

## 14.8.2: Foods- Production of Food Ingredients

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?

Buffering 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 ( $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ ) and 2.00 mol monosodium citrate ( $\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7$ ) are added to sufficient water to produce a solution of total volume 1 dm<sup>3</sup>. The stoichiometric concentration of citric acid, namely,  $c_a$ , is then 3.00 mol dm<sup>-3</sup>, while the stoichiometric concentration of sodium citrate,  $c_b$ , is 2.00 mol dm<sup>-3</sup>. As a result of mixing the two components, some of the citric acid, say  $x$  mol dm<sup>-3</sup>, 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.

Species	Initial Concentration mol dm <sup>-3</sup>	Change in Concentration mol dm <sup>-3</sup>	Equilibrium Concentration mol dm <sup>-3</sup>
$\text{H}_3\text{O}^+$	$10^{-7}$ (negligible)	$x$	$x$
$\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$	2.00	$x$	$2.00 + x$
$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	3.00	$(-x)$	$3.00 - x$

We can now substitute concentrations in the equilibrium expression  $K_a = \frac{[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]}$  from which we obtain  $1.4 \times 10^{-3} \text{ mol dm}^{-3} = \frac{(2.00 + x)x}{3.00 - x} \text{ mol dm}^{-3}$  (1) In order to solve this equation, we make the approximation that  $x$  is negligibly small compared with both 2.00 and 3.00, that is, that only a minute fraction of citric acid has converted to citrate ion. We then have  $\frac{2.00x}{3.00} = 1.4 \times 10^{-3}$

or

$$x = \frac{3.00}{2.00} \times 1.4 \times 10^{-3} \quad (14.8.2.1)$$

$$= 2.1 \times 10^{-3} \quad (14.8.2.2)$$

Since  $x$  is only 0.1 percent of 2.00 or 3.00, the approximation is valid and there is no need to obtain a second approximation by feeding  $x$  back into Eq. (1). We can thus conclude that  $[\text{H}_3\text{O}^+] = 2.1 \times 10^{-3} \text{ mol dm}^{-3}$  and  $\text{pH} = 2.67$  This example demonstrates two obvious features: **1** When the acid and its conjugate base are mixed, very little of the acid is converted to base, or vice versa. ( $x$  is small compared with 2.00 and 3.00.)

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

### The Henderson-Hasselbalch 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:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]} \quad (2) \text{ Taking negative logarithms of both sides, we obtain } -\log [H_3O^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$$

$pH = pK_a + \log \frac{[A^-]}{[HA]}$  (3) Equation (3) is called the **Henderson-Hasselbalch equation** and is often used by chemists and biologists to calculate the pH of a buffer.

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,

$$[HA] \approx c_a \text{ and } [A^-] \approx c_b$$

We can substitute these values into Eqs. (2) and (3) to obtain the very useful approximations  $[H_3O^+] \approx K_a \times \frac{c_a}{c_b}$  (4) and  $pH \approx pK_a + \log \frac{c_a}{c_b}$  (5)

#### ✓ Example 14.8.2.1 pH of Buffer

Calculate the pH of a buffer containing 3.93 g of  $NaH_2PO_4$  and 4.31 g of  $Na_2HPO_4$  per 450 mL of solution

**Solution:** First, we need to calculate the concentration of both the acid ( $NaH_2PO_4$ ) and the base ( $Na_2HPO_4$ ) in solution. For  $NaH_2PO_4$  we have that the number of moles is

$$n_{NaH_2PO_4} = \frac{3.93 \text{ g}}{119.98 \text{ g mol}^{-1}} \quad (14.8.2.3)$$

$$= 3.27 \times 10^{-2} \text{ mol} \quad (14.8.2.4)$$

and its concentration

$$[NaH_2PO_4] = \frac{3.27 \times 10^{-2} \text{ mol}}{0.45 \text{ dm}^3} \quad (14.8.2.5)$$

$$= 7.27 \times 10^{-2} \text{ mol dm}^{-3} \quad (14.8.2.6)$$

and for  $Na_2HPO_4$

$$n_{Na_2HPO_4} = \frac{4.31 \text{ g}}{141.96 \text{ g mol}^{-1}} \quad (14.8.2.7)$$

$$= 3.04 \times 10^{-2} \text{ mol} \quad (14.8.2.8)$$

$$[Na_2HPO_4] = \frac{3.04 \times 10^{-2} \text{ mol}}{0.45 \text{ dm}^3} \quad (14.8.2.9)$$

$$= 6.75 \times 10^{-2} \text{ mol dm}^{-3} \quad (14.8.2.10)$$

Which means that the concentrations of  $H_2PO_4^-$  and  $HPO_4^{2-}$  are respectively  $7.27 \times 10^{-2} \text{ mol dm}^{-3}$  and  $6.75 \times 10^{-2} \text{ mol dm}^{-3}$ . Using these values and a  $pK_{a2} = 7.21$  for the pair  $H_2PO_4^-/HPO_4^{2-}$  (calculated from  $K_{a2}$ ) in the Henderson Hasselbach equation, the pH of the buffer becomes

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (14.8.2.11)$$

$$= 7.21 + \log \frac{6.75 \times 10^{-2} \text{ mol dm}^{-3}}{7.27 \times 10^{-2} \text{ mol dm}^{-3}} \quad (14.8.2.12)$$

$$= 7.17 \quad (14.8.2.13)$$

Phosphate buffers help to control the pH of physiological fluids and are often used in carbonated soft drinks.

#### Buffer solutions and the production of food ingredients

Another example of the importance of buffers in food is the production of food ingredients and bioactive compounds derived from foods. In the last few years, numerous research papers have been published regarding the enzymic modification of food proteins to improve their functionality, sensory, and bioavailability properties. Buffer solutions are employed to conduct enzymic reactions maintaining the pH for optimum enzyme activity throughout the process.

As example of enzymic modification of food proteins we have the oligomerization of milk proteins. The enzymes employed in this process include transglutaminase, peroxidase, laccase, monoamine oxidase, and tyrosine. They act via the oxidation of aromatic and sulphur containing amino acid residues and bonding of oxidized protein groups. Buffer systems for these enzymes include sodium borate decahydrate, potassium phosphate, tris, succinate, and sodium phosphate. <sup>[1]</sup>

Oligomerization with lactoperoxidase, lipoxygenase, and  $\beta$ -galactosidase of milk proteins is significantly enhanced when conducted in buffer solutions instead of demineralized water. The extent of oligomerization and therefore the size of the resulting molecules depends on the buffer system. Besides the expected effect on the three-dimensional structure and catalytic activity of the enzyme and substrate, the buffers have shown further effects on the oligomerization of milk proteins, it appears that there exists a complex interaction between the buffer, protein, and enzyme accounting for the difference in the molecular weight of the oligomers.<sup>[1]</sup> In addition, polymerization of hemoglobin and milk proteins has been observed in borate and phosphate buffers without the addition of enzyme.<sup>[2] [3]</sup>

### Boric acid

What is the pH of a solution prepared by mixing 250 mL of 0.5 M boric acid ( $\text{B}(\text{OH})_3(\text{H}_2\text{O})$ ) and 750 mL of 0.8 M sodium borate ( $\text{NaB}(\text{OH})_4$ )?

Since both the acid and the base were diluted when the solution was prepared we need to calculate their concentrations with the new volume of  $1000 \text{ mL} = 1 \text{ dm}^3$ .

Using the relationship

$V_{old} \times c_{old} = V_{new} \times c_{new}$  The new concentration becomes  $c_{new} = \frac{V_{old} \times c_{old}}{V_{new}}$  So, for boric acid we have

$$c_{new \text{ B}(\text{OH})_3\text{H}_2\text{O}} = \frac{0.50 \text{ mol dm}^{-3} \times 0.25 \text{ dm}^{-3}}{1.0 \text{ dm}^{-3}} \quad (14.8.2.14)$$

$$= 0.125 \text{ mol dm}^{-3} \quad (14.8.2.15)$$

Similarly for borate The  $K_a$  for the equilibrium  $\text{B}(\text{OH})_3(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{B}(\text{OH})_4^-$  From our collection of acid-base resources is  $K_a = 5.8 \times 10^{-10}$  Thus, using equation (4)

$$[\text{H}_3\text{O}^+] \approx K_a \times \frac{c_a}{c_b} \quad (14.8.2.16)$$

$$\approx 5.8 \times 10^{-10} \text{ mol dm}^{-3} \times \frac{0.125 \text{ mol dm}^{-3}}{0.60 \text{ mol dm}^{-3}} \quad (14.8.2.17)$$

$$\approx 1.2 \times 10^{-10} \text{ mol dm}^{-3} \quad (14.8.2.18)$$

The pH of the solution is then and

$$\text{pH} = -\log(1.2 \times 10^{-10}) \quad (14.8.2.19)$$

$$= 9.92 \quad (14.8.2.20)$$

Boric acid tends to accumulate in adipose tissue, specially in the central nervous system. Since the risks associated with this compound in the human body are still unknown, it is no longer used in food.<sup>[4]</sup> However, food additives obtained through enzymic processes usually undergo several separation or purification steps which would eliminate or significantly reduce the amount of residual borate buffer in the final product.

**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  $0.50 \text{ mol}$  sodium hydroxide to  $1 \text{ dm}^3$  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

$\text{H}_3\text{C}_6\text{H}_5\text{O}_7 + \text{OH}^- \rightarrow \text{H}_2\text{C}_6\text{H}_5\text{O}_7^- + \text{H}_2\text{O}$  will go virtually to completion, and  $0.50 \text{ mol}$  citric acid will be consumed. The same amount of citrate ion will be produced. In tabular form:

Species	Initial Concentration $\text{mol dm}^{-3}$	Change in Concentration $\text{mol dm}^{-3}$	Equilibrium Concentration $\text{mol dm}^{-3}$
$\text{H}_3\text{O}^+$	$2.1 \times 10^{-4}$ (negligible)	Small	approx. $2.1 \times 10^{-4}$
$\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$	2.00	0.5	$2.00 + 0.5 = 2.5$
$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	3.00	(-0.5)	$3.00 - 0.5 = 2.5$

Substituting the equilibrium concentrations of base (citrate ion) and conjugate acid (citric acid) into the Henderson-Hasselbalch equation, Eq. (3), we have

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (14.8.2.21)$$

$$= -\log(1.4 \times 10^{-3}) + \log \frac{(2.50 \text{ mol dm}^{-3})}{(2.50 \text{ mol dm}^{-3})} \quad (14.8.2.22)$$

$$= -(0.15 - 3) + \log(1) \quad (14.8.2.23)$$

$$= 2.85 + 0 = 2.85 \quad (14.8.2.24)$$

The addition of  $0.5 \text{ mol}$  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  $0.5 \text{ mol}$  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  $0.5 \text{ M}$  of hydroxide ions with a pOH equal to

$\text{pOH} = -\log(0.5) = 0.3$  and  $\text{pH} = 14 - 0.3 = 13.7$  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  $\frac{[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]}{[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]}$ . 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  $[\text{H}_3\text{O}^+] = K_a \frac{[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]}{[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]}$ . 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 14.8.2.3 pH of Solution

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

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

$$K_a(\text{H}_3\text{C}_6\text{H}_5\text{O}_7) = \frac{K_w}{K_b(\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-)} \quad (14.8.2.25)$$

$$= \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{7.1 \times 10^{-12} \text{ mol dm}^{-3}} \quad (14.8.2.26)$$

$$= 1.4 \times 10^{-3} \text{ mol dm}^{-3} \quad (14.8.2.27)$$

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

$$[\text{H}_3\text{O}^+] \approx K_a \times \frac{c_a}{c_b} \quad (14.8.2.28)$$

$$\approx 1.4 \times 10^{-3} \text{ mol dm}^{-3} \times \frac{0.32 \text{ mol dm}^{-3}}{0.80 \text{ mol dm}^{-3}} \quad (14.8.2.29)$$

$$\approx 5.6 \times 10^{-4} \text{ mol dm}^{-3} \quad (14.8.2.30)$$

from which

and  $\text{pH} = 3.25$

From ChemPRIME: [14.7: Buffer Solutions](#)

## References

1. Hiller, B. and Lorenzen P.-C. 2008 Effect of buffer systems on the oligomerization of milk proteins. LWT-Food Sci. Technol. 41:1140-1144.
2. Chen, K., Ballas, S.K., Hantgan, R.R., and Kim-Shapiro, D.B. 2004 Aggregation of normal and sickle hemoglobin in high concentration phosphate buffer. Biophys. J. 87:4113-4121.
3. Parker, W.C., and Bearn, A.G. 1963. Boric acid-induced heterogeneity of conalbumin by starch-gel electrophoresis. Nature, 199, 1184-1186.
4. Food Chemistry 3rd Ed. 2004 Belitz, et al.

## 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.

---

This page titled [14.8.2: Foods- Production of Food Ingredients](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [Ed Vitz](#), [John W. Moore](#), [Justin Shorb](#), [Xavier Prat-Resina](#), [Tim Wendorff](#), & [Adam Hahn](#).