So far you have learned about pH in solutions where either a single acid, such as citric acid, or a single base, such as the citrate ion have been added to water. Now, let us consider solutions prepared with both an acid and a base. The simplest case of such a solution occurs when the acid and base are conjugate to each other and also are present in comparable amounts. Solutions of this special kind are called **buffer solutions** because it is difficult to change their pH even when an appreciable amount of strong acid or strong base is added.

**Why are buffer solutions important in foods?**

Buffer solutions in foods play an important role in maintaining specific pH values for optimum activity of enzymes, protein solubility, and functionality. As discussed in previous exemplars, pH may also modify the color and flavor of foods and it is a critical factor in the preservation of many processed foods. Buffering solutions are also used as reaction media in the production of food ingredients and additives. Overall pH control is a major factor in maintaining the physical, chemical, and microbiological stability of foods.

Foods contain numerous compounds able to form buffering systems. Molecules with acid-base properties naturally found in foods include amino acids, organic acids, proteins, and charged polysaccharides. Other buffering systems are intentionally added to processed foods, examples of these are the weak acids discussed in the pH of weak acids in foods and their corresponding conjugate bases.

**How do we calculate the pH of buffer solutions?**

As an example of a buffer solution, let us consider the solution obtained when 3.00 mol citric acid (H$_3$C$_6$H$_5$O$_7$) and 2.00 mol monosodium citrate (NaH$_2$C$_6$H$_5$O$_7$) are added to sufficient water to produce a solution of total volume 1 dm$^3$. The stoichiometric concentration of citric acid, namely, c$_a$, is then 3.00 mol dm$^{-3}$, while the stoichiometric concentration of sodium citrate, c$_b$, is 2.00 mol dm$^{-3}$. As a result of mixing the two components, some of the citric acid, say $x$ mol dm$^{-3}$, is converted to citrate ion and hydronium ion. We can now draw up a table in order to find the equilibrium concentrations in the usual way.

<table>
<thead>
<tr>
<th>Species</th>
<th>Initial Concentration mol dm$^{-3}$</th>
<th>Change in Concentration mol dm$^{-3}$</th>
<th>Equilibrium Concentration mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$O$^+$</td>
<td>$10^{-7}$ (negligible)</td>
<td>$x$</td>
<td>$x$</td>
</tr>
<tr>
<td>H$_2$C$_6$H$_5$O$_7^-$</td>
<td>2.00</td>
<td>$x$</td>
<td>2.00 + $x$</td>
</tr>
<tr>
<td>H$_3$C$_6$H$_5$O$_7$</td>
<td>3.00</td>
<td>($-x$)</td>
<td>3.00 – $x$</td>
</tr>
</tbody>
</table>

or

$xx$

$1x$
In a buffer mixture, the hydronium-ion concentration and the hydroxide-ion concentration are small compared with the concentrations of acid and conjugate base. ([H_3O^+] = 2.7 \times 10^{-5} \text{ mol dm}^{-3}; [\text{HO}^-] = 3.7 \times 10^{-10} \text{ mol dm}^{-3} \text{ as compared with } [\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-] = 2.00 \text{ mol dm}^{-3} \text{ and } [\text{H}_3\text{C}_6\text{H}_5\text{O}_7] = 3.00 \text{ mol dm}^{-3})

**The Henderson-Hasselbach equation**

Assuming that the above features are common to all buffer solutions, we make it very easy to handle them from a mathematical standpoint. Let us now consider the general problem of finding the pH of a buffer solution which is a mixture of a weak acid HA, of stoichiometric concentration $c_a$, and its conjugate base $A^-$, of stoichiometric concentration $c_b$. We can rearrange the expression for $K_a$ of the weak acid (Equation 2 on the pH of solutions of weak acids) as follows:

**Henderson-Hasselbalch equation**

As we saw in the case of the citric acid—sodium citrate buffer described earlier, the equilibrium concentrations of HA and $A^-$ are usually almost identical to the stoichiometric concentrations. That is,

and

**EXAMPLE 1** Calculate the pH of a buffer containing 3.93 g of NaH$_2$PO$_4$ and 4.31 g of Na$_2$HPO$_4$ per 450 mL of solution.

**SOLUTION** First, we need to calculate the concentration of both the acid (NaH$_2$PO$_4$) and the base (Na$_2$HPO$_4$) in solution. For NaH$_2$PO$_4$ we have that the number of moles is

Due to their sweetening properties, short chain polyols (compounds containing more than 2 alcohol groups) are often used to substitute sugars. Besides their sweetening properties, polyols can perform a variety of functions in food. They are added as bulking agents, antimicrobials, prebiotics, humectants, and modifiers of freezing point, crystallization, and mouth-feel. Polyols are naturally found in food or obtained by hydrogenation of the corresponding sugar. The compounds shown in the table on the side are used in the formulation of sugar-free dietary foods including products for diabetics, however their use is limited by their laxative and hygroscopic properties.
Polyols have been reported to lower the pH of hydrochloric acid solutions and phosphate buffers. The ability of lowering the pH of a buffer solution appeared to be directly proportional to the molecular weight of the polyol with phosphate buffers being more sensitive to the effect of polyols than citrate buffers.\cite{3} \cite{4} The lower pH value of phosphate buffer solutions when sucrose was added has been attributed to a reduction in the apparent pKa of the phosphate buffer.\cite{5} The apparent pKa values for the second dissociation of phosphoric acid decreased slightly from 6.79 to 6.74 when 2 molal glycerol was added into solution, while a significant decrease to 6.56 was observed with 2 molal sucrose. The authors of this investigation explained that such reduction in the apparent pKa value could be the result of a reduction in the hydration sphere around the buffer ions which would favor proton dissociation. The level of hydration of the ions in turn depends on polyol-water interactions and the charge density of the buffer ions.

**EXAMPLE 2** Calculate the pH of the phosphate buffer solution from **EXAMPLE 1** if in addition to NaH$_2$PO$_4$ and Na$_2$HPO$_4$, it contains 2 molal sucrose.

**SOLUTION** From **EXAMPLE 1** we know that the concentrations in solution for NaH$_2$PO$_4$ and Na$_2$HPO$_4$ are $7.27 \times 10^{-2}$ and $6.75 \times 10^{-2}$ mol dm$^{-2}$ respectively. A phosphate buffer solution like this containing 2 molal sucrose would register a shift in apparent pKa from 6.79 to 6.56. Under these conditions, the Henderson-Hasselbach equation becomes

\[
\text{pH} = \frac{\text{pK}_a}{2} \ln \left( \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \right)
\]

this pH value is lower compared to 6.82, the pH of this solutions in the absence of sucrose.

**How do buffers work?**

To better understand why a mixture of an acid and its conjugate base is resistant to a change in pH, let us go back to our first example: a mixture of citric acid ($3 \text{ mol dm}^{-3}$) and sodium citrate ($2 \text{ mol dm}^{-3}$). What would happen if we now added 0.50 mol sodium hydroxide to 1 dm$^3$ of this mixture? The added hydroxide ion will attack both the acids present, namely, the hydronium ion and citric acid. Since the hydronium-ion concentration is so small, very little hydroxide ion will be consumed by reaction with the hydronium ion. Most of it will be consumed by reaction with citric acid. Further, since the hydroxide ion is such a strong base, the reaction

will go virtually to completion, and 0.50 mol citric acid will be consumed. The same amount of citrate ion will be produced. In tabular form:

<table>
<thead>
<tr>
<th>Species</th>
<th>Initial Concentration mol dm$^{-3}$</th>
<th>Change in Concentration mol dm$^{-3}$</th>
<th>Equilibrium Concentration mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$O$^+$</td>
<td>$2.1 \times 10^{-4}$ (negligible)</td>
<td>Small</td>
<td>approx. $2.1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Substituting the equilibrium concentrations of base (citrate ion) and conjugate acid (citric acid) into the Henderson-Hasselbalch equation, Eq. (3), we have

The addition of 0.5 mol sodium hydroxide to the buffer mixture raised its pH from 2.5 to only 2.85.

Now, what would be the pH of the solution if the 0.5 mol of sodium hydroxide would have been added to a cubic decimeter of pure water in absence of citric acid?

This amount of sodium hydroxide would produce a solution containing 0.5 M of hydroxide ions with a pOH equal to

This shows you that the buffer is extremely effective at resisting a change in pH because the added hydroxide ion attacks the weak acid (in very high concentration) rather than the hydronium ion (in very low concentration). The major effect of the addition of the hydroxide ion is thus to change the ratio of acid to conjugate base, i.e., to change the value of

As long as the amount of weak acid is much larger than the amount of base added, this ratio is not altered by very much. Since the hydronium-ion concentration is governed by

Similarly, if instead of a strong base, a strong acid such as hydrochloric was added to the buffer mixture, it would react with the citrate in solution. Although, the pH would decrease, the change would be minor again.

**EXAMPLE 3** Find the pH of the solution obtained when 2.00 mol H$_2$C$_6$H$_5$O$_7^-$ and 0.80 mol H$_3$C$_6$H$_5$O$_7$ are mixed to give 2.5 dm$^3$ of solution. $K_b$(H$_2$C$_6$H$_5$O$_7^-$) = 7.1 × 10$^{-12}$ mol dm$^{-3}$.

**Solution** In order to use Eq. (4), we need first to have the value of

Given that the final volume of the solution is 2.5 dm$^3$, the concentration of the acid and base in solution are $c_a$ = 0.32 mol dm$^{-3}$ and $c_b$ = 0.80 mol dm$^{-3}$. Thus

from which

and
References


Contributors

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.