

18.2: Buffers- Solutions That Resist pH Change

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium involving a substance that adds an ion that is a part of the equilibrium.

Introduction

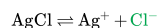
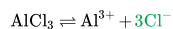
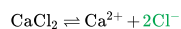
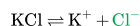
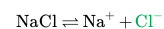
The solubility products K_{sp} 's are equilibrium constants in heterogeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[\text{Na}^+] + [\text{K}^+] = [\text{Cl}^-] \quad (18.2.1)$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion.

Common Ions

When NaCl and KCl are dissolved in the same solution, the Cl^- ions are *common* to both salts. In a system containing NaCl and KCl, the Cl^- ions are common ions.



For example, when AgCl is dissolved into a solution already containing NaCl (actually Na^+ and Cl^- ions), the Cl^- ions come from the ionization of both AgCl and NaCl. Thus, $[\text{Cl}^-]$ differs from $[\text{Ag}^+]$. The following examples show how the concentration of the common ion is calculated.

✓ Example 18.2.1

What are $[\text{Na}^+]$, $[\text{Cl}^-]$, $[\text{Ca}^{2+}]$, and $[\text{H}^+]$ in a solution containing 0.10 M each of NaCl, CaCl_2 , and HCl?

Solution

Due to the conservation of ions, we have

$$[\text{Na}^+] = [\text{Ca}^{2+}] = [\text{H}^+] = 0.10 \text{ M}$$

but

$$\begin{aligned} [\text{Cl}^-] &= 0.10 \text{ (due to NaCl)} \\ &\quad + 0.20 \text{ (due to CaCl}_2\text{)} \\ &\quad + 0.10 \text{ (due to HCl)} \\ &= 0.40 \text{ M} \end{aligned}$$

? Exercise 18.2.1

John poured 10.0 mL of 0.10 M NaCl, 10.0 mL of 0.10 M KOH, and 5.0 mL of 0.20 M HCl solutions together and then he made the total volume to be 100.0 mL. What is $[\text{Cl}^-]$ in the final solution?

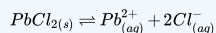
Solution

$$[\text{Cl}^-] = \frac{0.1 \text{ M} \times 10 \text{ mL} + 0.2 \text{ M} \times 5.0 \text{ mL}}{100.0 \text{ mL}} = 0.020 \text{ M}$$

Le Châtelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

✓ Example 18.2.2: Solubility of Lead Chloride

Consider the lead(II) ion concentration in this *saturated* solution of PbCl_2 . The balanced reaction is



Defining s as the concentration of dissolved lead(II) chloride, then:

$$[\text{Pb}^{2+}] = s$$

$$[\text{Cl}^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s :

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 \quad (18.2.2)$$

$$= s \times (2s)^2 \quad (18.2.3)$$

$$1.7 \times 10^{-5} = 4s^3 \quad (18.2.4)$$

$$s^3 = \frac{1.7 \times 10^{-5}}{4} \quad (18.2.5)$$

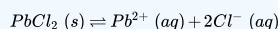
$$= 4.25 \times 10^{-6} \quad (18.2.6)$$

$$s = \sqrt[3]{4.25 \times 10^{-6}} \quad (18.2.7)$$

$$= 1.62 \times 10^{-2} \text{ mol dm}^{-3} \quad (18.2.8)$$

The concentration of lead(II) ions in the solution is $1.62 \times 10^{-2} \text{ M}$. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression again:



What happens to that equilibrium if extra chloride ions are added? According to [Le Châtelier](#), the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

✓ Example 18.2.3

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[\text{Pb}^{2+}] = s \quad (18.2.9)$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution.

In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[\text{Cl}^{-}] = 0.100 \text{ M} \quad (18.2.10)$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [\text{Pb}^{2+}][\text{Cl}^{-}]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.0100 \end{aligned}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3} \text{ M} \end{aligned} \quad (18.2.11)$$

Finally, compare that value with the simple saturated solution:

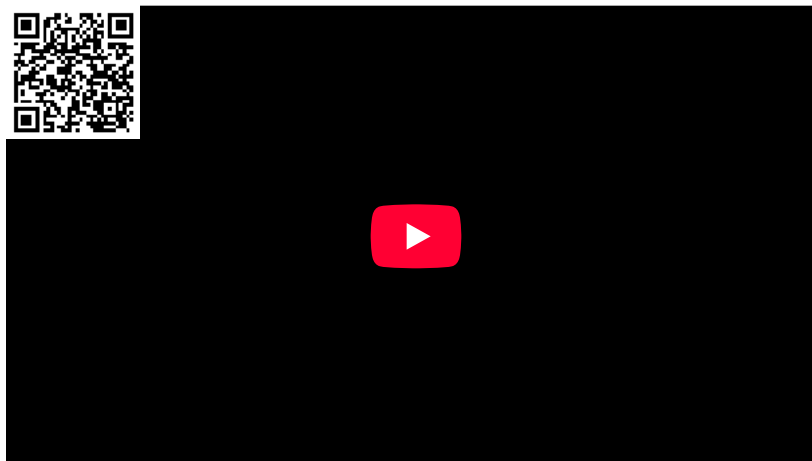
Original solution:

$$[\text{Pb}^{2+}] = 0.0162 \text{ M} \quad (18.2.12)$$

Solution in 0.100 M NaCl solution:

$$[\text{Pb}^{2+}] = 0.0017 \text{ M} \quad (18.2.13)$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.



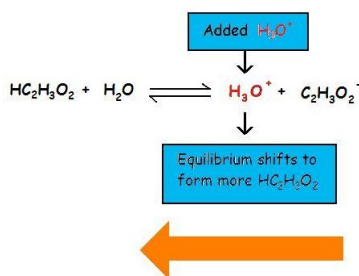
A Video Discussing Finding the Solubility of a Salt: [Finding the Solubility of a Salt\(opens in new window\)](#) [youtu.be]

Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.

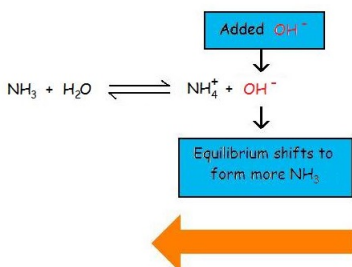
The common ion effect of H_3O^+ on the ionization of acetic acid



$\text{HC}_2\text{H}_3\text{O}_2$ reactions with H_2O to produce H_3O^+ plus and $\text{C}_2\text{H}_3\text{O}_2^-$. If more H_3O^+ plus is added to the reaction, the equilibrium would shift to form more $\text{HC}_2\text{H}_3\text{O}_2$.

When a strong acid supplies the common ion H_3O^+ the equilibrium shifts to form more $\text{HC}_2\text{H}_3\text{O}_2$.

The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium. Now consider the common ion effect of OH^- on the ionization of ammonia



When a strong base supplies the common ion OH^- the equilibrium shifts to form more NH_3 .

NH_3 reacts with H_2O to produce NH_4^+ plus and OH^- minus. If more OH^- minus is added to the reaction, the equilibrium would shift to form more NH_3 .

Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with [Le Chatelier's Principle](#)), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K .

Common Ion Effect on Solubility

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:



As you will discover in more advanced chemistry courses, basic anions, such as S^{2-} , PO_4^{3-} , and CO_3^{2-} , react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate. The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $\text{Ca}_3(\text{PO}_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2}{[\text{Ca}_3(\text{PO}_4)_2]} \quad (18.2.15)$$

$$[\text{Ca}_3(\text{PO}_4)_2]K = K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 \quad (18.2.16)$$

At 25°C and pH 7.00, K_{sp} for calcium phosphate is 2.07×10^{-33} , indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts vary dramatically for different compounds (Table E3). Although K_{sp} is not a function of pH in Equation 18.2.15, changes in pH can affect the solubility of a compound.

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. **Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions.** This dependency is another example of the common ion effect where adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion.

Consider, for example, the effect of adding a soluble salt, such as CaCl_2 , to a saturated solution of calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$. We have seen that the solubility of $\text{Ca}_3(\text{PO}_4)_2$ in water at 25°C is $1.14 \times 10^{-7} \text{ M}$ ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $\text{Ca}_3(\text{PO}_4)_2$ in water contains

- $3 \times (1.14 \times 10^{-7} \text{ M}) = 3.42 \times 10^{-7} \text{ M}$ of Ca^{2+}
- $2 \times (1.14 \times 10^{-7} \text{ M}) = 2.28 \times 10^{-7} \text{ M}$ of PO_4^{3-}

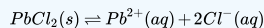
according to the stoichiometry shown in Equation 18.2.15 (neglecting hydrolysis to form HPO_4^{2-}). If CaCl_2 is added to a saturated solution of $\text{Ca}_3(\text{PO}_4)_2$, the Ca^{2+} ion concentration will increase such that $[\text{Ca}^{2+}] > 3.42 \times 10^{-7} \text{ M}$, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 18.2.15 to proceed to the left, resulting in precipitation of $\text{Ca}_3(\text{PO}_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

Note

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.

✓ Example 18.2.5

Consider the reaction:



What happens to the solubility of $\text{PbCl}_2(s)$ when 0.1 M NaCl is added?

Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: Cl^-

Notice: $Q_{sp} > K_{sp}$. The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of PbCl_2 is equivalent to the concentration of Pb^{2+} produced because they are in a 1:1 ratio.

Because K_{sp} for the reaction is 1.7×10^{-5} , the overall reaction would be $(s)(2s)^2 = 1.7 \times 10^{-5}$. Solving the equation for s gives $s = 1.62 \times 10^{-2}$ M. The coefficient on Cl^- is 2, so it is assumed that twice as much Cl^- is produced as Pb^{2+} , hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^- added would be 0.1 M because Na^+ and Cl^- are in a 1:1 ratio in the ionic salt, NaCl. Therefore, the overall molarity of Cl^- would be $2s + 0.1$, with 2s referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$Q_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 \quad (18.2.17)$$

$$1.8 \times 10^{-5} = (s)(2s + 0.1)^2 \quad (18.2.18)$$

$$s = [\text{Pb}^{2+}] \quad (18.2.19)$$

$$= 1.8 \times 10^{-3} \text{ M} \quad (18.2.20)$$

$$2s = [\text{Cl}^-] \quad (18.2.21)$$

$$\approx 0.1 \text{ M} \quad (18.2.22)$$

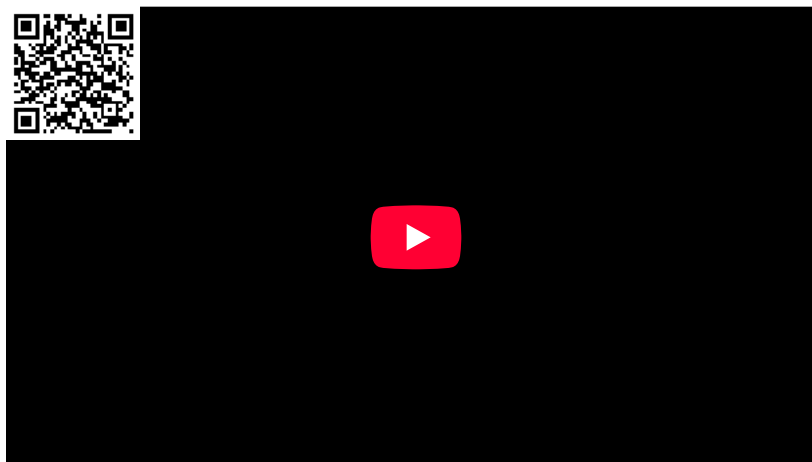
Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[\text{Cl}^-]$ is approximately 0.1M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for PbCl_2 is greater than the equilibrium constant because of the added Cl^- . This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

? Exercise 18.2.5

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



A Video Discussing the Common Ion Effect in Solubility Products: [The Common Ion Effect in Solubility Products \(opens in new window\)](#) [youtu.be]

References

1. Harwood, William S., F. G. Herring, Jeffrey D. Madura, and Ralph H. Petrucci. General Chemistry Principles and Modern Applications. 9th ed. New Jersey: Prentice Hall, 2007.

Contributors and Attributions

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Learning Objectives

- To understand how adding a common ion affects the position of an acid–base equilibrium.
- To know how to use the Henderson-Hasselbalch approximation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or “buffer,” other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect: Weak Acids Combined with Conjugate Bases

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H^+). Le Chatelier's principle can be used to predict the effect on the equilibrium position of the solution. A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. The dissociation reaction of acetic acid is as follows:



and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3CO_2H]} \quad (18.2.24)$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 18.2.23 will shift to the left, consuming some of the added CH_3COO^- and some of the H^+ ions originally present in solution.

Because Na^+ is a **spectator ion**, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding any base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3CO_2^-]$ than before. In both cases, only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is via the common ion effect.

Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.

✓ Example 18.2.1

A 0.150 M solution of formic acid at 25°C ($pK_a = 3.75$) has a pH of 2.28 and is 3.5% ionized.

- Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
- What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a , and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

- Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.
- Substitute the expressions for the final concentrations into the expression for K_a . Calculate $[H^+]$ and the pH of the solution.
- Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

A Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid-base properties of the solution are determined solely by the formic acid ionization equilibrium:



The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

| Final Concentration | | | |
|---------------------|----------------|-----------------------|-----------------|
| ICE | $[HCO_2H(aq)]$ | $[H^+(aq)]$ | $[HCO_2^-(aq)]$ |
| Initial | 0.150 | 1.00×10^{-7} | 0.100 |
| Change | -x | +x | +x |
| Equilibrium | $(0.150 - x)$ | x | $(0.100 + x)$ |

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$\begin{aligned}
 K_a &= \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(x)(0.100 + x)}{0.150 - x} \\
 &\approx \frac{x(0.100)}{0.150} \\
 &\approx 10^{-3.75} \\
 &\approx 1.8 \times 10^{-4}
 \end{aligned}$$

Rearranging and solving for x,

$$\begin{aligned}
 x &= (1.8 \times 10^{-4}) \times \frac{0.150 \text{ M}}{0.100 \text{ M}} \\
 &= 2.7 \times 10^{-4} \\
 &= [H^+]
 \end{aligned}$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover,

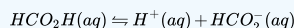
$$K_a C_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

which is greater than 1.0×10^{-6} , so again, our assumption is justified. The final pH is:

$$pH = -\log(2.7 \times 10^{-4}) = 3.57$$

compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

C Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.



initial concentrations, changes in concentration, and final concentrations

| | $[HCO_2H(aq)]$ | $[H^+(aq)]$ | $[HCO_2^-(aq)]$ |
|---------|----------------|---------------|-----------------|
| initial | 0.150 | 0.200 | 0 |
| change | $-x$ | $+x$ | $+x$ |
| final | $(0.150 - x)$ | $(0.200 + x)$ | x |

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[HCO_2^-]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200 + x)(x)}{0.150 - x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for x ,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150 M}{0.200 M} \\ = 1.35 \times 10^{-4} = [HCO_2^-]$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4} M}{0.150 M} \times 100\% = 0.0900\%$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding H^+ ions drives the dissociation equilibrium to the left.

? Exercise 18.2.1

A 0.225 M solution of ethylamine ($CH_3CH_2NH_2$ with $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

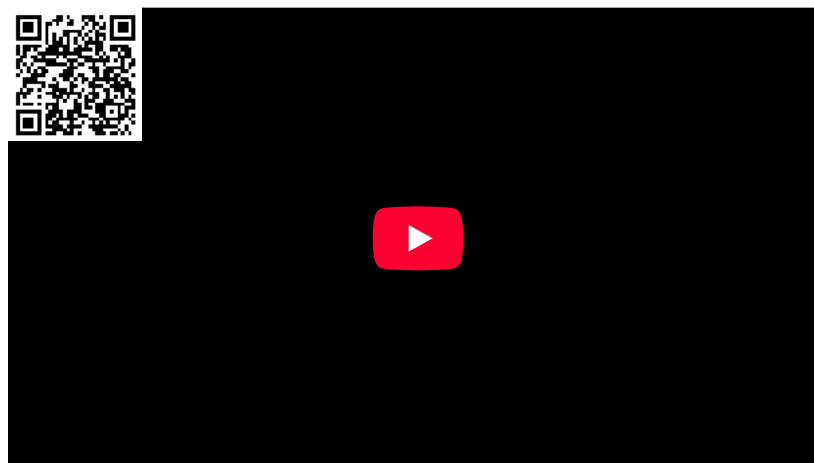
- the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$
- the percentage of ethylamine that is ionized if enough solid NaOH is added to the original solution to give a final concentration of 0.050 M NaOH

Answer a

11.16

Answer b

1.3%



A Video Discussing the Common Ion Effect: [The Common Ion Effect \(opens in new window\)](#) [youtu.be]

The Common Ion Effect: Weak Bases Combined with Conjugate Acids

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:



If the equilibrium constant for the reaction as written in Equation 18.2.25 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \frac{1}{K_b} = 10^5$.

Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 18.2.25 to shift to the left, consuming the added OH^- . As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is

$$pK_a = pK_w - pK_b = 14.0 - 5.0 = 9.0.$$

Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:



Again, the equilibrium constant for the reverse of this reaction is very large: $K = 1/K_a = 10^9$. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 18.2.26 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 18.2.1, when $NaOH$ is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

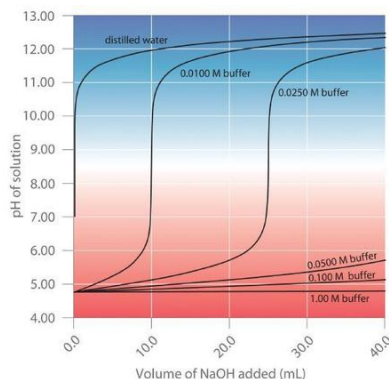


Figure 18.2.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M $NaOH$ to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of $NaOH$ solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the $NaOH$ solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 18.2.1 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \rightleftharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (18.2.27)$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \quad (18.2.28)$$

Taking the logarithm of both sides and multiplying both sides by -1 ,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \quad (18.2.29)$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad (18.2.30)$$

Replacing the negative logarithms in Equation 18.2.30

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad (18.2.31)$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \quad (18.2.32)$$

Equation 18.2.31 and Equation 18.2.32 are both forms of the Henderson-Hasselbalch approximation, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

$$\frac{[base]}{[acid]} = 1$$

in Equation 18.2.32 Because $\log 1 = 0$,

$$pH = pK_a$$

regardless of the actual concentrations of the acid and base. Recall that this corresponds to the midpoint in the titration of a weak acid or a weak base.

- $[base]/[acid] = 10$: In Equation 18.2.32 because $\log 10 = 1$,

$$pH = pK_a + 1.$$

- $[base]/[acid] = 100$: In Equation 18.2.32 because $\log 100 = 2$,

$$pH = pK_a + 2.$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then $\text{pH} = \text{p}K_a - 1$. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

If [base] = [acid] for a buffer, then $\text{pH} = \text{p}K_a$. Changing this ratio by a factor of 10 either way changes the pH by ± 1 unit.

✓ Example 18.2.2

What is the pH of a solution that contains

- 0.135 M HCO_2H and 0.215 M HCO_2Na ? (The $\text{p}K_a$ of formic acid is 3.75.)
- 0.0135 M HCO_2H and 0.0215 M HCO_2Na ?
- 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The $\text{p}K_b$ of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and $\text{p}K_a$; concentration of base, conjugate acid, and $\text{p}K_b$

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equations 18.2.31 or 18.2.32) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 18.2.31), the pH of a solution that contains both a weak acid and its conjugate base is

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

A

Inserting the given values into the equation,

$$\begin{aligned}\text{pH} &= 3.75 + \log\left(\frac{0.215}{0.135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95\end{aligned}$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the $\text{p}K_a$ (3.75) and $\text{p}K_a + 1$, or 4.75.

B

This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch approximation,

$$\begin{aligned}\text{pH} &= 3.75 + \log\left(\frac{0.0215}{0.0135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95\end{aligned}$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends only on the ratio of the concentrations of the conjugate base and the acid, not on the magnitude of the concentrations. Because the $[A^-]/[HA]$ ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

C

In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 18.2.32 the more general form of the Henderson-Hasselbalch approximation, in which “base” and “acid” refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and [acid] = $[\text{HPy}^+] = 0.234 \text{ M}$. We also are given $\text{p}K_b = 8.77$ for pyridine, but we need $\text{p}K_a$ for the pyridinium ion. Recall from Equation 16.23 that the $\text{p}K_b$ of a weak base and the $\text{p}K_a$ of its conjugate acid are related:

$$\text{p}K_a + \text{p}K_b = \text{p}K_w.$$

Thus $\text{p}K_a$ for the pyridinium ion is $\text{p}K_w - \text{p}K_b = 14.00 - 8.77 = 5.23$. Substituting this $\text{p}K_a$ value into the Henderson-Hasselbalch approximation,

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \\ &= 5.23 + \log\left(\frac{0.119}{0.234}\right) \\ &= 5.23 - 0.294 \\ &= 4.94\end{aligned}$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the $\text{p}K_a$ (5.23) and $\text{p}K_a - 1$, or 4.23.

? Exercise 18.2.2

What is the pH of a solution that contains

- 0.333 M benzoic acid and 0.252 M sodium benzoate?
- 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The $\text{p}K_a$ of benzoic acid is 4.20, and the $\text{p}K_b$ of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68



A Video Discussing Using the Henderson Hasselbalch Equation: [Using the Henderson Hasselbalch Equation](#) (opens in new window) [youtu.be] (opens in new window)

The Henderson-Hasselbalch approximation (Equation 18.2.3) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 18.2.3

✓ Example 18.2.3

The buffer solution in Example 18.2.2 contained 0.135 M HCO_2H and 0.215 M HCO_2Na and had a pH of 3.95.

- What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
- What is the final pH if 5.00 mL of 1.00 M NaOH are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A. Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 18.2.1. Then calculate the amount of acid or base added.

B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 18.2.3) to obtain the pH.

Solution:

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

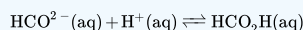
$$100 \text{ mL} \left(\frac{0.135 \text{ mmol } \text{HCO}_2\text{H}}{\text{mL}} \right) = 13.5 \text{ mmol } \text{HCO}_2\text{H}$$

$$100 \text{ mL} \left(\frac{0.215 \text{ mmol } \text{HCO}_2^-}{\text{mL}} \right) = 21.5 \text{ mmol } \text{HCO}_2^-$$

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00 \text{ mL} \left(\frac{1.00 \text{ mmol } \text{H}^+}{\text{mL}} \right) = 5 \text{ mmol } \text{H}^+$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:



initial amounts, changes in amounts, and final amounts:

| | $\text{HCO}_2^-(\text{aq})$ | $\text{H}^+(\text{aq})$ | $\text{HCO}_2\text{H}(\text{aq})$ |
|----------------|-----------------------------|-------------------------|-----------------------------------|
| Initial | 21.5 mmol | 5.00 mmol | 13.5 mmol |
| Change | -5.00 mmol | -5.00 mmol | +5.00 mmol |
| Final | 16.5 mmol | ~0 mmol | 18.5 mmol |

The final amount of H^+ in solution is given as “~0 mmol.” For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[\text{H}^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 18.2.1 or the Henderson-Hasselbalch approximation. Because we have performed many equilibrium calculations in this chapter, we’ll take the latter approach. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H , which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation (Equation 18.2.3):

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \left(\frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} \right) \\ &= \text{p}K_a + \log \left(\frac{n_{\text{HCO}_2^-}/V_f}{n_{\text{HCO}_2\text{H}}/V_f} \right) \\ &= \text{p}K_a + \log \left(\frac{n_{\text{HCO}_2^-}}{n_{\text{HCO}_2\text{H}}} \right) \end{aligned}$$

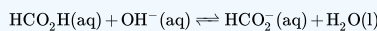
Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{n_{\text{HCO}_2^-}}{n_{\text{HCO}_2\text{H}}}\right) \\ &= 3.75 + \log\left(\frac{16.5 \text{ mmol}}{18.5 \text{ mmol}}\right) \\ &= 3.75 - 0.050 = 3.70 \end{aligned}$$

Once again, this result makes sense on two levels. First, the addition of HCl has decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the $\text{p}K_a$ and $\text{p}K_a - 1$.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^- . The number of millimoles of OH^- in 5.00 mL of 1.00 M NaOH is as follows:

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.



initial amounts, changes in amounts, and final amounts

| | $\text{HCO}_2\text{H}(\text{aq})$ | OH^- | $\text{HCO}_2^-(\text{aq})$ |
|----------------|-----------------------------------|---------------|-----------------------------|
| Initial | 13.5 mmol | 5.00 mmol | 21.5 mmol |
| Change | -5.00 mmol | -5.00 mmol | +5.00 mmol |
| Final | 8.5 mmol | ~0 mmol | 26.5 mmol |

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{n_{\text{HCO}_2^-}}{n_{\text{HCO}_2\text{H}}}\right) \\ &= 3.75 + \log\left(\frac{26.5 \text{ mmol}}{8.5 \text{ mmol}}\right) \\ &= 3.75 + 0.494 = 4.24 \end{aligned}$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the $\text{p}K_a$ and $\text{p}K_a + 1$, as expected for a solution with a $\text{HCO}_2^-/\text{HCO}_2\text{H}$ ratio between 1 and 10.

? Exercise 18.2.3

The buffer solution from Example 18.2.2 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

- What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
- What is the final pH if 12.0 mL of 1.5 M HCl are added?

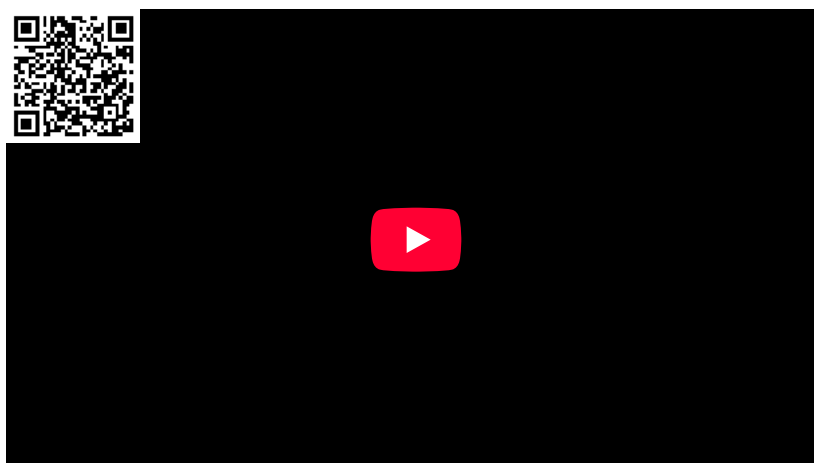
Answer a

5.30

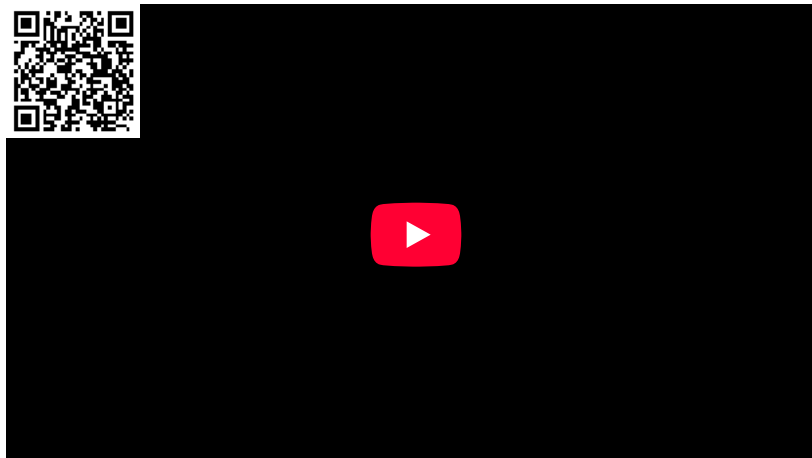
Answer b

4.42

Only the amounts (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch approximation, not their concentrations.



A Video Discussing the Change in pH with the Addition of a Strong Acid to a Buffer: [The Change in pH with the Addition of a Strong Acid to a Buffer](https://www.youtube.com/watch?v=392355) (opens in new window) [youtu.be]



The Change in pH with the Addition of a Strong Base to a Buffer:

[The Change in pH with the Addition of a Strong Base to a Buffer \(opens in new window\)](#) [youtu.be]

The results obtained in Example 18.2.3 and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or $NaOH$ solution to 100 mL of an unbuffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M $NaOH$ would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

The most effective buffers contain equal concentrations of an acid and its conjugate base.

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure 18.2.2 for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

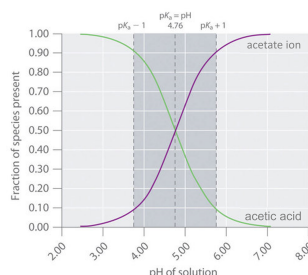
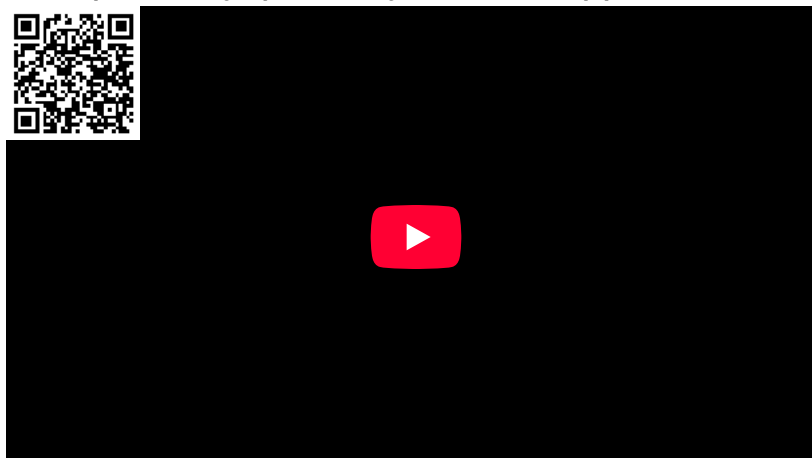


Figure 18.2.2: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $pH = pK_a \pm 1$). (CC BY-SA-NC; Anonymous by request)

Graph of mole fraction against pH of solution. The green line is acetic acid and the purple line is the acetate ion.



A Video Discussing The Buffer Region: [The Buffer Region \(opens in new window\)](#) [youtu.be]

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5. Consider the schematic titration curve of a weak acid with a strong base shown in Figure 18.2.3. As indicated by the labels, the region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a , which is why buffer solutions usually have a pH that is within ± 1 pH units of the pK_a of the acid component of the buffer.

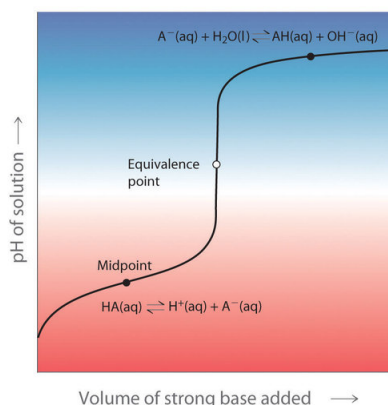


Figure 18.2.3: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)
Titration curves graph pH of solution against volume of strong base added. On the curve we look for the midpoints and equivalence points.

This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

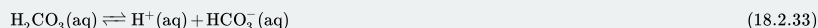
In the region of the titration curve at the lower left, before the midpoint, the acid-base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a . In the region of the titration curve at the upper right, after the midpoint, the acid-base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to K_b . However, we can calculate either K_a or K_b from the other because they are related by K_w .

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

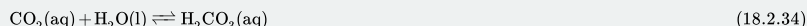
Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the $\text{CO}_2/\text{HCO}_3^-$ system, which dominates the buffering action of blood plasma.

The acid-base equilibrium in the $\text{CO}_2/\text{HCO}_3^-$ buffer system is usually written as follows:

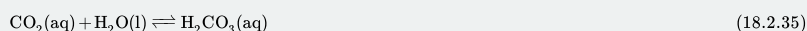


with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C . In fact, Equation 18.2.33 is a grossly oversimplified version of the $\text{CO}_2/\text{HCO}_3^-$ system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3 . Thus Equation 18.2.33 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C .

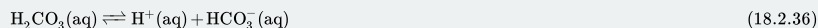
As shown in Equation 18.2.34 CO_2 is in equilibrium with H_2CO_3 , but the equilibrium lies far to the left, with an $\text{H}_2\text{CO}_3/\text{CO}_2$ ratio less than 0.01 under most conditions:



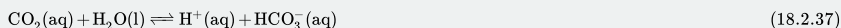
with $K' = 4.0 \times 10^{-3}$ at 37°C . The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4} , which makes it a much stronger acid than Equation 18.2.33 suggests. Adding Equation 18.2.33 and Equation 18.2.34 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:



with $K' = 4.0 \times 10^{-3}$ (37°C)



with $K_a = 2.0 \times 10^{-4}$ (37°C)



with $K = 8.0 \times 10^{-7}$ (37°C)

The K value for the reaction in Equation 18.2.37 is the product of the true ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $\text{CO}_2(\text{aq})$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = 8.0 \times 10^{-7} \quad (18.2.38)$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to Henry's law,

$$[\text{CO}_2] = kP_{\text{CO}_2}$$

where k is the Henry's law constant for CO_2 , which is $3.0 \times 10^{-5} \text{ M/mmHg}$ at 37°C . Substituting this expression for $[\text{CO}_2]$ in Equation 18.2.38

$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{(3.0 \times 10^{-5} \text{ M/mmHg})(P_{\text{CO}_2})}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$\text{pH} = 6.10 + \log \left(\frac{[\text{HCO}_3^-]}{(3.0 \times 10^{-5} \text{ M/mmHg})(P_{\text{CO}_2})} \right) \quad (18.2.39)$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[\text{HCO}_3^-]$. Figure 18.2.4 plots the relationship between pH and $[\text{HCO}_3^-]$ under physiological conditions for several different values of P_{CO_2} , with normal pH and $[\text{HCO}_3^-]$ values indicated by the dashed lines.

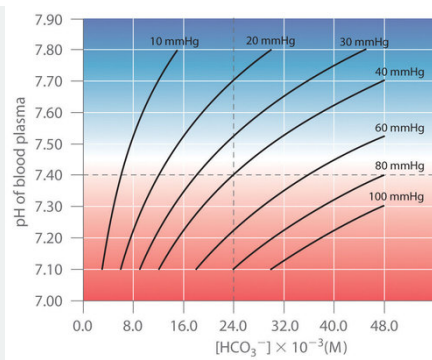
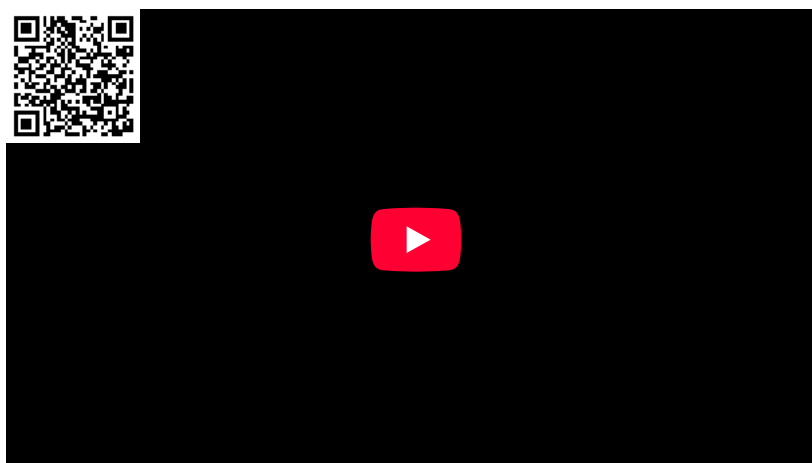


Figure 18.2.4: Buffering in Blood: pH versus $[\text{HCO}_3^-]$ Curves for Buffers with Different Values of P_{CO_2} . Only those combinations of pH and $[\text{HCO}_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[\text{HCO}_3^-]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 18.2.39 adding a strong acid to the $\text{CO}_2/\text{HCO}_3^-$ system causes $[\text{HCO}_3^-]$ to decrease as HCO_3^- is converted to CO_2 . Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in P_{CO_2} . Because the change in $[\text{HCO}_3^-]/P_{\text{CO}_2}$ is small, Equation 18.2.39 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form HCO_3^- , but CO_2 is replenished by the body, again limiting the change in both $[\text{HCO}_3^-]/P_{\text{CO}_2}$ and pH. The $\text{CO}_2/\text{HCO}_3^-$ buffer system is an example of an open system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower P_{CO_2} at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[\text{HCO}_3^-]$. The increase in pH and decrease in $[\text{HCO}_3^-]$ in response to the decrease in P_{CO_2} are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.



A Video Summary of the pH Curve for a Strong Acid/Strong Base Titration:

[Summary of the pH Curve for a Strong Acid/Strong Base Titration](#)(opens in new window) [youtu.be]

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the common ion effect. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its buffer capacity depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the Henderson-Hasselbalch approximation, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the $\text{CO}_2/\text{HCO}_3^-$ system, which dominates the buffering action of blood plasma.

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