

14.8: Buffer Solutions

So far in discussing pH we have dealt only with solutions obtained by adding a single acid, such as acetic acid, or a single base, such as the acetate ion, to water. We must now turn to a consideration of solutions to which both an acid and a base have been added. The simplest case of such a solution occurs when the acid and base are conjugate to each other and also present in comparable amounts. Solutions of this special kind are called **buffer solutions** because, as we shall shortly see in the video below, it is difficult to change their pH even when an appreciable amount of strong acid or strong base is added.



As a typical example of a buffer solution, let us consider the solution obtained when 3.00 mol acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) and 2.00 mol sodium acetate ($\text{Na C}_2\text{H}_3\text{O}_2$) are added to sufficient water to produce a solution of total volume 1 L. The stoichiometric concentration of acetic acid, namely, c_a , is then 3.00 mol L^{-1} , while the stoichiometric concentration of sodium acetate, c_b , is 2.00 mol L^{-1} . As a result of mixing the two components, some of the acetic acid, say $x \text{ mol L}^{-1}$, is converted to acetate 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 L^{-1})	Change in Concentration (mol L^{-1})	Equilibrium Concentration (mol L^{-1})
H_3O^+	10^{-7} (negligible)	x	x
CH_3COO^-	2.00	x	$2.00 + x$
CH_2COOH	3.00	$(-x)$	$3.00 - x$

We can now substitute concentrations in the equilibrium expression

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

from which we obtain

$$1.8 \times 10^{-5} \text{ mol L}^{-1} = \frac{(2.00 + x)x}{3.00 - x} \text{ mol L}^{-1} \quad (14.8.1)$$

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 acetic acid has converted to acetate ion. We then have

$$\frac{2.00x}{3.00} = 1.8 \times 10^{-5}$$

or

$$x = \frac{3.00}{2.00} \times 1.8 \times 10^{-5} \quad (14.8.2)$$

$$= 2.7 \times 10^{-5} \quad (14.8.3)$$

Obviously, our approximation is a very good one. Since x is only 0.001 percent of 2.00 or 3.00, there really is no point in obtaining a second approximation by feeding x back into Eq. 14.8.1. We can thus safely conclude that

$$[\text{H}_3\text{O}^+] = 2.7 \times 10^{-5} \text{ mol L}^{-1}$$

and

$$\text{pH} = 4.57$$

The example we have just considered 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 was 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. ($[\text{H}_3\text{O}^+] = 2.7 \times 10^{-5} \text{ mol L}^{-1}$; $[\text{HO}^-] = 3.7 \times 10^{-10} \text{ mol L}^{-1}$ as compared with $[\text{CH}_3\text{COO}^-] = 2.00 \text{ mol L}^{-1}$ and $[\text{CH}_3\text{COOH}] = 3.00 \text{ mol L}^{-1}$)

By assuming that these 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 .

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]} \quad (14.8.4)$$

Taking negative logarithms of both sides, we obtain

$$\begin{aligned} -\log [\text{H}_3\text{O}^+] &= -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]} \\ \text{pH} &= \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \end{aligned} \quad (14.8.5)$$

Equation 14.8.5 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 acetic acid—sodium acetate buffer described earlier, the equilibrium concentrations of HA and A^- are usually almost identical to the stoichiometric concentrations. That is,

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

We can substitute these values into Eqs. 14.8.4 and 14.8.5 to obtain the very useful approximations

$$[\text{H}_3\text{O}^+] \approx K_a \times \frac{c_a}{c_b} \quad (14.8.6)$$

and

$$\text{pH} \approx \text{p}K_a + \log \frac{c_b}{c_a}$$

✓ Example 14.8.1: pH of Solution

Find the pH of the solution obtained when 1.00 mol NH_3 and 0.40 mol NH_4Cl are mixed to give 1 L of solution. $K_b(\text{NH}_3) = 1.8 \times 10^{-5} \text{ mol L}^{-1}$.

Solution

In order to use Eq. 14.8.6, we need first to have the value of

$$K_a(\text{NH}_4^+) = \frac{K_w}{K_b(\text{NH}_3)} \quad (14.8.7)$$

$$= \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}}{1.8 \times 10^{-5} \text{ mol L}^{-1}} \quad (14.8.8)$$

$$= 5.56 \times 10^{-10} \text{ mol L}^{-1} \quad (14.8.9)$$

We also have $c_a = 0.40 \text{ mol L}^{-1}$ and $c_b = 1.00 \text{ mol L}^{-1}$. Thus

$$[\text{H}_3\text{O}^+] = K_a \times \frac{c_a}{c_b} \quad (14.8.10)$$

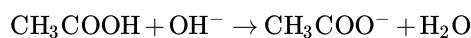
$$= 5.56 \times 10^{-10} \text{ mol L}^{-1} \times \frac{0.4 \text{ mol L}^{-1}}{1.0 \text{ mol L}^{-1}} \quad (14.8.11)$$

$$= 2.22 \times 10^{-10} \text{ mol L}^{-1} \quad (14.8.12)$$

from which

and $\text{pH} = 9.65$

To see 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 acetic acid (3 mol L^{-1}) and sodium acetate (2 mol L^{-1}). What would happen if we now added 0.50 mol sodium hydroxide to 1 L of this mixture? The added hydroxide ion will attack both the acids present, namely, the hydronium ion and acetic acid. Since the hydronium-ion concentration is so small, very little hydroxide ion will be consumed by reaction with the hydronium ion. Most will be consumed by reaction with acetic acid. Further, since the hydroxide ion is such a strong base, the reaction



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

Species	Initial Concentration mol L^{-1}	Change in Concentration mol L^{-1}	Equilibrium Concentration mol L^{-1}
H_3O^+	2.7×10^{-5}	Small	approx. 2.7×10^{-5}
CH_3COO^-	2.00	0.50	$2.50 + 2.7 \times 10^{-5} = 2.50$
CH_3COOH	3.00	(-0.50)	$2.50 - 2.7 \times 10^{-5} = 2.50$

Substituting the equilibrium concentrations of base (acetate ion) and conjugate acid (acetic acid) into the Henderson-Hasselbalch equation, Eq. 14.8.5, we have

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (14.8.13)$$

$$= -\log(1.8 \times 10^{-5}) + \log \frac{(2.50 \text{ mol L}^{-1})}{(2.50 \text{ mol L}^{-1})} \quad (14.8.14)$$

$$= -(0.25 - 5) + \log(1) \quad (14.8.15)$$

$$= 4.74 + 0 = 4.74 \quad (14.8.16)$$

The addition of 0.5 mol sodium hydroxide to buffer mixture has thus succeeded in raising its pH from 4.57 to only 4.74. If the same 0.5 mol had been added to a cubic decimeter of pure water, the pH would have jumped all the way from 7.00 up to 13.7! 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

$$\frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

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

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

the hydronium-ion concentration and pH are also altered to only a small extent.

The ability of a buffer solution to resist large changes in pH has a great many chemical applications, but perhaps the most obvious examples of buffer action are to be found in living matter. If the pH of human blood, for instance, gets outside the range 7.2 to 7.6, the results are usually fatal. The pH of blood is controlled by the buffering action of several conjugate acid-base pairs. The most important of these is undoubtedly the $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ pair, but side chains of the amino acid histidine in the hemoglobin molecule also play a part. (Hemoglobin, a protein, is the red substance in the blood. It is responsible for carrying oxygen away from the lungs.) Most enzymes (biological catalysts) can only function inside a rather limited pH range and must therefore operate in a buffered environment. The enzymes which start the process of digestion in the mouth at a pH of around 7 become inoperative in the stomach at a pH of 1.4. The stomach enzymes in turn cannot function in the slightly basic environment of the intestines.

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