

# Hydrolysis of Salts: Buffer Systems

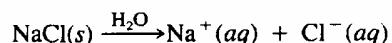
## OBJECTIVES

- Study how dissolving a salt in water affects hydronium ion concentration.
- Study the buffering activity of a system.
- Prepare specific buffer solutions, and evaluate their buffer capacity.

## INTRODUCTION

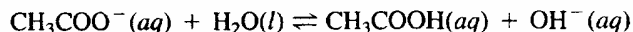
Salts are ionic compounds containing cations other than hydrogen ion and anions other than hydroxide ion. One might expect solutions of salts to be neutral in character, but such is not always the case. All ions in aqueous solution are **hydrated** — surrounded by water molecules — as a result of the electrical attraction between the ions and the polar water molecules. Some ions in aqueous solution undergo only hydration. Other ions react with the water molecules and enter into Brønsted-Lowry acid-base equilibria that result in the formation of acidic or alkaline solutions. For example, solutions of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), and potassium bromide (KBr) are acidic, basic, and neutral, respectively. Because pure water is neutral—contains equal amounts of hydronium and hydroxide ions—the obvious conclusion is that the ions of certain salts disturb the auto-ionization of water. In pure water only one molecule in approximately one-half billion is ionized. We classify solutions of salts into four general classes:

1. Salts of cations and anions, neither of which react with water, form *neutral solutions*. Common salts of this type are viewed as derived from reactions of strong acids with strong bases. Because neither ion reacts significantly with water, only hydration of the ions occurs and resulting solutions are neutral. For example, consider sodium chloride (NaCl):

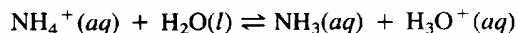


Neither the sodium cation nor the chloride anion react with the water to disturb the equilibrium that normally exists between  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ .

2. Salts of cations that do not react with water and of anions that are stronger bases than water form *alkaline solutions*. Common salts of this type are viewed as derived from the reaction of weak acids with strong bases. Only the anions react with water to a significant extent—producing hydroxide ions—which results in an alkaline solution. For example, consider sodium acetate ( $\text{NaCH}_3\text{COO}$ ):

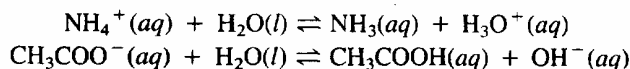


3. Salts of cations that are stronger acids than water and of anions that do not react with water form *acidic solutions*. Common salts of this type are viewed as derived from the reaction of a strong acid with a weak base. The hydrated cations are proton donors, and react with water to give  $\text{H}_3\text{O}^+$ ; thus, these salt solutions are acidic. For example, consider ammonium chloride ( $\text{NH}_4\text{Cl}$ ):



4. Salts of cations and anions both of which react with water may form *acidic, neutral, or basic solutions*. Common examples of these salts are viewed as derived from the

reaction of weak acids with weak bases. The pH of such solutions varies with the specific cation and anion. For example, consider ammonium acetate ( $\text{NH}_4\text{CH}_3\text{COO}$ ):



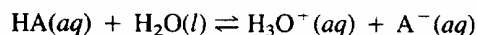
Common examples of each class of solutions of salts are given in Experiment Table 1.

Remember that the terms “strong” and “weak” above have no relationship to the concentration of the solution, as is sometimes the case in nonscientific usage (e.g., This tea is strong). A **strong electrolyte** (acid, base, or salt) dissociates 100% into its ions in an aqueous solution; **weak electrolyte** dissociates only partially into its ions. The degree of dissociation of a weak electrolyte is generally small—typically less than 10%—so that the predominant species in the solution is the molecular, nonionized form.

The common strong acids are hydrochloric (HCl), hydrobromic (HBr), hydriodic (HI), nitric ( $\text{HNO}_3$ ), perchloric ( $\text{HClO}_4$ ), and sulfuric ( $\text{H}_2\text{SO}_4$ ) acids. All other common acids are weak acids. Some familiar examples are acetic ( $\text{CH}_3\text{COOH}$ ), lactic ( $\text{HC}_3\text{H}_5\text{O}_3$ ), citric ( $\text{H}_3\text{C}_6\text{H}_7\text{O}_7$ ), carbonic ( $\text{H}_2\text{CO}_3$ ), and phosphoric ( $\text{H}_3\text{PO}_4$ ) acids. Ions such as hydrogen carbonate ( $\text{HCO}_3^-$ ), dihydrogen phosphate ( $\text{H}_2\text{PO}_4^-$ ), and ammonium ( $\text{NH}_4^+$ ) may also be considered weak acids.

Metal hydroxides such as NaOH,  $\text{Ca}(\text{OH})_2$ , or  $\text{Fe}(\text{OH})_3$  are strong bases. Note the lack of correlation between strength and volatility. Although  $\text{Fe}(\text{OH})_3$  is almost totally insoluble in water, the small amount that dissolves is 100% dissociated into  $\text{Fe}^{3+}$  and  $\text{OH}^-$  ions. The only common soluble strong bases are the hydroxides of the lithium family metals and barium. Most weak bases are molecular species, such as ammonia ( $\text{NH}_3$ ) or triethylamine ( $\text{C}_2\text{H}_5)_3\text{N}$ , or are conjugate bases of weak acids, such as phosphate ion ( $\text{PO}_4^{3-}$ ) or sulfide ion ( $\text{S}^{2-}$ ).

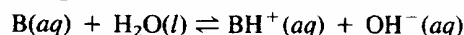
For any weak acid (HA), a chemical equilibrium



is established in aqueous solution. As with any equilibrium, the magnitude of the equilibrium constant is an indication of the extent of the reaction. The equilibrium constant for the preceding reaction is called the **acid dissociation constant** of the acid HA, and is symbolized by  $K_a$ :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

For a weak base the analogous equilibrium reaction would be



**EXPERIMENT TABLE 1 Acid-Base Properties of Aqueous Salt Solutions**

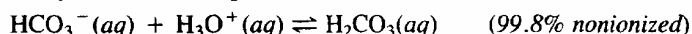
CATIONS ANIONS	Cations that simply become hydrated $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{Ba}^{2+}$	Cations that react with water to give $\text{H}_3\text{O}^+$ $\text{NH}_4^+$ , $\text{Be}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Al}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Cu}^{2+}$
Anions that simply become hydrated $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{ClO}_4^-$ , $\text{ClO}_3^-$	Salts give neutral solutions $\text{NaCl}$ $\text{CaCl}_2$ $\text{KNO}_3$	Salts give acidic solutions $\text{NH}_4\text{Cl}$ $\text{NH}_4\text{NO}_3$ $\text{AlCl}_3$ $\text{Fe}(\text{NO}_3)_3$
Anions that react with water to give $\text{OH}^-$ $\text{S}^{2-}$ , $\text{PO}_4^{3-}$ , $\text{CO}_3^{2-}$ , $\text{CN}^-$ , $\text{SO}_3^{2-}$ , $\text{HCO}_3^-$ , $\text{CH}_3\text{COO}^-$ , $\text{NO}_2^-$ , $\text{F}^-$	Salts give alkaline solutions $\text{Ba}(\text{CH}_3\text{COO})_2$ $\text{K}_2\text{CO}_3$ $\text{Na}_2\text{S}$ $\text{KCN}$	pH of salt solution varies weakly acidic or weakly alkaline $\text{NH}_4\text{CH}_3\text{COO}$ $\text{NH}_4\text{NO}_2$ $\text{NH}_4\text{CN}$

The **base dissociation constant** ( $K_b$ ) for the species is

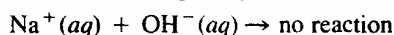
$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

Typical values for  $K_a$  and  $K_b$  are in the range  $10^{-1}$  to  $10^{-13}$ . For numbers this small, the negative logarithm or p function is commonly used. One often sees tables of  $\text{p}K_a$  or  $\text{p}K_b$  values, which are tabulations of  $-\log(K_a)$  and  $-\log(K_b)$ , respectively.

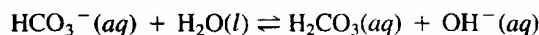
Let us examine one type of salt solution in greater detail, the salt of a strong base and weak acid such as sodium hydrogen carbonate ( $\text{NaHCO}_3$ ). Sodium hydrogen carbonate is the salt that contains the cation ( $\text{Na}_+$ ) derived from a strong base ( $\text{NaOH}$ ) and the anion ( $\text{HCO}_3^-$ ) derived from a weak acid ( $\text{H}_2\text{CO}_3$ ). As the conjugate base of the weak acid carbonic acid ( $\text{H}_2\text{CO}_3$ ), the hydrogen carbonate ion is a proton acceptor. The  $\text{HCO}_3^-$  ion disturbs the neutrality of water by tying up some of the hydronium ions produced in the auto-ionization of water



The  $\text{Na}^+$  ion—the cation of the strong base sodium hydroxide ( $\text{NaOH}$ )—has no tendency to tie up hydroxide ions because such bases are completely ionized:



The solution is neutral as long as  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  are equal. The overall result of the hydrolysis of  $\text{NaHCO}_3$  is that hydronium ions have been removed, leaving a predominance of hydroxide ion and causing the solution to be basic. The explanation of the basic properties of  $\text{NaHCO}_3$  can also be described in terms of the hydrolysis reaction



Because the reaction of  $\text{HCO}_3^-$  ion with the solvent increases the amount of  $\text{OH}^-$  ion present,  $\text{HCO}_3^-$  ion acts as a weak base. Here the water is acting as the Brønsted-Lowry acid, as it appears to donate a proton ( $\text{H}^+$ ) to the  $\text{HCO}_3^-$  ion. For this reason sodium hydrogen carbonate, sodium lactate, or sodium citrate solutions are frequently administered to increase the alkalinity of the extracellular fluids of the body. It is left for you to develop a similar explanation for the acidic properties of a solution containing the salt of a weak base and strong acid such as ammonium chloride ( $\text{NH}_4\text{Cl}$ ).

The effects on pH caused by adding a strong acid to a solution are dramatic. Just 1 mL of a 0.1 M HCl solution added to 100 mL of water releases a flood of hydronium ions. The pH drops instantly from 7.0 to 3.0. (The hydronium ion concentration increases from  $1 \times 10^{-7}$  to  $1 \times 10^{-3}$  mol/L.)

That life could not exist without some mechanism for absorbing excess acid or base is apparent from the narrow normal range of plasma pH, 7.35 to 7.45. This pH range is referred to as **physiological pH**. The living organism is intolerant of drastic changes in acidity levels. Life is impossible for most organisms outside the limits of 7.0 and 7.8. If blood pH falls below 7.35, a state of acidosis exists. Acidosis is a specific medical term, because chemically the entire physiological range is on the alkaline side of neutrality. Medical acidosis indicates that blood pH has fallen to the acidic side of the normal range. The major physiological effect of acidosis is a depression of the central nervous system. As the pH falls, progressive disorientation ensues and, finally, coma results. Below pH 7.0, death occurs in coma due to acidosis.

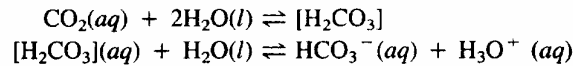
In **alkalosis** blood pH is above 7.45. Severe over-excitability of the nervous system characterizes alkalosis. The peripheral nerves are affected first and muscles undergo tetany, a spasmodic contraction and rigidity. Convulsions may occur as the central nervous system becomes involved. Above pH 7.8 death is imminent, and frequently occurs from tetany of the respiratory muscles.

The presence in the body of carbonic acid and sodium hydrogen carbonate provides a **buffer system** that is the primary defense against the influx of strong acid or base. Buffers act as chemical shock absorbers; their components team up to resist changes in pH. One member of the buffer team removes excess hydrogen ion; the other member ties up hydroxide ion. Thus the pH is kept at an almost constant level.

An effective buffer may be described in Brønsted-Lowry terminology as a conjugate acid–base pair, such as acetic acid and the acetate ion or ammonia and the ammonium ion. Buffering is a

team effort requiring the presence of both weak acid and weak base in solution. The team effort is depicted in Experiment Table 2.

In blood plasma the hydrogen carbonate/carbonic acid ratio is maintained at 20 parts  $\text{HCO}_3^-$  ion to 1 part  $\text{H}_2\text{CO}_3$ , and is termed the **alkaline reserve**. The alkaline reserve represents the base available for buffering acid. This ratio of  $\text{HCO}_3^-/\text{H}_2\text{CO}_3$  results in the normal slightly alkaline plasma pH of 7.4.



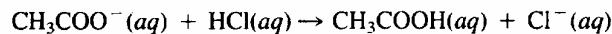
An equation that describes the pH of this and many dilute buffer systems in which the concentration of weak base and weak acid do not differ greatly is the **Henderson-Hasselbalch Equation**, which may be stated as

$$\text{pH} = \text{p}K_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

The  $\text{p}K_a$  in this equation is the negative logarithm of the ionization constant of the weak acid. For carbonic acid the  $\text{p}K_a$  is 6.1—the pH of the solution when the concentration of the conjugate base equals the concentration of the weak acid. Substituting normal plasma concentrations of  $[\text{HCO}_3^-] = 27 \text{ mmol/L}$  and  $[\text{H}_2\text{CO}_3] = 1.35 \text{ mmol/L}$ , the pH is

$$\begin{aligned}\text{pH} &= 6.1 + \log \frac{(27 \text{ mmol/L})}{(1.35 \text{ mmol/L})} \\ \text{pH} &= 6.1 + \log 20 \\ \text{pH} &= 6.1 + 1.3 \\ \text{pH} &= 7.4\end{aligned}$$

A buffer ceases to retard pH change when all the reacting component is consumed by the stronger acid or base. For example, if a buffer solution contains 0.050 mol of acetate ions ( $\text{CH}_3\text{COO}^-$ ), the addition of 100 mL of 0.50 M HCl consumes all the acetate ion by reaction:



Further addition of strong acid causes a rapid drop in pH because there is nothing present to react with the added  $\text{H}_3\text{O}^+$ . The amount of strong acid or base that can be added to a given volume of a buffer system without a significant change in pH is known as the **buffer capacity**. The buffer capacity is defined as the number of moles of acid/base necessary to change the pH of 1 liter of the buffer solution by one unit. Buffer capacity can be calculated using the following equation:

$$\text{buffer capacity} = \frac{(\text{number moles of } \text{H}_3\text{O}^+ \text{ or } \text{OH}^- \text{ consumed})}{(\text{pH change}) \times (\text{volume of buffer in L})}$$

Examination of the Henderson-Hasselbalch Equation shows that the pH of a buffer depends on both the  $\text{p}K_a$  of the acid and the ratio of concentration of proton acceptor to proton donor species. To produce a buffer with a pH value different from the  $\text{p}K_a$  value of the acid, one must simply adjust this ratio appropriately. If the ratio differs significantly from 1, however, the buffer capacity toward a strong acid is different from its capacity toward a strong base. Consequently, a buffer is usually formulated using an acid whose  $\text{p}K_a$  approximates the pH desired in the buffer.

The Henderson-Hasselbalch Equation allows a more precise definition of buffer capacity. When the ratio  $[\text{A}^-]/[\text{HA}]$  is less than 0.10 or greater than 10.0, the buffer capacity is exceeded. Thus the pH range of a buffer extends one pH unit above and below the  $\text{p}K_a$  of the weak acid used. An acetic acid–acetate ion buffer, for example, has a pH range of 3.75 to 5.75, because acetic acid has a  $\text{p}K_a$  of 4.75.

**EXPERIMENT TABLE 2** Some Common Buffer Systems

Species	Examples				Function
Weak base	$\text{CH}_3\text{COO}^-$	$\text{HPO}_4^{2-}$	$\text{HCO}_3^-$	$\text{NH}_3$	Neutralizes $\text{H}_3\text{O}^+$
	and	and	and	and	
Weak acid	$\text{CH}_3\text{COOH}$	$\text{H}_2\text{PO}_4^-$	$\text{H}_2\text{CO}_3$	$\text{NH}_4^+$	Neutralizes $\text{OH}^-$