Aqueous Equilibria: Acids and Bases

Ch. 16

What is an acid? What is a base?

There are actually multiple definitions

**Arrhenius:** Dealt with species in aqueous solutions. Most basic definition of acid-base.

- Acid: increases H\(^+\) in water.
- Base: increases OH\(^-\) in water

**Børnested-Lowrey:** Acid-Base need not be in aqueous solutions. Acid and bases are part of a related conjugate pair.

- Acid: Proton (H\(^+\)) donor
- Base: Proton (H\(^+\)) acceptor

**Lewis:** No need for hydrogen in definitions

- Acid: Electron (e\(^-\)) acceptor
- Base: Electron (e\(^-\)) donor

\[ \text{Ag}^+ + 2 \cdot \text{NH}_3 \rightarrow \text{[H}_3\text{N:Ag:NH}_3]^{+} \]
Weak vs. Strong Acids/Bases

What does “strong” as in strong acids and bases mean?

- Highly Concentrated?
- Dangerous?

Strong just mean 100% dissociation
That’s all.

HCl in the gas phase

\[ \text{HCl(g)} \rightarrow \text{HCl(aq)} \]

K’s large
HCl = \(1.3 \times 10^6\)

HCl in the aqueous phase

HCl is strong acid

HCl in the gas phase

HF in the gas phase

\[ \text{HF(g)} \leftrightarrow \text{HF(aq)} \]

K’s are very small
HF = \(6.6 \times 10^{-4}\)

HF in the aqueous phase

HF is weak acid

Most HF molecules are actually NOT dissociated
**Weak vs. Strong Acids/Bases**

Just like with acids, strong bases are those with 100% dissociation.

**NaOH in the solid phase**

NaOH in the aqueous phase

NaOH(s) → NaOH(aq)  K’s large  NaOH is a strong base

**Weak vs. Strong Acids/Bases**

Weak just means much less than 100% dissociation! For NH₃, it itself is not dissociated, however, it takes an H⁺ from water to create OH⁻

NH₃(l) + H₂O(l) → NH₄⁺(aq) + OH⁻(aq)

Most NH₃ molecules are actually NOT converted to NH₄⁺

NH₄⁺ in the aqueous phase

NH₃ in the liquid phase

NH₃(l) ⇌ NH₄⁺(aq)  K’s are very small  NH₃ is a weak base

NH₃ = 1.8x10⁻⁵
### Strong vs. Weak acids

If you know the strong acids/bases, assume the rest are weak

<table>
<thead>
<tr>
<th>Strong Acids</th>
<th>Strong Bases</th>
<th>Examples of weak acids</th>
<th>Examples of weak bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl(aq)</td>
<td>LIOH</td>
<td>HF</td>
<td>(nitrogen-containing bases)</td>
</tr>
<tr>
<td>HBr(aq)</td>
<td>NaOH</td>
<td>CH₃COOH (acetic)</td>
<td>NH₃R R = anything</td>
</tr>
<tr>
<td>HI(aq)</td>
<td>KOH</td>
<td>HCOOH (formic)</td>
<td>NH₃ (ammonia)</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Ca(OH)₂</td>
<td>NH₄⁺ (ammonium)</td>
<td>(“Insoluble” hydroxides)</td>
</tr>
<tr>
<td>HClO₃</td>
<td>Sr(OH)₂</td>
<td>H₂PO₄</td>
<td></td>
</tr>
<tr>
<td>HClO₄</td>
<td>Ba(OH)₂</td>
<td>HClO</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄**</td>
<td></td>
<td>(small, highly-charged metal ions)</td>
<td></td>
</tr>
</tbody>
</table>

**Only the 1st H⁺ removed is "strong"**

A common rule for oxo-acids: if there are at least 2 more O’s than H⁺’s in the molecule, it is strong

100% ionization

<100% ionization

### Auto ionization of water – $K_w$

At any time in a sample of pure water, some water molecules, very few, will dissociate by themselves

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

The amount (concentration) that dissociates is quantified by $K_w$
The pH scale
A simple way of expressing concentration of H⁺ ions in solution.

<table>
<thead>
<tr>
<th>[H⁺] in M</th>
<th>pH</th>
<th>Common solutions</th>
<th>[OH⁻] in M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000000000001</td>
<td>14</td>
<td>1</td>
<td>0.000000000001</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>13</td>
<td>Bleach</td>
<td>0.1</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>12</td>
<td>Soapy Water</td>
<td>0.01</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>11</td>
<td>Ammonia Sulfate</td>
<td>0.001</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>10</td>
<td>Milk of Magnesia</td>
<td>0.0001</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>9</td>
<td>Baking Soda</td>
<td>0.0000000001</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>8</td>
<td>Sea Water</td>
<td>0.000001</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>7</td>
<td>Distilled Water</td>
<td>0.000000001</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>6</td>
<td>Urine</td>
<td>0.00000001</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>5</td>
<td>Black Coffee</td>
<td>0.0000000001</td>
</tr>
<tr>
<td>0.000000000001</td>
<td>4</td>
<td>Tomato Juice</td>
<td>0.000000000001</td>
</tr>
<tr>
<td>0.00000000001</td>
<td>3</td>
<td>Orange Juice</td>
<td>0.000000000001</td>
</tr>
<tr>
<td>0.0001</td>
<td>2</td>
<td>Lemon Juice</td>
<td>0.000000000001</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>Gastric Acid</td>
<td>0.000000000000001</td>
</tr>
</tbody>
</table>

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

\[ [\text{H}^+] = 10^{-\text{pH}} \]

Notice the relationship:

\[ [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} = K_w \]

Also notice the logarithmic nature of pH vs. [H⁺]

For example, what is the difference in [H⁺] between the pH of 7 and 4?

pH of 4 has \(10^{3}\), (or 1,000x) more H⁺ ions in solution than pH 7.

<table>
<thead>
<tr>
<th>pH</th>
<th>[H⁺] in M</th>
<th>[OH⁻] in M</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.000000000001</td>
<td>0.000000000001</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>0.000000000001</td>
</tr>
</tbody>
</table>

Determine the pH of a solution with 1.55x10⁻⁶ M H⁺. Also, what will be the concentration of OH⁻?

\[ \text{pH} = -\log(1.55 \times 10^{-6} \text{M}) = 5.810 \]

\[ [\text{H}^+] = 1.0 \times 10^{-6} \text{M} \]

\[ [\text{OH}^-] = 1.0 \times 10^{-8} \text{M} \]

Determine the pH of a solution with 0.977 M OH⁻. Also, what will be the concentration of H⁺?

\[ \text{pH} = -\log(0.977 \text{M}) = 13.991 \]

\[ [\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.977 \text{M}} = 1.02 \times 10^{-14} \text{M} \]

Determine the H⁺ and OH⁻ concentrations for a solution with a pH of 7.02

\[ [\text{H}^+] = 10^{-7.02} = 9.8 \times 10^{-8} \text{M} \]

\[ [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{9.8 \times 10^{-8} \text{M}} = 1.0 \times 10^{-6} \text{M} \]

Notice that the closer to pH = 7, the closer the [H⁺] and [OH⁻].
**pH and pOH**

Although most people know about pH, we can also calculate something called pOH

\[
[H^+][OH^-] = 1.0 \times 10^{-14} = K_w
\]

So, let's say we have a solution with a \([H^+]\) of \(2.9 \times 10^{-5}\) M. Determine the concentration of \([OH^-]\), find pH and pOH.

\[
\text{[OH]} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-5}} = 3.4 \times 10^{-10} \text{M}
\]

\[
\text{pOH} = \log(3.4 \times 10^{-10}) = 9.54
\]

\[
\text{pH} = 14 - \text{pOH} = 4.46
\]

**Qualitatively:**
- The larger the \([H^+]\), the lower the \([OH^-]\).
- The smaller the pH, the larger the pOH.

**pH of a strong acid/strong base**

Remember that when a strong acid or a strong base is placed in water, we assume that it is 100% dissociated.

So, for HCl, all of the “H” becomes dissociated as \(H^+\). If we know the concentration of HCl, we also know the concentration of \(H^+\).

What is the pH of a 0.050M solution of HCl?

Since HCl is 100% dissociated, the \([H^+]\) is also 0.050M

\[
pH = -\log([H^+]) = -\log(0.050) = 1.30
\]

And for NaOH, all of the “OH” becomes dissociated as \(OH^-\). If we know the concentration of NaOH, we also know the concentration of \(OH^-\).

What is the pH of a 0.050M solution of NaOH?

Since NaOH is 100% dissociated, the \([OH^-]\) is also 0.050M

\[
pOH = -\log([OH^-]) = -\log(0.050) = 1.30
\]

\[
pH = 14 - \text{pOH} = 14.00 - 1.30 = 12.70
\]
Conjugate Acid/Base pairs

Conjugate acid/base pairs are acids and bases that differ by only an H⁺.

HCl(aq) + H₂O(l) → H₃O⁺(aq) + Cl⁻(aq)

The stronger the acid, the weaker its conjugate base.

HCl(aq) + H₂O(l) → H₃O⁺(aq) + Cl⁻(aq)

Stronger acid weaker base

Stronger base weaker acid

The reaction will not proceed in the forward direction.

HCl(aq) + H₂O(l) → H₃O⁺(aq) + Cl⁻(aq)

Reaction proceeds in direction that results in a weaker acid and weaker base produced.

NO₃⁻ (aq) + H₂O(l) → OH⁻(aq) + HNO₃(aq)

Weaker base weaker acid

Stronger base stronger acid

The reaction will not proceed in the forward direction.

NH₄⁺ (aq) + CH₃COO⁻(aq) ⇌ NH₃(aq) + CH₃COOH(aq)

Weaker acid weaker base

Stronger base stronger acid
The Acid and Base Equilibrium constants: $K_a$ and $K_b$

The strength of acid or base can be related to an equilibrium constant:

$$\text{HA(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$$

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

$$\text{B(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{OH}^-(aq) + \text{BH}^+(aq)$$

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

The larger the $K_a$ and thus smaller the $pK_a$, the stronger the acid.

The larger the $K_b$ and thus smaller the $pK_b$, the stronger the base.

A certain acid has a $K_a$ of $1.2 \times 10^{-7}$.

Calculate its $pK_a$.

A certain acid has a $pK_a$ of 9.23.

Calculate its $K_a$.

Based on $pK_a$ or $K_a$ values, which acid is stronger?

Conjugate Acid/Base pair relationship – $K_a$ and $K_b$

How are conjugate acid/base pairs related?

$$K_b \cdot K_a = K_w = 1 \times 10^{-14}$$

For conjugate acid/base pairs

$\text{H}_3\text{PO}_4$ $K_a = 7.6 \times 10^{-3}$

$\text{H}_3\text{PO}_4$ $pK_a = 2.12$

$\text{CH}_3\text{COOH}$ $K_a = 1.6 \times 10^{-5}$

$\text{CH}_3\text{COOH} \ pK_a = 4.79$

$\text{NH}_4^+$ $K_a = 5.4 \times 10^{-10}$

$\text{NH}_4^+ \ pK_a = 9.27$

$\text{H}_2\text{PO}_4$ $K_a = 1.3 \times 10^{12}$

$\text{H}_2\text{PO}_4\ pK_a = 11.88$

$\text{CH}_3\text{COO}^- \ K_a = 6.2 \times 10^{10}$

$\text{CH}_3\text{COO}^- \ pK_a = 9.21$

$\text{NH}_3 \ K_a = 1.9 \times 10^5$

$\text{NH}_3 \ pK_a = 4.73$

We can also take the negative log of $K_a$, $K_b$, and $pK_a$.

$pK_b + pK_a = pK_w = 14$
Polyprotic Acids

While binary acids only have one H\(^+\) to donate, some oxoacids have multiple protons. They can be diprotic or triprotic.

\[
\begin{align*}
\text{H}_2\text{SO}_4 & \quad pK_{a1} = -3 \\
\text{HSO}_4^- & \quad pK_{a2} = 1.99 \\
\text{SO}_4^{2-} & \quad < 100\% \text{ dissociation}
\end{align*}
\]

Only the first H\(^+\) is considered strong. Each subsequent H\(^+\) dissociates less.

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \quad pK_{a1} = 2.12 \\
\text{H}_2\text{PO}_4^- & \quad pK_{a2} = 7.20 \\
\text{HPO}_4^{2-} & \quad pK_{a3} = 12.38 \\
\text{PO}_4^{3-} & \quad < 100\% \text{ dissociation}
\end{align*}
\]

Acidic, Basic, and Neutral Salts

Remember: in chemistry, a salt is just an ionic compound containing an anion and cation, but is neutral overall.

The anion and cation in this case can be viewed as conjugate acid/bases of something else...

Rules to remember:
• The child of a strong acid or base is negligible in strength.
• The child of weak acid or base is also weak
Acidic, Basic, and Neutral Salts

<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion (Conjugate Base)</th>
<th>Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>From strong base</td>
<td>...of a strong acid</td>
<td>Neutral salts</td>
</tr>
<tr>
<td>Conjugate acid of weak base</td>
<td>...of a strong acid</td>
<td>Acidic salts</td>
</tr>
<tr>
<td>Small/highly-charged metal ion</td>
<td>...of a strong acid</td>
<td>Acidic salts</td>
</tr>
<tr>
<td>From strong base</td>
<td>...of a weak acid</td>
<td>Basic salts</td>
</tr>
<tr>
<td>Conjugate acid weak base or small/highly-charged metal ion</td>
<td>...of a weak acid</td>
<td>Neutral salts</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
K_a &= K_b & \text{Neutral salts} \\
K_a &< K_b & \text{Basic salts} \\
K_a &> K_b & \text{Acidic salts}
\end{align*}
\]

Whether a salt is neutral, acidic, or basic will depend on the specific anion and anion.

Metal ions as acids

Certain metal ions act as acids, increasing the H⁺ concentration in water.

When these ions dissolve in water, water ions “coordinate” with the ions creating a “complex”.

The metal ions pull enough electron density from one water molecule outside the complex to allow it to dissociate into H₃O⁺ while an OH⁻ stays bound to the complex. Thus, increasing H₃O⁺ concentration.

Acidity increases with higher charge and smaller size of ion.
Determining the pH of a Weak Acid Solution

Determine the pH of a 0.123M aqueous solution of HClO. \( K_a = 2.95 \times 10^{-8} \).

Write the balanced equation for the acid in \( H_2O \)…producing \( H_3O^+ \).

Just like any other equilibrium problem, plug in what we know. Since \( H_2O \) is a pure liquid (and does not change appreciably over time), we don’t need to deal with it.

\[
K_a = \frac{[H_3O^+][ClO^-]}{[HClO]}
\]

\[
2.95 \times 10^{-8} = \frac{x^2}{0.123}
\]

\[
\sqrt{3.63 \times 10^{-5}} = x = 6.02 \times 10^{-5}
\]

\[
[H_3O^+] = [OH^-] = x = 6.02 \times 10^{-5}M
\]

\[
pH = -\log(6.02 \times 10^{-5}M) = 4.220
\]

\[
\text{pH} = 14.00 - 2.503 = 11.497
\]

Less than 5%, good assumption

\[
0.0487\% \times 100 = 0.0487\%
\]

Determining the pH of a Weak Base Solution

Determine the pH of a 0.555M aqueous solution of \( NH_3 \). \( pK_b = 4.75 \).

First, we need to deal with \( pK_b \).

\[
K_b = 10^{-4.75} = 1.78 \times 10^{-5}
\]

Write the balanced equation for the base in \( H_2O \)...producing \( OH^- \) and the conjugate acid, \( NH_4^+ \).

\[
K_b = \frac{[OH^-][NH_4^+]}{[NH_3]}
\]

\[
1.78 \times 10^{-5} = \frac{x^2}{0.555}
\]

\[
\sqrt{9.88 \times 10^{-5}} = x = 3.14 \times 10^{-3}
\]

\[
[OH^-] = x = 3.14 \times 10^{-3}M
\]

\[
pOH = -\log(3.14 \times 10^{-3}M) = 2.503
\]

\[
pH = 14.00 - 2.503 = 11.497
\]

Less than 5%, good assumption

\[
0.566\% \times 100 = 0.566\%
\]
Calculating $K_a$ from pH

If 1.55M solution of an acid has a pH of 5.15, determine the $K_a$ for the acid (assume it is monoprotic).

Since we know pH, we also know $[H^+]$ at equilibrium

$[H^+] = 10^{-5.15} = 7.1 \times 10^{-6}$

$K_a = \frac{[H_3O^+][A^-]}{[HA]}$

$K_a = \frac{(7.1 \times 10^{-6})(7.1 \times 10^{-6})}{(1.55 - 7.1 \times 10^{-6})} = 3.3 \times 10^{-11}$

“Short-Cuts”

If you complete enough ice tables, you will start noticing trends.

For example, placing a weak acid or base in water will give you the following expression using an ice table:

$K_c = \frac{x^2}{[\text{weak acid or base}]_{\text{initial}}}$

This assumes that $K_c$ is small enough where $x$ will also be small. Therefore we leave it out.

This also assumes that there are no products of ionization in the water before the weak base or acid is added.

If you are ever unsure of a short cut...always do it the long way!!
Percent ionization

Percent ionization is the amount of a weak acid or base that has become $H_3O^+$ or $OH^-$. 

$$\% \text{ionization of an acid} = \frac{[H_3O^+]}{[HA]_{\text{initial}}} \times 100$$

$$\% \text{ionization of a base} = \frac{[OH^-]}{[B]_{\text{initial}}} \times 100$$

Determine the percent ionization if 0.76M aqueous solution of an unknown acid mixed with water resulted in a $[H_3O^+]$ of $9.05 \times 10^{-4} M$.

$$\% \text{ionization} = \frac{9.05 \times 10^{-4} M}{0.76 M} \times 100 = 0.12\%$$

Determine the percent ionization if 5.00M aqueous solution of an unknown acid mixed with water resulted in a pH of 3.12.

$$[H_3O^+] = 10^{-pH} = 10^{-3.12} = 7.6 \times 10^{-4} M$$

$$\% \text{ionization} = \frac{7.6 \times 10^{-4} M}{5.00 M} \times 100 = 0.15\%$$

Determine the percent ionization of a weak acid with a $K_a$ of $1.0 \times 10^{-5}$ with the initial concentrations of 1.28M, 0.040M, and 0.010M.

$$\% \text{ionization} = \frac{x^2}{0.010} \times 100$$

$$x = 0.0032M$$

$$\% \text{ionization} = 3.2\%$$

$$\% \text{ionization} = \frac{x^2}{0.040} \times 100$$

$$x = 0.00063M$$

$$\% \text{ionization} = 1.6\%$$

$$\% \text{ionization} = \frac{x^2}{1.28} \times 100$$

$$x = 0.0036M - [H_3O^+]$$

$$\% \text{ionization} = 0.28\%$$

The more concentrated a weak base solution, the lower the % ionization.

Percent Ionization and Concentration

Weak acids and bases do not ionize to the same extent in every solution. The amount to which it ionizes depends on, among other things, the initial concentration of the weak acid or base.

Let's use the "short-cut" $K_b = \frac{x^2}{[\text{weak acid or base}]_{\text{initial}}}$

$$K_b = 10^{-4.75} = 1.8 \times 10^{-5}$$

$$\% \text{ionization} = \frac{1.8 \times 10^{-5}}{0.100 M} \times 100 = 1.8\%$$

The more concentrated a weak base solution, the lower the % ionization.
Binary Acid Strengths

<table>
<thead>
<tr>
<th>Acid</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>15.74</td>
</tr>
<tr>
<td>HF</td>
<td>3.17</td>
</tr>
<tr>
<td>H₂S</td>
<td>6.9</td>
</tr>
<tr>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td>HBr</td>
<td>3.9</td>
</tr>
<tr>
<td>HI</td>
<td></td>
</tr>
<tr>
<td>H₂Se</td>
<td>2.6</td>
</tr>
<tr>
<td>H₂Te</td>
<td></td>
</tr>
<tr>
<td>H₂Se</td>
<td></td>
</tr>
<tr>
<td>H₂Te</td>
<td></td>
</tr>
</tbody>
</table>

Moving down a group, the bond length gets longer. Longer bond length = weaker X-H bond.

Carboxylic Acid Strengths

<table>
<thead>
<tr>
<th>Acid</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂CO₂H</td>
<td>4.79</td>
</tr>
<tr>
<td>H₂CO₂H</td>
<td>2.86</td>
</tr>
<tr>
<td>H₂CO₂H</td>
<td>1.35</td>
</tr>
<tr>
<td>H₂CO₂H</td>
<td>0.77</td>
</tr>
</tbody>
</table>
Oxoacid Strengths – Inductive effects

In oxoacids, the weaker the O-H bond, the stronger the acid.

What can make the O-H bond weaker? Highly electronegative atoms withdraw electron density from the O-H bond, making it weaker.

- Chlorous acid: 7.53
- Chloric acid: 1.96
- Pershloric acid: -1
- Hypothioclyric acid: -8

Shift in electron density away from O-H makes the bond weaker (more acidic).

Less electron density at the H.

Carboxylic Acid Strengths

NaOH

H      H
H      C      C      O      H
H      H

4.74

Explain the following trend in acid strength:

- H      O
H      C      C      O      H
H
4.74

- H      O
H      C      C      O      H
H
2.86

- H      O
H      C      C      O      H
H
1.35

- H      O
H      C      C      O      H
H
0.77
Oxoacid Strengths – Inductive effects

Across each row, electron density of being shifted away from the O-H bond.

Stabilizes negative charge after proton loss

<table>
<thead>
<tr>
<th>Acid Strength</th>
<th>Electronegativity of central atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄⁺</td>
<td>9.84</td>
</tr>
<tr>
<td>H₂SO₃⁻</td>
<td>2.15</td>
</tr>
<tr>
<td>H₂SO₂⁻</td>
<td>-3</td>
</tr>
<tr>
<td>H₂SO₁⁻</td>
<td>-8</td>
</tr>
</tbody>
</table>