Polyprotic Acids & Bases

According to Brønsted and Lowry an acid is a proton donor and a base is a proton acceptor. This idea of proton donor and proton acceptor is important in understanding monoprotic and polyprotic acids and bases because monoprotic corresponds to the transfer of one proton and polyprotic refers to the transfer of more than one proton. Therefore, a monoprotic acid is an acid that can donate only one proton, while polyprotic acid can donate more than one proton. Similarly, a monoprotic base can only accept one proton, while a polyprotic base can accept more than one proton.

Introduction

One way to display the differences between monoprotic and polyprotic acids and bases is through titration, which clearly depicts the equivalence points and acid or base dissociation constants. The acid dissociation constant, signified by $K_a$, and the base dissociation constant, $K_b$, are equilibrium constants for the dissociation of weak acids and weak bases. The larger the value of either $K_a$ or $K_b$ signifies a stronger acid or base, respectively.

Here is a list of important equations and constants when dealing with $K_a$ and $K_b$:

For the general equation of a weak acid, $\text{HA}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{A}^-_{(aq)}$), you need to solve for the $K_a$ value.

In order to do that you use $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$

Another necessary value is the $pK_a$ value, and that is obtained through $pK_a = -\log K_a$

The procedure is very similar for weak bases. The general equation of a weak base is $\text{BOH} \rightarrow \text{B}^+ + \text{OH}^-$

Solving for the $K_b$ value is the same as the $K_a$ value. You use the formula $K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$

The $pK_b$ value is found through $pK_b = -\log K_b$

The $K_w$ value is found with $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$. 

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Monoprotic Acids

Monoprotic acids are acids that can release only one proton per molecule and have one equivalence point.

Here is a table of some common monoprotic acids:

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid (strong)</td>
<td>HCl</td>
<td>$1.3 \times 10^6$</td>
</tr>
<tr>
<td>Nitric acid (strong)</td>
<td>HNO₃</td>
<td>$2.4 \times 10^1$</td>
</tr>
<tr>
<td>Acetic acid (weak)</td>
<td>CH₃COOH</td>
<td>$1.74 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Monoprotic Bases

Monoprotic bases are bases that can only react with one proton per molecule and similar to monoprotic acids, only have one equivalence point. Here is a list of some common monoprotic bases:

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$K_b$</th>
</tr>
</thead>
</table>

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<table>
<thead>
<tr>
<th>Sodium hydroxide (strong)</th>
<th>NaOH</th>
<th>$6.3 \times 10^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium hydroxide (strong)</td>
<td>KOH</td>
<td>$3.16 \times 10^{-1}$</td>
</tr>
<tr>
<td>Ammonia (weak)</td>
<td>NH$_3$</td>
<td>$1.80 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

**Example 1**

What is the pH of the solution that results from the addition of 200 mL of 0.1 M CsOH(aq) to 50 mL of 0.2M HNO$_2$(aq)? (pKa= 3.14 for HNO$_2$)

**SOLUTION**

\[
\dfrac{0.1\text{ mol}}{L} \times 200\text{ mL} \times \dfrac{1\text{ L}}{1000\text{ mL}} = 0.02\text{ mol CsOH} \\
\dfrac{0.2\text{ mol}}{L} \times 50\text{ mL} \times \dfrac{1\text{ L}}{1000\text{ mL}} = 0.01\text{ mol HNO}_2
\]

Then do an ICE Table for \(\text{CsOH} + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{CsNO}_2\), yielding \([\text{CsOH}] = [\text{OH}^-] = 0.01\text{M}\)

Then to find pH first we find pOH \(\text{pOH} = -\log[\text{OH}^-] = -\log[\dfrac{0.01}{0.25}] = 1.4\)

Then \(\text{pH} = {14 - \text{pOH}}\), plugging in \(\text{pH} = 14 - 1.4 = 12.6\)

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**Polyprotic Acids and Bases**

So far, we have only considered monoprotic acids and bases, however there are various other substances that can donate or accept more than proton per molecule and these are known as polyprotic acids and bases. Polyprotic acids and bases have multiple dissociation constants, such as \(K_{a1}\), \(K_{a2}\), \(K_{a3}\) or \(K_{b1}\), \(K_{b2}\), and \(K_{b3}\), and equivalence points depending on the number of times dissociation occurs.

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**Polyprotic Acids**

*Polyprotic acids* are acids that can lose several protons per molecule. They can be further categorized into *diprotic acids* and *triprotic acids*, those which can donate two and three protons, respectively. The best way to demonstrate polyprotic acids and bases is with a titration curve. A titration curve displays the multiple acid dissociation constants (\(K_a\)) as portrayed below.
Here is a list of some common polyprotic acids:

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$K_{a1}$</th>
<th>$K_{a2}$</th>
<th>$K_{a3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid</td>
<td>H$_2$SO$_4$</td>
<td>1.0 x 10$^3$</td>
<td>1.2 x 10$^{-2}$</td>
<td>-</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>H$_2$CO$_3$</td>
<td>4.2 x 10$^{-7}$</td>
<td>4.8 x 10$^{-11}$</td>
<td>-</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H$_3$PO$_4$</td>
<td>7.1 x 10$^{-3}$</td>
<td>6.3 x 10$^{-8}$</td>
<td>4.2 x 10$^{-13}$</td>
</tr>
</tbody>
</table>

**Polyprotic Bases**

*Polyprotic bases* are bases that can attach several protons per molecule. Similar to polyprotic acids, polyprotic bases can be categorized into *diprotic bases* and *triprotic bases*.

Here is a list of some common polyprotic bases:

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium hydroxide</td>
<td>Ba(OH)$_2$</td>
<td></td>
</tr>
</tbody>
</table>
Example 2

For a 4.0 M \( \text{H}_3\text{PO}_4 \) solution, calculate (a) \([\text{H}_3\text{O}^+]\) (b) \([\text{HPO}_4^{2-}]\) and (c) \([\text{PO}_4^{3-}]\).

\[
\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-
\]

**SOLUTION**

(a) Using ICE Tables you get:

\[
[K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}]
\]

So,

\[
(x^2) = 0.284
\]

\[
(x) = 0.17 \text{ M}
\]

(b) From part (a), \((x) = [\text{H}_2\text{PO}_4^-] = [\text{H}_3\text{O}^+] = 0.17 \text{ M}

(c) To determine \([\text{H}_3\text{O}^+]\) and \([\text{H}_2\text{PO}_4^-]\), it was assumed that the second ionization constant was insignificant.

The new equation is as follows:

\[
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}
\]

Using ICE Tables again:

\[
(K_{a2} = [\text{HPO}_4^{2-}] = 6.3 \times 10^{-8})
\]

Example 3

The polyprotic acid \( \text{H}_2\text{SO}_4 \) can ionize two times (\(K_{a1} >> 1\), \(K_{a2} = 1.1 \times 10^{-2}\)). If we start with 9.50*10^{-3} M solution of \( \text{H}_2\text{SO}_4 \), what are the final concentrations of \( \text{H}_2\text{SO}_4 \), \( \text{HSO}_4^- \), \( \text{SO}_4^{2-} \), and \( \text{H}_3\text{O}^+ \).

**SOLUTION**
The equation for the first ionization is \((H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-)\). This equation goes to completion because \(H_2SO_4\) is a strong acid and \(K_{a1} \gg 1\).

So since the reaction goes to completion, doing an ICE Table you get \([H_3O^+] = 9.50 \times 10^{-3}\) M and \([HSO_4^-] = 9.50 \times 10^{-3}\) M (after the first ionization).

The equation of the second ionization is \((HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-})\). Using the equation \(K_{a2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}\), \(K_{a2} = 1.1 \times 10^{-2}\), and an ICE Table to get \((x^2 + 0.0205x - 0.0001045 = 0)\).

Then you use the quadratic equation to solve for \(X\), to get \(x = 0.004226\).

Now we need to solve for the necessary concentrations

\[([H_2SO_4]) = 0 \text{ (because the first ionization reaction went to completion)}\]

\[([HSO_4^-]) = (k_{a1}) - (k_{a2}) = 9.50 \times 10^{-3} \text{ M} - 0.004226 \text{ M} = 5.27 \times 10^{-3} \text{ M}\]

\[([SO_4^{2-}]) = (k_{a2}) = 0.004226 \text{ M}\]

\[([H_3O^+]) = (k_{a1}) + (k_{a2}) = 9.50 \times 10^{-3} \text{ M} + 0.004226 \text{ M} = 1.37 \times 10^{-2} \text{ M}\]

**Summary**

- \(K_a\) and \(K_b\) are equilibrium constants and a high value signifies a stronger acid or base.
- Acid are proton donors and bases are proton acceptors.
- Monoprotic acid/base corresponds to the donation/acceptance of *only one* proton.
- Polyprotic acid/base corresponds to the donation/acceptance of *more than one* proton.
  - Remember diprotic and triprotic.
- \((K_{a1})/(K_{a2})/(K_{a3})\)

**Common Errors**

- Assuming that the \([H_3O^+]\) is the same for all the ionizations.
  - In fact, the pH is dominated by only the first ionization, but the later ionizations do contribute very slightly.
References


Contributors

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