Learning Objectives

• Predict and calculate the pH of a solution of salts of polyprotic acids

Salts can be thought of as being derived from the neutralization of an acid and a base. A salt formed from a strong acid and a strong base will not hydrolyze (e.g., extract a proton from water). When placed in water, these salts dissociate completely, and their ions remain uncombined in solution (e.g., the NaCl salt is formed from a strong acid (HCl) and a strong base (NaOH).

In discussing the titration of acids and bases, the acid or basic properties of the corresponding salts after a neutralization reaction must be addressed to calculate the final pH of a solution. To calculate the pH of a salt solution one needs to know the concentration of the salt solution, whether the salt is an acidic, basic, or neutral salt, the equation for the interaction of the ion with the water, the equilibrium expression for this interaction and the $K_a$ or $K_b$ value.

Note: The Hydrolysis of Salts

As a quick review, the general rules for the hydrolysis of monoprotic salts are:

1. If neither the cation/anion can affect the pH, the solution is neutral
2. If only the cation of the salt is acidic, the solution is acidic
3. If only the anion of the salt is basic, the solution will be basic
4. If a salt has a cation that is acidic and an anion that is basic, the pH of the solution is determined by the relative strengths of the acid and base
   - if $(K_a = K_b)$, then no net effect on pH
   - if $(K_a > K_b)$, then the solution is slightly acidic
   - if $(K_b > K_a)$, then the solution is slightly basic

Salts of Polyprotic Acids

Do not be intimidated by the salts of polyprotic acids. Yes they're bigger and "badder" than most other salts, but they can be handled the exact same way as other salts, just with a bit more math.

• All of the rules from above still apply, e.g., the pH of a salt of polyprotic acid will always be greater than 7.
• The same way that polyprotic acids lose $H^+$ stepwise, salts of polyprotic acids gain $H^+$ in the same manner, but in reverse order of the polyprotic acid.

Take for example dissociation of carbonic acid ($H_2CO_3$):

$$\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq)$$

with $(K_{a1} = 2.5 \times 10^{-4})$

$$\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CO}_3^{2-}(aq)$$

$1$
with \(K_{a2} = 5.61 \times 10^{-11}\). This means that when calculating the values for \(K_b\) of \(\ce{CO3^{2-}}\), the \(K_b\) of the first hydrolysis reaction will be \(K_{b1} = \dfrac{K_w}{K_{a2}}\) since it will go in the reverse order.

Example 17.5.1: \(\text{(NaHSO}_4\text{)}\)

What is the pH of a 0.100 M \(\text{(NaHSO}_4\text{)}\) solution? Sulfuric acid is a strong acid, and the \(\text{pK}_a\) of \(\ce{HSO4^-}\) is 1.92.

**Solution**

First review the ions generated immediate upon dissociation of the salt.

- \(\text{Na}^+\) is a non-acidic "spectator ion" that does not affect the acidity or basicity of a solution and can be ignored.
- The \(\text{HSO}_4^-\) anion will affect the pH

\(\text{HSO}_4^-\) is part of the dissociation chain of diprotic sulfuric acid \(\text{(Na}_2\text{SO}_4\text{)}\) with the following steps

\[
\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^- \quad \text{label(step1SO3)}
\]

Because \(\text{H}_2\text{SO}_4\) is a strong acid, this step goes to completion and no \(\text{H}_2\text{SO}_4\) exists in the solution. The \(\text{HSO}_4^-\) ion is a weak acid and dissociates to a small extent:

\[
\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-} \quad \text{label(step2SO3)}
\]

with \(K_{a2} = 1.0 \times 10^{-2}\) from Table E1. The equilibrium favors the reactants.

The \(\text{(NaHSO}_4\text{)}\) salt is completely ionized in its solution.

\[
\text{\text{NaHSO}_4_{(s)} \rightarrow Na^+_{(aq)} + HSO_4^-_{(aq)}} \quad \text{label(step2SO3)}
\]

The anion then further ionizes (Equation \(\text{ref(step2SO3)}\)). We can construct an **ICE table** to solve for the final value of this ionization and hence \(\text{[H}_3\text{O}^+\text{]}\)

<table>
<thead>
<tr>
<th>ICE Table</th>
<th>(\text{HSO}_4^-)</th>
<th>(\text{H}_2\text{O})</th>
<th>(\text{H}_3\text{O}^+)</th>
<th>(\text{SO}_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.1 M</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>-</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.1 M -x</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\(K_{a2} = \dfrac{x^2}{0.100-x} = 0.0100 \ \text{nonumber}\)

\[
\begin{align}
\text{[H}_3\text{O}^+] &= \dfrac{-0.120 + \sqrt{0.012^2 + 4\times0.00120}}{2} \\
&= \text{0.0292 M}
\end{align}
\]
Thus,

$$\text{pH} = -\log 0.0292 = 1.54$$

Note that while the dissociation is weak, the quadratic equation cannot be avoided since 0.0292 cannot be ignored when compared to 0.1 M.

Exercise 17.5.1

Which of the following solutions are acidic, basic, or neutral?

a. $\ce{Na2SO4}$
b. $\ce{NaH2PO4}$
c. $\ce{Na2HPO4}$
d. $\ce{Na3PO4}$
e. $\ce{NaNO3}$

Example 17.5.2: Qualitatively Estimating the pH of a Polyprotic Salt Solution

Predict whether the $\ce{Na2HPO4}$ salt will form an acidic or basic solution when dissolved in water. You will need values from Table E1 to address this.

Solution

First review the ions generated upon dissociation of the salt.

- The $\ce{Na^+}$ ion is a non-acidic "spectator ion" that does not affect the acidity or basicity of a solution and can be ignored.
- The $\ce{HPO4^{2-}}$ anion will affect the pH and does so via competing hydrolysis steps as discussed below.

From Table E1, the three equilibria values for the three acid/base reactions of the phosphate ion are:

$$\ce{H3PO4(sq) <=> H+(aq) + H2PO4-(aq)} \quad \text{with} \quad K_{a1} = 6.9 \times 10^{-3}$$

$$\ce{H2PO4-(aq) <=> H+(aq) + HPO4^{2-}(aq)} \quad \text{with} \quad K_{a2} = 6.2 \times 10^{-8}$$

$$\ce{HPO4^{2-}(aq) <=> H+(aq) + PO4^{3-}(aq)} \quad \text{with} \quad K_{a3} = 4.8 \times 10^{-11}$$

The low $K_{a1}$ value for the deprotonation of $\ce{HPO4^{2-}(aq)}$ means that it is a poor acid and better functions as a
(Brønsted-Lowry) base:

\[
[HPO^{2-}_{4 (aq)} + H_2O_{(l)} \rightleftharpoons H_2PO^-_{4 (aq)} + OH^-_{ (aq)}] \label{3b} 
\]

The two possible reactions that \(HPO^{2-}_{4(aq)}\) undergoes are the acid reaction in Equation \(\ref{2}\) and the basic reaction in Equation \(\ref{3b}\). Whether this ion will cause the solution to be acidic or basic depends on whether the \(K_a\) for Equation \(\ref{2}\) is bigger than the \(K_b\) for Equation \(\ref{3b}\).

The \(K_b\) of this reaction is related to the \(K_{a2}\) by

\[
K_b = \frac{K_w}{K_{a2}} \nonumber
\]

\[
K_b = \frac{1 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7} \text{ for } HPO_4^{2-} \nonumber
\]

Since \(K_b > K_a\), the solution will be basic. To determine just how basic requires the use of an ICE table as discussed in Example 17.5.3.

Solving the final pH for a \((Na_2HPO_4)\) salt solution is more complex than for the \((NaHSO_4)\), since the latter involves a single equilibrium. Two equilibria must be simultaneously solved for \((Na_2HPO_4)\). However, often time (but not always), they can be easily approximated given the relative \(pk_a\) describing the reversible reaction.

Example 17.5.3: Quantitatively Estimating the pH of a Polyprotic Salt Solution

Calculate the pH of the solution containing 3.875 g of \((Na_2HPO_4)\) that has been dissolved in a 250 mL of water.

Solution

First it is best to identify the molarity of \((Na_2HPO_4)\) that was initially generated (i.e., before any hydrolysis reactions happens).

\[
c = \frac{3.875 \; g}{141.98 \; g/mol} = 0.027 \; M \nonumber
\]

As discussed in Example 17.5.1, the low \(K_a\) value for the deprotonation of \((HPO_{4(sq)}^{2-})\) means that it is a poor acid and instead functions as a base instead. From comparing the ionization constant in Example 17.5.1, the \((Na_2HPO_4)\) is a far better base than acid. If we ignore the acid properties of the ion and focus on the basic we get the following reaction

\[
[HPO^{2-}_{4 (aq)} + H_2O_{(l)} \rightleftharpoons H_2PO^-_{4 (aq)} + OH^-_{ (aq)}] \nonumber
\]

with a \(K_b\) of \(1.6 \times 10^{-7}\). Now do an \textit{ICE table} to get the final \([H^+]\) concentration.

<table>
<thead>
<tr>
<th>ICE Table</th>
<th>([HPO^{2-}_{4 (aq)}])</th>
<th>([H_2O_{(l)}])</th>
<th>([H_2PO^-_{4 (aq)}])</th>
<th>([OH^-_{ (aq)}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.11 M</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>
\[ K_b = \text{H}_2\text{PO}_{4 (aq)}^- \cdot [\text{OH}^-_{(aq)}] / [\text{HPO}^{2-}_{4 (aq)}] = 1.6 \times 10^{-7} \]

\[ x^2 / (0.11 \text{ M} - x) = 1.6 \times 10^{-7} \]

if \(x << 0.11 \text{ M}\) then \(0.11 \text{ M} - x \approx 0.11 \text{ M}\)

\[ x = 1.3 \times 10^{-4} = [\text{OH}^-] \]

\[ pOH = -\log_{10} [\text{OH}^-] = 3.8 \]

\[ pH = pK_w - pOH \]

Assuming that the reaction is at 25°, then \(pK_w = 14\) and

\[ pH = 14 - 3.8 = 10.2 \]

As expected, the solution is basic.