Monoprotic Acid/Base Equilibria

Strong acids and bases:
What is the pH of 0.10 M HCl? How do you calculate it? Why?

Based on our typical method for calculating pH, at 10^-8 M HCl, pH is greater than 7.00, does this make sense? Where have we gone wrong?

<table>
<thead>
<tr>
<th>Concentration (F)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 (10^-1)</td>
<td>1</td>
</tr>
<tr>
<td>0.01 (10^-2)</td>
<td>2</td>
</tr>
<tr>
<td>0.001 (10^-3)</td>
<td>3</td>
</tr>
<tr>
<td>0.0001 (10^-4)</td>
<td>4</td>
</tr>
<tr>
<td>0.00001 (10^-5)</td>
<td>5</td>
</tr>
<tr>
<td>0.000001 (10^-6)</td>
<td>6</td>
</tr>
<tr>
<td>0.0000001 (10^-7)</td>
<td>7</td>
</tr>
<tr>
<td>0.00000001 (10^-8)</td>
<td>8</td>
</tr>
</tbody>
</table>

Monoprotic Acid/Base Equilibria

We have to consider autoprotolysis of water:

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

As well as HCl → H^+ + Cl^-.

Charge Balance:

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

Mass Balance:

\[ \frac{[\text{H}^+]}{[\text{OH}^-]} = \frac{[\text{Cl}^-]}{[\text{H}^+]} \]

So:

\[ [\text{H}^+]^2 = Kw + 10^{-8}M \]

\[ [\text{H}^+] = \frac{\text{K}_w}{[\text{H}^+] + 10^{-8}M} \]

\[ [\text{H}^+] = 1.0 \times 10^{-7}M \]

\[ \text{pH} = \log [\text{H}^+] \]

\[ \text{pH} = 6.98 \]
**Autoprotolysis**

**Question:** When do we have to be concerned with autoprotolysis?

**Answer:** When the (strong) acid or base concentration is around $K_w^{1/2}$ ($\sim 10^{-6}$ to $10^{-8}$ F),

\[
\frac{[A_{tot}]}{[B_{tot}]} \approx 10^{-8} M, \quad p[H] \approx 7.00
\]

Why not just when the concentration is $< 10^{-8}$ F?

Lets look back at our strong acid calculation (charge balance)

\[
[OH^-] = [H^+] - [\text{Strong Acid}]
\]

as [Strong Acid] gets smaller and smaller, [OH^-] approaches [H^+]

So, for extremely low strong acid or base concentration ($< 10^{-8}$ F),

\[
pH = 7.00
\]

**Problem:** What is the pOH, and pH of a 2.48 x $10^{-7}$ F solution of NaOH?

\[
\begin{align*}
2.48 \times 10^{-7} M & \quad \text{NaOH} \\
\text{NaOH} & \rightarrow \text{Na}^+ + \text{OH}^- \\
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^- \quad \rightarrow K_w : \text{[H}^+][\text{OH}^-] \\
\text{C.B.} & \rightarrow \text{[H}^+] + \text{[Na}^+] = \text{[OH}^-]\] \\
\text{M.B.} & \rightarrow \text{[Na}^+] = 2.48 \times 10^{-7} M \\
\text{[H}^+] + 2.48 \times 10^{-7} M & = \frac{K_w}{\text{[H}^+]} \\
\text{[H}^+]^2 + 2.48 \times 10^{-7} \text{(H}^+) - K_w & = 0 \\
\text{[H}^+] & = 3.53 \times 10^{-8} M, \\
\text{[OH}^-] & = 2.88 \times 10^{-2} M \\
pH & = 7.15 \\
pOH & = 6.55 \\
\text{pH} + \text{pOH} & = 14
\end{align*}
\]
\[2.48 \times 10^{-7} \text{M} \quad \text{NH}_3\]

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad \text{K}_b = 1.75 \times 10^{-5}
\]

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad \text{K}_w = 10^{-14}
\]

C.B. \[\text{[NH}_4^+\text{]} + \text{[H}^+\text{]} = \text{[OH}^-\text{]} \quad \frac{\text{[NH}_4^+\text{]} + \text{[H}^+\text{]} - \text{[OH}^-\text{]} = 0}{\text{K}_w = \frac{\text{[CH}_3\text{OH}]}{\text{[CH}_3\text{]+}}} \]

M.B. \[\frac{\text{[OH}^-\text{]} + \text{[NH}_4^+\text{]} + \text{[H}^+\text{]}}{\text{[NH}_4^+\text{]}} = \frac{2.48 \times 10^{-7}}{\text{[CH}_3\text{OH}]} \]

\[\text{K}_b = \frac{\text{[NH}_4^+\text{]} \cdot \text{[OH}^-\text{]} \cdot \text{[CH}_3\text{OH}]}{\text{[NH}_3\text{]}} \]

\[\text{[NH}_3\text{]} = 2.48 \times 10^{-7} - \text{[NH}_4^+\text{]} \]

\[
\text{K}_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{2.48 \times 10^{-7} - [\text{NH}_4^+]} \]

\[
\text{K}_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{2.48 \times 10^{-7}} \]

\[
2.48 \times 10^{-7} \text{K}_b - \text{K}_b [\text{NH}_4^+] = [\text{NH}_4^+][\text{OH}^-] \]

\[
2.48 \times 10^{-7} \text{K}_b = [\text{NH}_4^+][\text{OH}^-] + \text{K}_b [\text{NH}_4^+] \]

\[
[\text{NH}_4^+] = \frac{2.48 \times 10^{-7} \text{K}_b}{\text{[OH}^-] + \text{K}_b} = \frac{2.48 \times 10^{-7} \text{K}_b}{\text{K}_w / \text{[CH}_3\text{OH}] + \text{K}_b} \]

\[
[\text{NH}_4^+] + [\text{H}^+] = \text{[OH}^-\text{]} \]

\[
2.48 \times 10^{-7} \text{K}_b + [\text{H}^+] = \frac{\text{K}_w}{[\text{CH}_3\text{OH}]} \]

\[
[\text{H}^+] = \frac{2.48 \times 10^{-7} \text{K}_b [\text{OH}^-]}{\text{K}_w [\text{CH}_3\text{OH}] - [\text{OH}^-]^2} - [\text{OH}^-]^2 - [\text{H}^+]^2 = 0 \]
Weak Acids and Bases: Quick Review

Acid Dissociation: Base Hydrolysis:

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

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

For any conjugate acid base pair

\[ K_aK_b = K_w \]

What is the pH of a solution prepared by dissolving 0.10 moles of acetic acid in 1.00 L solution? This is tougher than it sounds!

\[ HOAc = H^+ + OAc^- \]

\[ H_2O = H^+ + OH^- \quad Kw = [OH^-][H^+] = 1.0 \times 10^{-14} \]

Charge Balance:

\[ [H^+] = [OH^-] + [OAc^-] \]

Mass Balance:

\[ [HOAc] + [OAc^-] = 0.10 \text{ F} \]

Four unknowns, four equations, time to solve.

We end up with a third order equation! What to do?!?
pH of a Weak Acid Solution

Let's make a simplifying approximation.

- Since HOAc is a much stronger acid than H₂O (look at the Kₐ's), the overwhelming majority of the protons in solution will come from the dissociation of HOAc
- Every time a proton (H⁺) is liberated, an acetate (OAc⁻) is liberated as well
- So, [H⁺] ≈ [OAc⁻], and therefore, [OH⁻] << [OAc⁻]

What does that do for us?

\[ K_a = \frac{[H^+]^2}{[HA]} = \frac{0.10 - [H^+]}{[H^+]} \]

\[ [H^+] = \sqrt{0.10 K_a} \]

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

where x = [H⁺].
**pH of a Weak Acid Solution**

This equation can be solved using the quadratic formula, BUT:

In some instances, we can make things easier yet:

- Remember, HA is a weak acid, so it only dissociates slightly (the $K_a$ equilibrium lies to the left b/c $K_a << 1$)
- So, [HA] at equilibrium will not vary much from its initial value, as long its initial concentration (F) isn’t extremely dilute.
- This allows us to approximate $F-x$ as $F$, the equation now becomes:

$$K_a = \frac{x^2}{F} \quad \text{or} \quad x = \sqrt{K_a F}$$

- This approximation is usually good as long as $K_a < 0.01 F$**

$$F > 100 K_a$$

\[\begin{align*}
K_a &= \frac{x^2}{0.1 - x} \\
0.1K_a - K_a x &= x^2 \\
x^2 + K_a x - 0.1K_a &= 0
\end{align*}\]

1. Ignore $H_2O$, $pH = 2.88 \approx 2.9$ 
   Solve quadratic

2. \(x\) is $\text{[H]}_x \approx \text{[HA]}_i$
   $pH = 2.878 \approx 2.88$
Fraction of Dissociation

Just how much (what fraction) HA dissociates? It depends on a couple of things:

1. $K_a$ (acid strength)

2. $pH$

To calculate fraction of dissociation, $\alpha$, for a monoprotic weak acid:

$$\alpha = \frac{[A^-]}{[HA] + [A^-]} = \frac{\frac{K_a[HA]}{[H^+]} + [A^-]}{[HA]} = \frac{K_a}{[H^+] + K_a} = \frac{K_a}{1 + \frac{K_a}{[H^+]}}$$

This reduces to:

$$0 < \alpha < 1 \quad \frac{K_a}{[H^+] + K_a} \quad \alpha \approx \frac{K_a}{K_a} \approx 1$$

$\alpha_{HA} = 1 - \alpha_A$

pH of a Weak Base Solution

The process is basically the same.

$$NH_3 + H_2O = NH_4^+ + OH^- \quad K_b = 1.75 \times 10^{-5}$$

What is the pH of 0.025 F ammonia?

Equilibrium Constants:

Charge Balance:

Mass Balance:

Simplifying assumption:

$$[NH_4^+] >> [H^+], \quad [OH^-] \approx \frac{[NH_4^+]}{[NH_3]}$$

Simplified solution:

$$[OH^-] = \frac{7 \times 10^{-4}}{M} \quad pH = 10.83$$

What is the fraction of association of ammonia under these conditions?

$$\alpha_{NH_3} = \frac{[NH_3]}{[NH_4^+][OH^-]} = \frac{6.7 \times 10^{-5}}{2.025} \approx 3.32 \%$$
Conjugate Acid-Base Pairs and Buffers

Items to remember about conjugate acid-base pairs:
• The conjugate acid of a weak base is a weak acid and the conjugate base of a weak acid is a weak base.
• For any conjugate acid-base pair, $K_a \times K_b = K_w$, where $K_a$ is the acid dissociation constant for the weak acid, and $K_b$ is the base hydrolysis constant for the conjugate base.
• Therefore, the conjugate base of a moderately weak acid is a stronger base than the conjugate of a very weak acid:

$$\text{If } K_a > K_b \text{ then } K_b < K_a$$


Why would you ever need a buffer?

How does a buffer work?

$K_a = 1.75 \times 10^{-5}$  $pK_a = 4.75$ Buffer pH

Calculate the pH of a solution prepared by mixing 0.010 mol of acetic acid with 0.010 mol of sodium acetate in 1.0 L solution.

$K_a = \frac{x(0.010)}{(0.010)}$

$K_a = \frac{1.75 \times 10^{-5} \times X(0.010)}{(0.010)}$

$\text{b/c } K_a \text{ small } A^- \text{ present}$

$\text{Expect little change in } [HA]$

$X \ll 0.010 M$
Buffer pH and the Henderson-Hasselbach Equation

H-H Relates pH to relative equilibrium concentrations of acid and conjugate base in solution.

\[ \text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \]

Buffer pH and the Henderson-Hasselbach Equation

We use the H-H equation to predict pH using non-equilibrium concentrations. How can we get by not accounting for dissociation?

To a first approximation, the pH of a buffer is essentially independent of dilution. Why?

- Activity and ionic strength considerations
- Concentrations of HA and A⁻ may not be equal to their formalities
- Dilute solutions, extreme pH

Critical Consideration: How would you prepare a buffer solution?
Buffer Behavior and Selection

Buffer Capacity:

\[ \beta = \frac{dC_a}{d\text{pH}} = -\frac{dC_a}{d\text{pH}} \]

- Buffer capacity is a maximum when \( \text{pH} = pK_a \)
- Best to choose a buffer system whose \( pK_a \) is within \( \pm 1 \) pH unit of your desired pH (since capacity diminishes greatly outside this range).

**PROBLEMS:**

1. Calculate the pH of a solution prepared by mixing 0.010 mol of acetic acid with 0.010 mol of sodium acetate in 1.0 L solution.

2. Calculate the new pH of this buffer after the addition of 15 mL of 0.100 F NaOH.

3. Would you expect a larger or smaller pH change if the buffer had been prepared from 0.10 mol HOAc and 0.10 mol NaOAc? Verify your prediction with a calculation.

\[ pH = pK_a + \log \left( \frac{\text{mol A}^-}{\text{mol HA}} \right) \]
PH 7.00 phosphate buffer | 0.10 M assume 1L

\[ H_3PO_4 \rightleftharpoons H_2PO_4^- \rightleftharpoons HPO_4^{2-} \rightleftharpoons PO_4^{3-} \]

\[ \text{pK}_1 = 1.91 \]
\[ \text{pK}_2 = 6.71 \]
\[ \text{pK}_3 = 11.82 \]

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[A^-]}{[HA]} \right) \]

Prepare using \( \text{Na}_2\text{HPO}_4 \), \( \text{Na}_3\text{PO}_4 \)

\[ \text{pH} = \text{pK}_a + \log \left( \frac{[A^-]}{[HA]} \right) \]

\[ \log \frac{[A^-]}{[HA]} = 7.00 - 6.71 = 0.29 \]

\[ \frac{[A^-]}{[HA]} = 10 \]

\[ \text{mol } A^- = 1.95 \text{ mol } HA \]

\[ 1.95 \text{ mol } HA + \text{mol } HA = 0.1 \text{ mol } \]

\[ \frac{\text{mol } HA}{\text{mol } A^-} = \frac{0.1}{1.95} \]

\[ \frac{\text{mol } A^-}{\text{mol } HA} = 10 \]