

# Mixtures of Acids and Bases

## PURPOSE

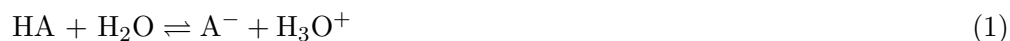
To investigate the resulting pH's of different mixtures of acid and base solutions.

## GOALS

- To calculate the pH of pure acid and base solutions.
- To calculate the pH of mixtures of acid and base solutions.
- To measure the pH of pure acid and base solutions and mixtures of these solutions.
- To compare the resulting pH's of different mixtures of acid and base solutions.

## INTRODUCTION

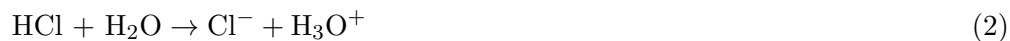
Brønsted acids are defined as proton donors. When placed in water, Brønsted acids (HA) donate a proton to water to produce the conjugate base of the acid ( $A^-$ ) and a hydronium ion ( $H_3O^+$ ) according to the following reaction.



This is defined as the **acid dissociation reaction** and the equilibrium constant for this reaction is called the **acid dissociation constant**,  $K_a$ .  $K_a$ 's can be found in the tables of physical data, and may be found in an appendix in your textbook. The larger the  $K_a$  for an acid, the stronger the acid is. The Brønsted acids are divided into two main groups: strong acids and weak acids.

### Strong Acids:

The  $K_a$ 's for strong acids, such as HCl and  $HNO_3$ , are simply listed as  $\gg 1$  which indicates that they dissociate 100% when placed in water.



Since strong acids dissociate completely, the  $[H_3O^+] = [\text{strong acid concentration}]$  and  $pH = -\log[H_3O^+]$ .

### Weak Acids:

Weak acids, such as  $NH_4^+$  and  $HC_2H_3O_2$ , only partially dissociate in water according to their  $K_a$ 's. As with any equilibrium reaction, the equilibrium concentrations can be calculated by generating a reaction table and substituting into the  $K_a$  expression. For example, acetic acid,  $HC_2H_3O_2$ , has a  $K_a$  of  $1.8 \times 10^{-5}$ . So for a 0.2 M aqueous solution of  $HC_2H_3O_2$ , the equilibrium concentrations can be calculated as follows.

	$\text{HC}_2\text{H}_3\text{O}_2$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{C}_2\text{H}_3\text{O}_2^-$	+	$\text{H}_3\text{O}^+$
initial	$0.2\text{ M}$				$0.0\text{ M}$		$0.0\text{ M}$
$\Delta$	$-x$				$+x$		$+x$
<hr/>							
equilibrium	$0.2 - x\text{ M}$				$x\text{ M}$		$x\text{ M}$

$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(x)}{(0.2 - x)} \simeq \frac{x^2}{0.2} = 1.8 \times 10^{-5} \quad (3)$$

$$x = 1.9 \times 10^{-3}\text{ M}$$

Thus the equilibrium concentrations are  $[\text{HC}_2\text{H}_3\text{O}_2] = 0.2\text{M}$  and  $[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{H}_3\text{O}^+] = 1.9 \times 10^{-3}\text{M}$ .

Equation 3 shows the detailed method to calculate  $[\text{H}_3\text{O}^+]$  for a weak acid. In cases where the percent ionization of the acid is less than 5%, equation 3 simplifies to the expression below, where  $c_{\text{wa}}$  represents the original concentration of the weak acid in  $M$ .

$$[\text{H}_3\text{O}^+] = (K_a \times c_{\text{wa}})^{1/2} = (1.8 \times 10^{-5} \times 0.2)^{1/2} = 1.9 \times 10^{-3}\text{ M} \quad (4)$$

The pH of this solution can now be calculated by taking the  $-\log[\text{H}_3\text{O}^+]$  to get 2.72.

Similarly, Brønsted bases ( $\text{B}^-$ ) are defined as proton acceptors and when placed in water will accept a proton from water to produce the base's conjugate acid (HB) and a hydroxide ion ( $\text{OH}^-$ ).



This reaction is defined as the **base association reaction** and the equilibrium constant for it is the **base association constant**,  $K_b$ .  $K_b$ 's cannot be found in tables as  $K_a$ 's are.  $K_b$ 's must be calculated according to the following equation at 25°C.

$$K_a \times K_b = K_w = 1.0 \times 10^{-14} \quad (6)$$

The Brønsted bases are also divided up into two main groups: strong bases and weak bases.

### Strong Bases:

The most common strong bases found in the laboratory are the Group IA salts of hydroxide, which completely dissociate in water to give one equivalent of  $\text{OH}^-$ .



Since the salts dissociate completely, the  $[\text{OH}^-] = [\text{strong base concentration}]$  and the  $\text{pOH} =$

$-\log[\text{OH}^-]$ . At 298 K, the relationship between pH and pOH is:

$$\text{pH} = 14 - \text{pOH}. \quad (8)$$

### Weak Bases:

Sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2$ , is considered a weak base. Using equation 6 above, the  $K_b$  for  $\text{C}_2\text{H}_3\text{O}_2^-$  is  $(1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$ . Using this value and a reaction table, the equilibrium composition of a 0.2 M  $\text{NaC}_2\text{H}_3\text{O}_2$  solution can be calculated as follows.

	$\text{C}_2\text{H}_3\text{O}_2^-$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HC}_2\text{H}_3\text{O}_2$	+	$\text{OH}^-$
initial	0.2 M				0.0 M		0.0 M
$\Delta$	$-x$				$+x$		$+x$
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equilibrium	$0.2 - x$ M				$x$ M		$x$ M

$$K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = \frac{(x)(x)}{(0.2 - x)} \simeq \frac{x^2}{0.2} = 5.6 \times 10^{-10} \quad (9)$$

$$x = 1.1 \times 10^{-5} \text{ M}$$

Thus the equilibrium concentrations are  $[\text{C}_2\text{H}_3\text{O}_2^-] = 0.2 \text{ M}$  and  $[\text{HC}_2\text{H}_3\text{O}_2] = [\text{OH}^-] = 1.1 \times 10^{-5} \text{ M}$ .

Equation 9 shows the detailed method to calculate  $[\text{OH}^-]$  for a weak base. In cases where the percent ionization of the base is less than 5%, equation 9 simplifies to the expression below, where  $c_{\text{wb}}$  represents the original concentration of the weak base in M.

$$[\text{OH}^-] = (K_b \times c_{\text{wb}})^{1/2} = (5.6 \times 10^{-10} \times 0.2)^{1/2} = 1.1 \times 10^{-5} \text{ M} \quad (10)$$

The pOH of this solution can now be calculated by taking the  $-\log[\text{OH}^-]$  to get 4.98. Using equation 8, the pH of the 0.2 M  $\text{C}_2\text{H}_3\text{O}_2^-$  solution is  $14 - 4.98 = 9.02$ .

When acids and bases are mixed together, things become more complicated. No matter how complicated, all mixtures of acids and bases should be approached the same way.

- 1 *Determine what species actually exist in solution.* Any sodium or potassium salt will dissociate completely as will any strong acid or base.
- 2 *Write out a balanced chemical reaction to describe any interactions that will occur.* Remember that the reactants must be present in the original solution as identified in step 1. Look for possible  $K_a$  or  $K_b$  reactions. Or for reactions of a weak base with a hydronium ion or a weak acid with a hydroxide ion that will react 100%. Sometimes there will not be an appropriate chemical reaction!
- 3 *Generate a reaction table based on the balanced chemical reaction.* Remember that the initial concentrations for the products are not necessarily zero!

- 4 Calculate the equilibrium composition of the mixture. This is only possible if the equilibrium constant for the reaction is known or if the reaction goes to completion.
- 5 Calculate the pH. Once the  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  is known, the pH can be calculated as above in the pure solutions.

Figure 1 demonstrates the potential combinations that can occur when mixing acids and bases.

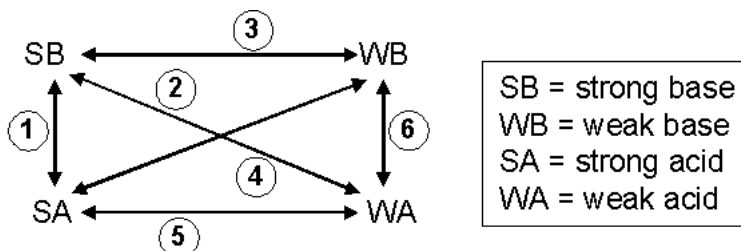


Figure 1: Combinations of Acids and Bases

### Mixture 1:

Mixture 1, reaction of a strong acid and strong base, goes to completion. A reaction table can be used to determine if excess acid or base remains. For example, consider the addition of 10. mL of 0.10 M HCl to 15 mL of 0.20 M NaOH. Since two solutions are being mixed, it is better to use moles or mmol in your reaction table.

	$\text{H}_3\text{O}^+$	+	$\text{OH}^-$	$\rightarrow$	$\text{H}_2\text{O}$	+	$\text{H}_2\text{O}$
given	10. mL $\times$ 0.10 M		15 mL $\times$ 0.20 M				
initial	1.0 mmol		3.0 mmol		—		—
$\Delta$	−1.0 mmol		−1.0 mmol		—		—
final	0 mmol		2.0 mmol		—		—

In this example, only strong base remains. The  $[\text{OH}^-]$  can be calculated from the final mmol/(total volume) to give 2.0 mmol/(10 + 15 mL) = 0.08 M. Table 1 contains the necessary formulas to calculate pOH and pH from this information. The pH of this mixture is 12.90.

Table 1. pH Formula Summary

Remaining Species	Formulas			
Strong Acid	$[\text{H}_3\text{O}^+] = [\text{SA}]$		$\text{pH} = -\log[\text{H}_3\text{O}^+]$	
Weak Acid	$[\text{H}_3\text{O}^+] = (K_a \times c_{\text{wa}})^{1/2}$		$\text{pH} = -\log[\text{H}_3\text{O}^+]$	
Strong Base	$[\text{OH}^-] = [\text{SB}]$	$\text{pOH} = -\log[\text{OH}^-]$	$\text{pH} = 14 - \text{pOH}$	
Weak Base	$K_b = K_w / K_a$	$[\text{OH}^-] = (K_b \times c_{\text{wb}})^{1/2}$	$\text{pOH} = -\log[\text{OH}^-]$	$\text{pH} = 14 - \text{pOH}$
Weak Acid & Weak Base	$\text{pH} = \text{pKa} + \log(\text{mmol base} / \text{mmol acid})$			

### Mixture 2:

Mixture 2, reaction of a strong base and weak acid, also goes to completion. Depending upon the relative amounts of material, the final solution may be composed of only strong base, only weak base, or a mixture of weak acid and weak base. For example, consider the addition of 15. mL of 0.20 *M* NaOH to 10. mL of 0.30 *M* HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. Since two solutions are being mixed, it is better to use moles or mmoles in your reaction table.

	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	+	OH <sup>-</sup>	→	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	+	H <sub>2</sub> O
given	10. mL × 0.30 <i>M</i>		15 mL × 0.20 <i>M</i>				
initial	3.0 mmol		3.0 mmol		—		—
Δ	-3.0 mmol		-3.0 mmol		+3.0 mmol		—
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final	0 mmol		0 mmol		3.0 mmol		—

In this example, only weak base remains. The [C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>] can be calculated from the final mmol/(total volume) to give 3.0 mmol/(10 + 15 mL) = 0.120 *M*. Table 1 contains the necessary formulas to calculate the pH, given the concentration of weak base. The pH of this mixture is 8.91.

### Mixture 3:

Mixture 3, a strong base and weak base, does not have any reaction. Rather, the [OH<sup>-</sup>] associated with the strong base tends to suppress generation of [OH<sup>-</sup>] from the reaction of the weak base and water. Please consult your textbook for more details. In compositions such as this, the pH can be readily obtained by focusing upon the concentration of strong base. For example, consider the addition of 20. mL of 0.20 *M* NaOH to 10. mL of 0.20 *M* NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. This results in dilution of the strong base. In this example, [OH<sup>-</sup>] = mmol NaOH/total volume = 20 mL × 0.20 *M* OH<sup>-</sup>/(20. + 10. mL) = 0.13 *M*. Table 1 contains the necessary formulas to calculate pOH and pH from this information. The pH of this mixture is 13.12.

### Mixture 4:

Mixture 4, reaction of a strong acid and weak base, also goes to completion. Depending upon the relative amounts of material, the final solution may be composed of only strong acid, only weak acid, or a mixture of weak acid and weak base. For example, consider the addition of 15. mL of 0.20 *M* HCl to 20. mL of 0.20 *M* NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. Since two solutions are being mixed, it is better to use moles or mmoles in your reaction table.

	H <sub>3</sub> O <sup>+</sup>	+	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	→	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	+	H <sub>2</sub> O
given	15. mL × 0.20 <i>M</i>		20 mL × 0.20 <i>M</i>				
initial	3.0 mmol		4.0 mmol		—		—
Δ	-3.0 mmol		-3.0 mmol		+3.0 mmol		—
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final	0 mmol		1.0 mmol		3.0 mmol		—

In this example, weak acid and weak base remain. This type of solution is known as a buffer and will be explored in greater detail in experiment 7. The pH can be calculated using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_{\text{a}} + \log \left( \frac{[\text{base}]}{[\text{acid}]}\right) \text{ or } \text{pH} = \text{p}K_{\text{a}} + \log \left( \frac{\text{moles of base}}{\text{moles of acid}} \right). \quad (11)$$

For the current example,

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log(1.0 \text{ mmol } \text{C}_2\text{H}_3\text{O}_2^- / 3.0 \text{ mmol } \text{HC}_2\text{H}_3\text{O}_2) = 4.26.$$

### Mixture 5:

Mixture 5, a strong acid and weak acid, also does not have any reaction. The  $[\text{H}_3\text{O}^+]$  associated with the strong acid tends to suppress generation of  $[\text{H}_3\text{O}^+]$  from the reaction of the weak acid and water. In compositions such as this, the pH can be readily obtained by focusing upon the concentration of strong acid. For example, consider the addition of 30. mL of 0.20 M HCl to 20. mL of 0.15 M  $\text{HC}_2\text{H}_3\text{O}_2$ . This results in dilution of the strong acid. In this example,  $[\text{H}_3\text{O}^+] = \text{mmol HCl} / \text{total volume} = 30 \text{ mL} \times 0.20 \text{ M } \text{H}_3\text{O}^+ / (30. + 20. \text{ mL}) = 0.12 \text{ M}$ . The  $\text{pH} = -\log[\text{H}_3\text{O}^+] = 0.92$ .

### Mixture 6:

Mixture 6, the combination of a weak acid and a weak base, is also a buffer. The pH can be calculated using the Henderson-Hasselbalch equation. For example, consider the mixture of 10. mL of 0.1 M  $\text{NH}_4\text{Cl}$  and 15 mL of 0.10 M  $\text{NH}_3$ . For this example,

$$\text{pH} = -\log(5.6 \times 10^{-10}) + \log(1.5 \text{ mmol } \text{NH}_3 / 1.0 \text{ mmol } \text{NH}_4^+) = 9.43.$$

This is a brief summary of calculating the pH of pure acid and base solutions as well as mixtures of acid and base solutions. In this lab, you will explore these solutions in more detail and gain a greater understanding of equilibrium in aqueous acid/base mixtures.

## EQUIPMENT

- 1 25 × 150 mm test tube
- 1 400 mL beaker (to hold the test tube)
- 1 glass stir rod
- 1 10 mL graduated cylinder
- 1 100 mL beaker
- 2 30 mL beakers
- 1 MicroLab interface
- 1 MicroLab pH measurement instruction sheet
- 1 pH electrode in pH 7.00 buffer
- 1 ring stand
- 1 clamp

1 250 mL beaker for electrode rinsings

1 deionized water squirt bottle

1 box Kimwipes

## REAGENTS

~60 mL 0.1 *M* NaOH

10 mL 0.1 *M* HCl

10 mL 0.1 *M* NH<sub>4</sub>Cl

10 mL 0.1 *M* NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

~15 mL pH 4.00 buffer

~15 mL pH 7.00 buffer

~15 mL pH 10.00 buffer

## SAFETY

HCl and NaOH are corrosive. They can attack the skin and cause permanent damage to the eyes. If either solution splashes into your eyes, use the eyewash immediately. Hold your eyes open and flush with water. If contact with skin or clothing occurs, flush the affected area with water. Have your lab partner notify your instructor about the spill.

## WASTE DISPOSAL

All solutions can be flushed down the sink with plenty of water.

## PRIOR TO CLASS

Please enter the calculated pH values from the WebAssign pre-lab assignment in Table A on your printed worksheet.

## LAB PROCEDURE

Please print the worksheet for this lab. You will need this sheet to record your data.

In this experiment, you will be using pH electrodes connected to the MicroLab interface. pH electrodes have a thin glass bulb at the tip. **They break easily and are costly to replace.** Be careful not to shove the electrode into the bottom of a beaker or drop the electrode. There is a protective guard around the tip, which should remain in place at all times. The guard will not protect against careless treatment. Please use extreme care when using this equipment.

Best results in using the electrodes are obtained if:

- Electrodes are kept in standard pH 7 buffer solution when not in use.
- Immediately prior to use, the electrodes are rinsed with deionized water and gently blotted with a tissue, then placed in the test solution.

- The electrodes are rinsed and blotted again after the measurement and returned to the pH 7 buffer solution.

## Part A: Calibrating the MicroLab™ pH Electrode

- 1 Open the MicroLab program.
- 2 Make sure the pH electrode is plugged into the interface.
- 3 Calibrate the pH electrode using the MicroLab instructions provided in the lab. The calibration standards for the pH electrode will be a pH = 4.00 (red) buffer solution, a pH = 7.00 (yellow) buffer solution, and a pH = 10.00 (blue) buffer solution. Use about 15 mL of each in 30 mL beakers.
- 4 After the calibration is complete, configure the MicroLab program to collect data as described in the lab.

## Part B: Measuring the pH of Acid/Base Mixtures

- 1 In a 100 mL beaker, obtain ~70 mL of 0.1 M NaOH from the side shelf.
- 2 Measure 10.0 mL of deionized water using the 10 mL graduated cylinder. Carefully pour the water into the 25 × 150 mm test tube and place it in the 400 mL beaker for support.
- 3 Measure the pH of the deionized water and record it in Table A.
  - a Remove the electrode from the buffer, rinse the electrode with deionized water and blot it with a Kimwipe.
  - b During measurement, place the electrode such that it is immersed in the sample solution and swirl the beaker gently, allowing a few seconds for equilibration.
  - c After the measurement is recorded, rinse the electrode with deionized water and blot it with a Kimwipe. Then return it to the pH 7 buffer provided.
- 4 Measure 5.0 mL of 0.1 M NaOH using the graduated cylinder. Carefully add the NaOH to the water in the test tube. Use the glass stir rod to gently mix the solution.
- 5 Measure the pH of the deionized water plus 5.0 mL of NaOH and record it in Table A.
- 6 Again measure 5.0 mL of 0.1 M NaOH using the graduated cylinder and carefully add it to the solution in the test tube. Use the glass stir rod to gently mix the solution.
- 7 Measure the pH of the deionized water plus 10.0 mL of NaOH and record it in Table A.
- 8 One more time measure 5.0 mL of 0.1 M NaOH using the graduated cylinder and carefully add it to the solution in the test tube. Use the glass stir rod to gently mix the solution.
- 9 Measure the pH of the deionized water plus 15.0 mL of NaOH and record it in Table A.
- 10 Pour your solution down the sink and flush with tap water. Rinse out the test tube with deionized water and dry as best as you can.

- 11** Repeat steps 2 - 10 substituting 0.1 *M* HCl for the deionized water.
- 12** Repeat steps 2 - 10 substituting 0.1 *M* NH<sub>4</sub>Cl for the deionized water.
- 13** Repeat steps 2 - 10 substituting 0.1 *M* NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> for the deionized water.
- 14** After your last measurement, stop and close the MicroLab software. Rinse all of your glassware with water, dry it and return it to the set-up area where you found it. Make sure the pH electrode is submerged in the pH 7 buffer solution.
- 15** Before leaving, enter your results in the in-lab assignment. If all results are scored as correct, log out. If not all results are correct, try to find the error or consult with your lab instructor. When all results are correct, note them and log out of WebAssign. The in-lab assignment must be completed by the end of the lab period. If additional time is needed, please consult with your lab instructor.