffer consists of a mixture of a weak acid and its conjugate base.

• The buffer is most useful when pH ≈ pKa.

• Over a reasonable range of concentration, the pH of a buffer is nearly independent of concentration.

• A buffer resists changes in pH because it reacts with added acids or bases.

• If too much acid or base is added, the buffer will be consumed and will no longer resist changes in pH.
Buffers in Biochemistry

Macrophages are white blood cells that fight infection by ingesting and dissolving foreign cells (i.e., phagocytosis). The compartment containing the ingested foreign cell merges with compartments called lysosomes, which contain digestive enzymes that are most active in acid. Low enzyme activity above pH 7 protects the cell from enzymes that leak into the cell.

The neutral cytoplasm, into which these enzymes may leak, is buffered, since they have low reactivity and do less damage to the cell than they would at their optimum pH (i.e., acidic).

Many enzyme-catalysed reactions are optimum at very specific pH’s; hence, natural buffered solutions are useful at protecting cells and organs within most organisms.

(a) Mouse macrophage engulfs two foreign red blood cells as phagocytosis begins. (b) Macrophages with ingested 1.6-μm-diameter fluorescent beads. (c) Fluorescence image of panel b.
Mixing: Weak Acid and Conjugate Base

If you mix $A$ moles of a weak acid with $B$ moles of its conjugate base, the moles of acid remain close to $A$ and the moles of base remain close to $B$. Little reaction occurs to change either concentration. Why? Consider $K_a$ and $K_b$ in terms of Le Chatelier’s principle:

Calculate the fraction of acid with $pK_a = 4.00$ that dissociates in a 0.10 M solution of HA:

$$\begin{align*}
    \text{HA} & \rightleftharpoons \text{H}^+ + \text{A}^- \\
    0.10 - x & = x + x
\end{align*}$$

$$\frac{x^2}{F - x} = K_a \Rightarrow x = 3.1 \times 10^{-3} \text{ M}$$

Fraction of dissociation $= \alpha = \frac{x}{F} = 0.031$

Thus, there is only 3.1% of the acid dissociated under these conditions.

For a 0.10 M solution of the conjugate acid $A^-$ ($pK_a = 10.00$), the extent of the reaction of $A^-$ with water is even smaller.

$$\begin{align*}
    \text{A}^- + \text{H}_2\text{O} & \rightleftharpoons \text{HA} + \text{OH}^- \\
    0.10 - x & = x + x
\end{align*}$$

$$\frac{x^2}{F - x} = K_b \Rightarrow x = 3.2 \times 10^{-6}$$

Fraction of association $= \alpha = \frac{x}{F} = 3.2 \times 10^{-5}$
You get what you mix!

HA dissociates very little, and adding extra A\(^-\) to the solution makes HA dissociate even less. Similarly, A\(^-\) does not react much with water, and adding extra HA makes A\(^-\) react even less.

This approximation, that the concentrations of HA and A\(^-\) remain unchanged upon mixing, breaks down only for very dilute solutions or at the extremes of pH.

e.g., If 0.050 mol of A\(^-\) plus 0.036 mol of HA are added to water, there will be close to 0.050 mol of A\(^-\) and close to 0.036 mol of HA in the solution at equilibrium.

However, buffers will react with any addition of strong acid or strong base, as we shall see!
Henderson-Hasselbalch Equation

The *Henderson-Hasselbalch equation*, which is derived from a rearrangement of the equilibrium expression for $K_a$, is the master equation for treatment of all buffers - it is not an approximation (only the concentrations of acids and bases may be approximate).

$$
\log K_a = \log \frac{[H^+][A^-]}{[HA]} = \log[H^+] + \log \frac{[A^-]}{[HA]}
$$

since \( \log xy = \log x + \log y \)

$$
-\log[H^+] = -\log K_a + \log \frac{[A^-]}{[HA]}
$$

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

For a solution prepared from a weak base $B$ and its conjugate acid:

$$
K_b
$$

$$
B + H_2O \rightleftharpoons BH^+ + OH^-
$$

$$
K_b = \frac{[BH^+][OH^-]}{[B]}
$$

$$
pH = pK_a + \log \frac{[B]}{[BH^+]}\]
A buffer in action

A widely used buffer is tris(hydroxymethyl)aminomethane (called “tris” for short).

\[
\begin{align*}
\text{NH}_3 & \quad \text{C} \quad \text{CH}_2\text{OH} \\
\text{HOCH}_2 & \quad \text{HOCH}_2 \\
& \quad \text{HOCH}_2
\end{align*}
\Rightarrow
\begin{align*}
\text{NH}_2 & \quad \text{C} \quad \text{CH}_2\text{OH} \\
\text{HOCH}_2 & \quad \text{HOCH}_2 \\
& \quad + \text{H}^+
\end{align*}
\]

The $pK_a = 8.072$ for the conjugate acid of tris.

An example of a salt containing the BH$^+$ cation is tris hydrochloride, which is BH$^+$Cl$^-$. When dissolved in water, it dissociates to BH$^+$ and Cl$^-$.

**Note:** the volumes of solution are irrelevant, since they cancel in the numerator and denominator of the log term.

**Example** A Buffer Solution

Find the pH of a 1.00-L aqueous solution prepared with 12.43 g of tris (FM 121.135) plus 4.67 g of tris hydrochloride (FM 157.596).

**Solution** The concentrations of B and BH$^+$ added to the solution are

\[
[B] = \frac{12.43 \text{ g/L}}{121.135 \text{ g/mol}} = 0.1026 \text{ M} \quad \quad [\text{BH}^+] = \frac{4.67 \text{ g/L}}{157.596 \text{ g/mol}} = 0.0296 \text{ M}
\]

Assuming that what we mixed stays in the same form, we plug these concentrations into the Henderson-Hasselbalch equation to find the pH:

\[
\text{pH} = pK_a + \log \frac{[B]}{[\text{BH}^+]} = 8.072 + \log \frac{0.1026}{0.0296} = 8.61
\]

**Test Yourself** Find the pH if we add another 1.00 g of tris hydrochloride. (Answer: 8.53)
A buffer in action, 2

The effect of adding a strong acid to a buffer should be considered.

**EXAMPLE**  Effect of Adding Acid to a Buffer

If we add 12.0 mL of 1.00 M HCl to the solution in the previous example, what will be the new pH?

**Solution**  The key is to realize that, when a strong acid is added to a weak base, they react completely to give BH⁺ (Box 8-3). We are adding 12.0 mL of 1.00 M HCl, which contains (0.012 0 L)(1.00 mol/L) = 0.012 0 mol of H⁺. This much H⁺ consumes 0.012 0 mol of B to create 0.012 0 mol of BH⁺:

<table>
<thead>
<tr>
<th></th>
<th>B Tris</th>
<th>H⁺ From HCl</th>
<th>BH⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moles</td>
<td>0.102 6</td>
<td>0.012 0</td>
<td>0.029 6</td>
</tr>
<tr>
<td>Final moles</td>
<td>0.090 6</td>
<td>—</td>
<td>0.041 6</td>
</tr>
</tbody>
</table>

\[(0.102 6 - 0.012 0)\]
\[(0.029 6 + 0.012 0)\]

Information in the table allows us to calculate the pH:

\[
pH = pK_a + \log \frac{\text{moles of } B}{\text{moles of } BH^+}
\]

\[
= 8.072 + \log \frac{0.090 6}{0.041 6} = 8.41
\]

The volume of the solution is irrelevant.
We see that the pH of a buffer does not change very much when a limited amount of strong acid or base is added.

**e.g.**, Addition of 12.0 mL of 1.00 M HCl changed the pH from 8.61 to 8.41. Addition of 12.0 mL of 1.00 M HCl to 1.00 L of unbuffered solution would have lowered the pH to 1.93!

**But why does a buffer resist changes in pH?**

It does so because the strong acid or strong base is consumed by B or BH⁺.

- **e.g.**, If you add HCl to tris, B (weak base) is converted into BH⁺ (weak acid).
- **e.g.**, If you add NaOH, BH⁺ (weak acid) is converted into B (weak base).

As long as you don’t use up B or BH⁺ by adding too much HCl or NaOH, the log term of the HH equation does not change much and pH does not change much.

The buffer has its maximum capacity to resist changes of pH when pH = pKa (more on this later!).
A buffer in action, 4

If a strong acid is added to a buffer, the weak base, $A^-$, will react with the $H^+$ from the strong acid to form the weak acid $HA$.

If a strong base is added to a buffer, the weak acid, $HA$, will give up its $H^+$ in order to transform the base ($OH^-$) into water ($H_2O$) and the conjugate base, $A^-$. 
Preparing Buffers

How many mL of 0.500 M NaOH should be added to 10.0 g of tris hydrochloride to give a pH of 7.60 in a final volume of 250 mL?

**Solution**  The moles of tris hydrochloride are \( \frac{10.0 \text{ g}}{157.598 \text{ g/mol}} = 0.0635 \text{ mol} \). We can make a table to help solve the problem:

<table>
<thead>
<tr>
<th>Reaction with OH(^-):</th>
<th>BH(^+)</th>
<th>+</th>
<th>OH(^-)</th>
<th>→</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial moles</td>
<td>0.0635</td>
<td>x</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Final moles</td>
<td>0.0635 - x</td>
<td>—</td>
<td>x</td>
<td>—</td>
<td>x</td>
</tr>
</tbody>
</table>

The Henderson-Hasselbalch equation allows us to find \( x \), because we know pH and \( pK_a \).

\[
pH = pK_a + \log \frac{\text{mol B}}{\text{mol BH}^+} \\
7.60 = 8.072 + \log \frac{x}{0.0635 - x} \\
-0.472 = \log \frac{x}{0.0635 - x} \\
10^{-0.472} = \frac{x}{0.0635 - x} \Rightarrow x = 0.0160 \text{ mol}
\]

This many moles of NaOH is contained in

\[
\frac{0.0160 \text{ mol}}{0.500 \text{ mol/L}} = 0.0320 \text{ L} = 32.0 \text{ mL}
\]
Preparing Buffers, 2

In practice, you would probably not make a buffer as described on the previous slide. Suppose that you wish to prepare 1.00 L of buffer containing 0.100 M tris at a pH of 7.60. You have available solid tris hydrochloride and approximately 1 M NaOH.

1. Weigh out 0.100 mol of tris hydrochloride and dissolve it in a beaker containing about 800 mL of water.

2. Place a calibrated pH electrode in the solution and monitor the pH.

3. Add NaOH solution until the pH is exactly 7.60.

4. Transfer the solution to a volumetric flask and wash the beaker a few times. Add the washings to the volumetric flask.

5. Dilute to the mark and mix.

You do not simply add the calculated quantity of NaOH because it would not give exactly the desired pH. The reason for using 800 mL of water in the first step is so that the volume will be reasonably close to the final volume during pH adjustment. Otherwise, the pH will change slightly when the sample is diluted to its final volume and the ionic strength changes.
Buffers, Activities and Ionic Strengths

The true form of the HH equation is expressed in terms of activities:

$$\text{pH} = pK_a + \log \frac{\mathcal{A}_A}{\mathcal{A}_{HA}} = pK_a + \log \frac{[A^-]}{[HA] \gamma_{HA}}$$

The most important reason why the calculated pH of a buffer is not equal to the observed pH is because the ionic strength is not 0, so activity coefficients are not 1.

Table 8-2 (8th edition) gives structures and pK_a values for many common buffers.

**e.g.,** For instance, if we mix 0.200 mol boric acid with 0.100 mol NaOH in 1.00 L, we generate a 1:1 mixture of boric acid and its conjugate base with an ionic strength of 0.10 M:

$$\text{B(OH)}_3 + \text{OH}^- \rightarrow (\text{HO})_2\text{BO}^- + \text{H}_2\text{O}$$

Boric acid (HA)  Borate (A^-)

For boric acid in Table 8-2, pK_a = 9.24 at μ = 0 and pK_a = 8.98 at μ = 0.1 M. We predict that the pH of a 1:1 mixture of boric acid and borate will have a pH near pKa = 9.24 at low ionic strength and a pH near 8.98 at μ = 0.1 M.