Chapter 8

Monoprotic Acids and Bases

Bronsted and Lowry definitions
Acids are proton donars
Bases are proton acceptors

HCl(g) + NH₃(g) → NH₄⁺Cl⁻(s)
acid    base    salt

CH₃OOH + CH₃NH₂ ↔ CH₃OO⁻ + CH₃NH₃⁺
Acetic acid methyl amine acetate ion methyl ammonium ion
acid    base    conjugate base    conjugate acid
For aqueous solutions,

Acids react with water to yield $\text{H}_3\text{O}^+$

Bases react with water to yield $\text{OH}^-$

\[
\text{acid} \quad \text{CH}_3\text{COOH} \quad + \quad \text{H}_2\text{O} \quad \leftrightarrow \quad \text{CH}_3\text{COO}^- \quad + \quad \text{H}_3\text{O}^+
\]

Acetic acid water acetate ion hydronium ion

conjugate pairs

$\text{CH}_3\text{COOH}$
$\text{CH}_3\text{COO}^-$

base

\[
\text{base} \quad \text{CH}_3\text{NH}_2 \quad + \quad \text{H}_2\text{O} \quad \leftrightarrow \quad \text{CH}_3\text{NH}_3^+ \quad + \quad \text{OH}^- 
\]

Methyl amine water methyl ammonium ion hydroxide ion

conjugate pairs

$\text{CH}_3\text{NH}_2$
$\text{CH}_3\text{NH}_3^+$
Autoprotolysis of water

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

Equilibrium constant is Kw

\[ \text{Kw} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.01\cdot10^{-14} \text{ @ 25 C} \]

For pure water (what is pure water?)

\[ [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00\cdot10^{-7} \text{ M} \]

pH – a measure of the acidity of a solution

\[ \text{pH} = -\log [\text{H}_3\text{O}^+] \text{ or } -\log [\text{H}^+] \]

below 7 is acidic

above 7 is basic
**Strong acids and bases – complete dissociation in water**

Example of strong acid

What is the pH of a 0.2 M HCl solution

HCl is a strong acid

\[
\text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+ 
\]

The equilibrium constant for this reaction is large. There is virtually no HCl species remaining in solution. Therefore, 

\[
[\text{H}_3\text{O}^+] = 0.2 \text{ M and pH} = -\log (0.2) = 0.7 
\]

0.02 M solution \(\rightarrow 1.7\)

sig. fig. rule: the number of significant figures in the concentration is equal to the number of significant figures after the decimal point in the pH.
Example of strong base

What is the pH of a 0.020 M Ca(OH)$_2$ solution?

Ca(OH)$_2$ is a strong base.

Ca(OH)$_2$ $\rightarrow$ Ca$^{2+}$ + 2OH$^-$

The equilibrium constant for this reaction is large. There is virtually no Ca(OH)$_2$(s) remains. Therefore,

$[\text{OH}^-] = 0.040$ M, $[\text{H}_3\text{O}^+] = 2.5 \cdot 10^{-13}$ M, and pH = -log $(2.5 \cdot 10^{-13}) = 12.60$

sig. fig. rule: the number of significant figures in the concentration is equal to the number of significant figures after the decimal point in the pH.

However, in these examples we have made an assumption. The assumption that has implicitly been made is that the [H$^+$] from the strong acid (or [OH$^-$] from the strong base) is >>>>> the [H$^+$] (or the [OH$^-$]) from water hydrolysis. Certainly these assumptions have been true!!!

In the strong acid example,

$[\text{H}^+]_{sa} = 0.1$ M

$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.01 \cdot 10^{-14}$

$[\text{OH}^-] = 1.01 \cdot 10^{-13}$ M

$[\text{H}_3\text{O}^+]_{\text{water}} = [\text{H}^+]_{\text{water}} = 1.01 \cdot 10^{-13}$ M
**but what happens if this assumption breaks down?**

Example:
Calculate the pH of a $5.0 \cdot 10^{-8}$ M $\text{HClO}_4$ solution

$\text{HClO}_4$ is a strong acid, and thus completely dissociates to give $\text{H}_3\text{O}^+$ and $\text{ClO}_4^-$ ions.

Sources of $\text{H}_3\text{O}^+$

$\text{HClO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^-$

$2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$
pertinent equations;
mass balance Eq.

\[ [H_3O^+] = [H_3O^+]_{HClO4} + [H_3O^+]_{H2O} \]

\[ [OH^-] = [H_3O^+]_{H2O} \]

\[ 1.01 \times 10^{-14} = Kw = [H_3O^+] [OH^-] \]

\[ [H_3O^+]_{HClO4} = 5.0 \times 10^{-8} \text{ M} \]

let \( x = [H_3O^+]_{H2O} \)

substitutions;

\[ Kw = x(5.0 \times 10^{-8} + x) = 1.01 \times 10^{-14} \]
Or ICE BOX

<table>
<thead>
<tr>
<th></th>
<th>$[H_3O^+]$</th>
<th>$[OH^-]$</th>
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</thead>
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<tr>
<td>Initial</td>
<td>5.0e-8</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>5.0E-8 + x</td>
<td>x</td>
</tr>
</tbody>
</table>

or

<table>
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<tr>
<th></th>
<th>$[H_3O^+]$</th>
<th>$[OH^-]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1.5e-7</td>
<td>1.0E-7</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>-x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1.5e-7 - x</td>
<td>1.0e-7-x</td>
</tr>
</tbody>
</table>
\[ \text{Kw} = x(5.0 \cdot 10^{-8} + x) = 1.01 \cdot 10^{-14} \]

Assumption 1: Is \( [\text{H}_3\text{O}^+]_{\text{H}_2\text{O}} \ll [\text{H}_3\text{O}^+]_{\text{HA}} \)
If at first we make the assumption, we soon see that …
\[ [\text{H}_3\text{O}^+]_{\text{HA}} = 5.0 \cdot 10^{-8} \text{ M and } [\text{H}_3\text{O}^+]_{\text{H}_2\text{O}} = 2.0 \cdot 10^{-7} \text{ M, and the assumption is not valid!!!!} \]

Back to the original expression, \( x(5.0 \cdot 10^{-8} + x) = 1.01 \cdot 10^{-14} \)
This is a quadratic. Using excel, successive approximations gives,
\[ x = 7.86 \cdot 10^{-8} \text{ M} \]
\[ [\text{H}_3\text{O}^+] = 5.0 \cdot 10^{-8} + x = 1.286 \cdot 10^{-7} \text{ M,} \]
\[ \text{pH} = -\log(1.286 \cdot 10^{-7}) = 6.89 \]
This result makes sense. The pH of a dilute strong acid ought to be slightly acidic.
Weak Acids and Bases

**Treatment of Weak acids – HA**

\[ \text{HA} + \text{H}_2\text{O} \leftrightarrow \text{A}^- + \text{H}_3\text{O}^+ \]

Equilibrium constant is \( K_a \)

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

The autoprotolysis reaction must also be satisfied

\[ 2\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}_3\text{O}^+ \]

\[ K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 1.01 \cdot 10^{-14} \]

\[ K_a = [\text{A}^-][\text{H}_3\text{O}^+]_{\text{HA}} + [\text{H}_3\text{O}^+]_{\text{H}_2\text{O}})/(F_{\text{HA}} - [\text{A}^-]) \]

Define:

\[
\begin{align*}
\frac{[\text{H}_3\text{O}^+]_{\text{HA}}}{F_{\text{HA}}} \\
\frac{[\text{H}_3\text{O}^+]_{\text{H}_2\text{O}}}{F_{\text{HA}}} \\
\end{align*}
\]
**Assumptions that can often be made:**

1. \([\text{H}_3\text{O}^+]_{\text{H}_2\text{O}} \ll [\text{H}_3\text{O}^+]_{\text{HA}}, \text{ therefore HA is the only source of H}_3\text{O}^+, \text{ and } [A^-] = [\text{H}_3\text{O}^+]\)

2. If \(K_a\) is small, \([A^-] \ll [\text{HA}], \text{ and } [\text{HA}] = F_{HA}\)
Example of a weak acid problem:

Calculate the pH of a 0.10 M solution of acetic acid.

\[ K_a = 1.75 \cdot 10^{-5} \]

\[
\text{CH}_3\text{OOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OO}^- + \text{H}_3\text{O}^+ \\
\]

\[
K_a = 1.75 \cdot 10^{-5} = \frac{[\text{CH}_3\text{OO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{OOH}]} \\
\]

Let \( x = [\text{CH}_3\text{OO}^-] \)

\[
K_a = \frac{x(x + [\text{H}_3\text{O}^+]_{\text{H}_2\text{O}})}{(0.10 - x)} \\
\]

Make assumptions:

(1) \([\text{H}_3\text{O}^+]_{\text{H}_2\text{O}} \ll \ll [\text{H}_3\text{O}^+]_{\text{HA}}\)

(2) \([\text{HA}] = F_{\text{HA}}\)

The \(K_a\) expression reduces to

\[
K_a = \frac{x^2}{0.10} = 1.75 \cdot 10^{-5} \\
x = 0.001322876 \text{ M} = [\text{CH}_3\text{OO}^-] = [\text{H}_3\text{O}^+] \\
\]

\[
\text{pH} = -\log(0.001322876) = 2.88 \quad (2 \text{ sig fig after the decimal pt.})
\]
Are the assumptions valid?

Assumption 1:
Is \([H_3O^+]_{\text{H}_2\text{O}} \ll \ [H_3O^+]_{\text{HA}}\)?

\([H_3O^+] = 0.00132 \text{ M}, \text{ so } [O^\text{-}] = \frac{K_w}{[H_3O^+]} = 7.65 \cdot 10^{-12} \text{ M}\)

The only source of the \([O^\text{-}]\) is from autoprotolysis of water, therefore, \([H_3O^+]_{\text{H}_2\text{O}} = [O^\text{-}] = 7.65 \cdot 10^{-12} \text{ M}\)

Assumption 1 is valid

Assumption 2:
Is \([HA] \gg [A^-]?\)

If \([A^-]/[HA]_0 < 0.05\), we will call the assumption valid
In other words; the extent of dissociation is less than 5 %

\([A^-]/F_{HA} = (0.00132/0.1) = 0.0132\), assumption is valid
Treatment of Weak bases, B

\[ B + H_2O \leftrightarrow BH^+ + OH^- \]
Equilibrium constant is \( K_b \)

\[ K_b = [BH^+][OH^-]/[B] \]

The autoprotolysis reaction must also be satisfied
\[ 2H_2O \leftrightarrow OH^- + H_3O^+ \]
\[ K_w = [OH^-][H_3O^+] = 1.01 \cdot 10^{-14} \]

\[ K_b = [BH^+][[OH^-]_B + [OH^-]_{H_2O}]/(F_B - [BH^+]) \]

Define:
- \([OH^-]_{HA}\)
- \([OH^-]_{H_2O}\)
- \(F_B\)
Assumptions that can often be made:
1. $[\text{OH}^-]_{\text{H}_2\text{O}} \ll [\text{OH}^-]_B$, therefore B is the only source of OH$^-$, and $[\text{BH}^+] = [\text{OH}^-]$
2. If $K_b$ is small, $[\text{BH}^+] \ll [B]$, and $[B] = F_B$

Example of a weak base
Calculate the pH of a 0.10 M solution of sodium acetate.
Sodium acetate is a soluble salt
$\text{NaAc} \rightarrow \text{Na}^+ + \text{Ac}^-$

$\text{CH}_3\text{OO}^- + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{OOH} + \text{OH}^-$

$K_b(\text{acetic acid})$ is the equilibrium constant for this reaction
$K_b(\text{acetic acid}) = Kw/K_a(\text{acetic acid}) = 1.01 \times 10^{-14}/1.75 \times 10^{-5} = 5.77 \times 10^{-10}$

$K_b = 5.77 \times 10^{-10} = [\text{CH}_3\text{OOH}] [\text{OH}^-] / [\text{CH}_3\text{OO}^-]$

Let $x = [\text{CH}_3\text{OOH}]$

$K_b = x(x + [\text{OH}^-]_{\text{H}_2\text{O}}) / (0.10 - x)$

Make assumptions:
1. $[\text{OH}^-]_{\text{H}_2\text{O}} \ll [\text{OH}^-]_A$
2. $[A^-] = F_A$. 
Let $x = [\text{CH}_3\text{OOH}]$

$$K_b = \frac{x(x + [\text{OH}^-][\text{H}_2\text{O}])}{(0.10 - x)}$$

Make assumptions:
- (1) $[\text{OH}^-][\text{H}_2\text{O}] \ll [\text{OH}^-]_A$
- (2) $[A^-] = F_A$

The $K_b$ expression reduces to

$$K_b = \frac{x^2}{0.10} = 5.77 \cdot 10^{-10}$$

$$x = 7.596991886 \cdot 10^{-6} \text{ M} = [\text{CH}_3\text{OOH}] = [\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = \frac{\text{K}_w}{[\text{OH}^-]} = 1.01 \cdot 10^{-14} / 7.596991886 \cdot 10^{-6} = 1.3294735 \cdot 10^{-9} \text{ M}$$

$$\text{pH} = \log(1.3294735 \cdot 10^{-9}) = 8.88 \text{ (2 sig fig after the decimal pt.)}$$
Are the assumptions valid?

Assumption 1:
Is $[\text{OH}^-]_{\text{H}_2\text{O}} << [\text{OH}^-]_{\text{HA}}$?
$[\text{OH}^-] = 7.60 \cdot 10^{-6} \text{ M}$
therefore, $[\text{OH}^-]_{\text{H}_2\text{O}} = [\text{H}_3\text{O}^+] = 1.3 \cdot 10^{-9} \text{ M}$

If $[\text{OH}^-]_{\text{H}_2\text{O}} / [\text{OH}^-] < 0.05$, we will call the assumption valid
$[\text{OH}^-]_{\text{H}_2\text{O}} / [\text{OH}^-] = 1.3 \cdot 10^{-9} / 7.60 \cdot 10^{-6} = 0.0002$
Assumption 1 is valid

Assumption 2:
Is $[\text{B}] >> [\text{BH}^+]$?

If $[\text{BH}^+] / [\text{B}]_0 < 0.05$, we will call the assumption valid
In other words; the extent of dissociation is less than 5 %
$[\text{BH}^+] / F_B = (7.6 \cdot 10^{-6} / 0.1) = 7.6 \cdot 10^{-5}$, assumption is valid

For weak acids and bases, if assumption 1 fails it is a little more tricky. Some tricks that we will pick up from Chapter 13 are useful in such a case.
What if assumption 2 is not valid?

What is the pH of a 5.0 mM solution of ammonia?

Ammonia is a weak base

$$K_b = \frac{K_w}{K_a(NH_4^+)} = \frac{1.01 \cdot 10^{-14}}{5.70 \cdot 10^{-10}} = 1.77 \cdot 10^{-5}$$

\[ CH_3OO^- + H_2O \leftrightarrow CH_3OOH + OH^- \]

$$K_b = 1.77 \cdot 10^{-5} = \left[ NH_4^+ \right] \left[ OH^- \right] / [NH_3]$$

Let \( x = [NH_4^+] \)

$$K_b = x(x + [OH^-]_{H_2O}) / (0.005 - x)$$

Make assumptions:

1. \([OH^-]_{H_2O} \ll [OH^-]_{NH_3}\)
2. \([NH_3] = F_{NH_3}\)

The \( K_b \) expression reduces to

$$K_b = \frac{x^2}{0.0050} = 1.77 \cdot 10^{-5}$$

$$x = 2.97489 \cdot 10^{-4} \text{ M} = [NH_4^+] = [OH^-]$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.01 \cdot 10^{-14}}{2.97489 \cdot 10^{-9}} = 3.3950779 \cdot 10^{-11} \text{ M}$$

pH = -log(3.3950779 \cdot 10^{-11}) = 10.47 (2 sig fig after the decimal pt.)
Are the assumptions valid?

Assumption 1:
Is \([\text{OH}^-]_{\text{H}_2\text{O}} \ll [\text{OH}^-]_{\text{HA}}\) \\
\([\text{OH}^-] = 2.97 \cdot 10^{-4} \text{ M} \) \\
therefore, \([\text{OH}^-]_{\text{H}_2\text{O}} = [\text{H}_3\text{O}^+] = 3.40 \cdot 10^{-11} \text{ M} \)
If \([\text{OH}^-]_{\text{H}_2\text{O}} / [\text{OH}^-] \ll 0.05\), we will call the assumption valid \\
\([\text{OH}^-]_{\text{H}_2\text{O}} / [\text{OH}^-] = 3.40 \cdot 10^{-11} / 2.970 \cdot 10^{-4} \ll 0.05\)
Assumption 1 is valid

Assumption 2:
Is \([\text{B}] \gg [\text{BH}^+]?\)
If \([\text{BH}^+] / F_B < 0.05\), we will call the assumption valid \\
In other words; the extent of dissociation is less than 5% \\
\([\text{BH}^+] / F_B = (2.970 \cdot 10^{-4} / 0.005) = 0.06\), 
**assumption is not valid!!!!**
Rewrite expression without assumption 2!!

\[ K_b = \frac{x^2}{(0.0050-x)} = 1.77 \cdot 10^{-5} \]

This is a quadradic

\[ x^2 + 1.77 \cdot 10^{-5}x - (0.005)(1.77 \cdot 10^{-5}) \]

You can use solve using the quadratic equation by hand or by fancy calculator or use Excel and solve by successive approximation

\[ x = 2.8877 \cdot 10^{-4} \text{ M} \quad \text{instead of } (2.970 \cdot 10^{-4}) \]

\[ [\text{H}_3\text{O}^+] = 1.01 \cdot 10^{-14}/2.8877 \cdot 10^{-4} = 3.4976 \cdot 10^{-11} \]
\[ \text{pH} = 10.46 \]
Another example:

Calculate the pH of a 0.010 M solution of chlorous acid.

\[ K_a = 1.12 \cdot 10^{-2} \]

\[ \text{HOClO} + \text{H}_2\text{O} \leftrightarrow \text{OCIO}^- + \text{H}_3\text{O}^+ \]

\[ K_a = 1.12 \cdot 10^{-2} = \frac{[\text{OCIO}^-][\text{H}_3\text{O}^+]}{[\text{HOClO}]} \]

Let \( x = [\text{CH}_3\text{OO}^-] \)

\[ K_a = \frac{x(x + [\text{H}_3\text{O}^+]_{\text{H}_2\text{O}})}{(0.010 - x)} \]

Make assumptions:

1. \([\text{H}_3\text{O}^+]_{\text{H}_2\text{O}} \ll [\text{H}_3\text{O}^+]_{\text{HA}}\)
2. \([\text{HA}] = F_{\text{HA}}\)

The \( K_a \) expression reduces to

\[ K_a = \frac{x^2}{0.010} = 1.12 \cdot 10^{-2} \]

\[ x = 0.0105838 \text{ M} = [\text{CH}_3\text{OO}^-] = [\text{H}_3\text{O}^+] \]

\[ \text{pH} = 1.98 \]
Are the assumptions valid?

Assumption 1:
Is $[\text{H}_3\text{O}^+]_{\text{H}_2\text{O}} << [\text{H}_3\text{O}^+]_{\text{HA}}$?

$[\text{H}_3\text{O}^+] = 0.0106 \text{ M}$, so $[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = 9\cdot10^{-13} \text{ M}$

The only source of the $[\text{OH}^-]$ is from autoprotolysis of water, therefore, $[\text{H}_3\text{O}^+]_{\text{H}_2\text{O}} = [\text{OH}^-] = 7.65\cdot10^{-12} \text{ M}$

Assumption 1 is valid.

Assumption 2:
Is $[\text{HA}] >> [\text{A}^-]$?

Clearly not!!!

Using excel solve the full expression for $x$

$1.12\cdot10^{-2} = x(x + [\text{H}_3\text{O}^+]_{\text{H}_2\text{O}}) / (0.010 - x)$

$x = 0.006181 \text{ M}$  \quad $\text{pH} = 2.21$
Recognizing the weak acid/weak base system and finding $K_b$

**Sodium Benzoate**
- This is a weak base.
- There is no table of $K_b$ constants for weak bases.
- Appendix G is a table of $K_a$ constants for weak acids
- You must be able to recognize that sodium benzoate is the weak base conjugate salt of benzoic acid.
- Use $K_b = K_a/K_w$ to obtain the $K_b$ for the benzoate ion.
Conjugate acids and Bases

The stronger the weak acid, the weaker its conjugate base.
The weaker the weak acid the stronger its conjugate base.

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<thead>
<tr>
<th></th>
<th>$K_a$</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>$1.8 \times 10^{-4}$</td>
<td>$5.6 \times 10^{-11}$</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>$6.28 \times 10^{-5}$</td>
<td>$1.61 \times 10^{-10}$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>$1.75 \times 10^{-5}$</td>
<td>$5.77 \times 10^{-10}$</td>
</tr>
</tbody>
</table>
Buffers

A buffer is a solution that is resistant to pH changes. It usually consist of a mixture of an acid and its conjugate base in roughly equal proportions

Let’s look at weak acid, HA ($K_a = 1.00 \cdot 10^{-4}$)

$$\text{HA} + \text{H}_2\text{O} \leftrightarrow \text{A}^- + \text{H}_3\text{O}^+$$

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

Notice when $[\text{A}^-] = [\text{HA}]$, $[\text{H}_3\text{O}^+] = K_a$

HH eq is often convenient when working with buffers
Take the log of both sides

$$\log K_a = \log [\text{H}_3\text{O}^+] + \log \{[\text{A}^-]/[\text{HA}]\}$$

$$-pK_a = -p\text{H} + \log \{[\text{A}^-]/[\text{HA}]\}$$

$$p\text{H} = pK_a + \log \{[\text{A}^-]/[\text{HA}]\}$$ Henderson-Hasselbach equation
pH = pK_a + log ([A^-] / [HA])  Henderson-Hasselbach equation

Implication: For a solution containing an equal mixture of an acid and its conjugate base, pH = pK_a, and this result is relatively independent of F_{HA} ([HA] +[A^-])!!!

Since [HA] and [A^-] are components of the same solution, we can rewrite the Henderson-Hasselbach equation as follows:

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

As we shall see, it is often more convenient in this form.
**How does a buffer work?**

Add 1.0 mL of concentrated HCl to 1.0 L of water. What is the pH?

Concentrated HCl is 12.1 M
1 ml of concentrated HCl = 12.1 mmol

\[
[H_3O^+] = \frac{(12.1 \text{ mmol})}{1001 \text{ ml}} = 0.012 \text{ M}
\]

\[
pH = -\log(0.012) = 1.92
\]
Now add 1.0 mL of concentrated HCl to 1.0 L solution containing 0.50 mol of acetic acid (HA) and 0.50 mol of sodium acetate (NaA).

\[ K_a(\text{acetic acid}) = 1.75 \times 10^{-5} \]
\[ \text{pK}_a = 4.757 \]

pH before the addition of the HCl
\[ \text{pH} = 4.757 + \log(\frac{\text{mol A}^-}{\text{mol HA}}) = 4.757 + \log \left( \frac{0.50}{0.50} \right) = 4.76 \]
pH after the addition of the HCl

The HCl reacts rapidly and completely with the A⁻ (it is a strong acid)

\[ \text{HCl} + \text{A}^- \rightarrow \text{Cl}^- + \text{HA} \]

Initial conditions:
- HCl: 12.1 mmol
- A⁻: 500 mmol
- HA: 500 mmol

Final conditions:
- HCl: 0.00 mmol
- A⁻: (500-12.1) = 487.9 mmol
- HA: (500+12.1) = 512.1 mmol

pH = 4.757 + log(mol A⁻ / mol HA) = 4.757 + log(487.9/512.1) = 4.74
Try adding 1.0 mL of concentrated HCl to 1.0 L solution containing 0.050 mol of acetic acid (HA) and 0.050 mol of sodium acetate (NaA).

**Initial conditions:**
- HCl: 12.1 mmol
- A⁻: 50 mmol
- HA: 50 mmol

**Final conditions:**
- HCl: 0.00 mmol
- A⁻: (50-12.1) = 37.9 mmol
- HA: (50+12.1) = 62.1 mmol

\[ \text{pH} = 4.757 + \log(\frac{\text{mol A}^-}{\text{mol HA}}) = 4.757 + \log(\frac{37.9}{62.1}) = 4.54 \]
Try adding 1.0 mL of concentrated HCl to 1.0 L solution containing 0.0050 mol of acetic acid (HA) and 0.0050 mol of sodium acetate (NaA).

Initial conditions:
- HCl: 12.1 mmol
- A\(^-\): 5.0 mmol
- HA: 5.0 mmol

Final conditions:
- HCl: 7.1 mmol
- A\(^-\): (5.0-5.0) = 0 mmol
- HA: (5.0+5.0) = 10 mmol

\(pH = -\log(0.0071) = 2.2\), the capacity of the buffer solution was exceeded

Why doesn’t HA contribute somewhat to the \([H_3O^+]\)?

\[ Ka = [H^+][A^-]/[HA] = \frac{(0.0071+x)x}{(0.01-x)} = 1.75 \cdot 10^{-5}, x = 5.76 \cdot 10^{-5} \]
Buffer capacity \( b = \frac{dc}{dpH} = -\frac{dc_a}{dpH} \)

Depends upon

1) ratio of A⁻/HA, closer to 1, the greater the buffer capacity
2) the absolute concentration of A⁻ and HA
Try adding 1.0 g of NaOH to 1.0 L solution containing 0.050 mol of acetic acid (HA) and 0.050 mol of sodium acetate (NaA).

\[
\text{NaOH} + \text{HA} \rightarrow \text{Na}^+ + \text{H}_2\text{O} + \text{A}^-
\]

The NaOH reacts rapidly and completely with the HA (it is a strong base)

Initial conditions:
- \(\text{NaOH}: \frac{1.0 \text{ g}}{40.0 \text{ g/mol}} = 25 \text{ mmol}\)
- \(\text{A}^-: 50 \text{ mmol}\)
- \(\text{HA}: 50 \text{ mmol}\)

Final conditions:
- \(\text{NaOH}: 0.00 \text{ mmol}\)
- \(\text{A}^-: (50 + 25) = 75 \text{ mmol}\)
- \(\text{HA}: (50 - 25) = 25 \text{ mmol}\)

\[
\text{pH} = 4.757 + \log(\text{mol A}^-/\text{mol HA}) = 4.757 + \log(75/25) = 5.23
\]
Preparing buffers

Prepare 1.0 L of a 0.10 M phosphate based buffer at pH 7.00

pKa2 of phosphoric acid

\[ \text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{HPO}_4^{2-} \quad \text{pK}_{a2} = 7.198 \]

Strategy 1:

\[ \text{pH} = \text{pK}_{a2} + \log \left( \frac{\text{mol HPO}_4^{2-}}{\text{mol H}_2\text{PO}_4^-} \right) \]

\[ 7.00 = 7.198 + \log(\frac{\text{mol HPO}_4^{2-}}{\text{mol H}_2\text{PO}_4^-}) \]

\[ 10^{(7.00-7.198)} = \frac{\text{mol HPO}_4^{2-}}{\text{mol H}_2\text{PO}_4^-} = 0.6339 \]

\[ 0.10 = \text{mol HPO}_4^{2-} + \text{mol H}_2\text{PO}_4^- \]

Substitution

\[ \frac{\text{mol HPO}_4^{2-}}{0.10 - \text{mol HPO}_4^{2-}} = 0.6339 \]

\[ 0.06339 - 0.6339 \text{ mol HPO}_4^{2-} = \text{mol HPO}_4^{2-} \]

\[ 0.06339 = 1.6339 \text{ mol HPO}_4^{2-} \]

\[ \text{mol HPO}_4^{2-} = \frac{0.06339}{1.6339} = 0.0387 \text{ M} \]

\[ \text{mol H}_2\text{PO}_4^- = 0.0613 \text{ M} \]

NaH₂PO₄ and Na₂HPO₄ are the salts. Use the molecular mass of these to find the mass of the salts needed to dissolve in 1.00 L of water.

Strategy 2

Dissolve 0.10 mol of NaH₂PO₄ to 1.0 L of water. Add 6.0 M NaOH dropwise while measuring with a calibrated pH meter until the pH reads 7.00.
Dilute buffer problem

What is the pH of a solution prepared by mixing 0.0100 mol HA (with \( K_a = 1.00 \cdot 10^{-2} \)) and 0.0100 mol of \( A^- \) and diluting with water to 1.00 L?

Because HA is a moderately strong acid, the following reaction can occur to an appreciable extent.

\[
\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+
\]

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

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

\[
[\text{A}^-] = F_{\text{A}^-} + [\text{H}_3\text{O}^+]
\]

\[
[\text{HA}] = F_{\text{HA}} - [\text{H}_3\text{O}^+]
\]

\[
F_{\text{A}^-} = F_{\text{HA}} = 0.0100 \text{ M}
\]

Let \([\text{H}_3\text{O}^+] = x\)

\[
K_a = x(0.0100+x)/(0.0100-x)
\]
$1.00 \cdot 10^{-2} = x(0.0100+x)/(0.0100-x)$

Excel, successive approximations → $x = 0.00414$ M

$$[A^-] = F_{A^-} + [H_3O^+] = 0.0100 + 0.00414 = 0.01414 \text{ M}$$

$$[HA] = F_{HA} - [H_3O^+] = 0.0100 - 0.00414 = 0.00586 \text{ M}$$

$pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) = 2.000 + \log(0.01414/0.00586) = 2.383$

or alternatively, since you already have $[H_3O^+] = x$

$pH = -\log x = 2.38$