

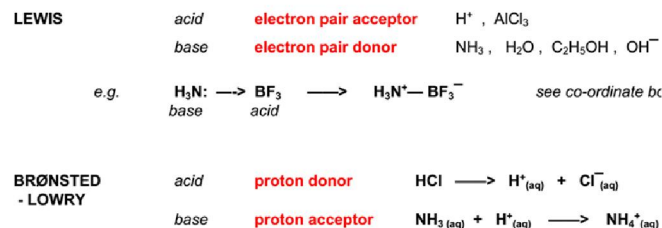
## Fundamental concepts of acid-base equilibrium

### Key terms and concepts

- Brønsted, and Lewis acids and bases
- Strength of acids and bases
- Dissociation of weak monoprotic acids and bases
- Autoionization of water and pH, pOH, pK<sub>a</sub>, pK<sub>b</sub>
- Percent ionization, Henderson-Hasselbach equation
- Buffer solutions and hydrolysis of salts

## Fundamental concepts of acid-base Chemistry

### Defining acids and bases



**Q.1** Classify the following according to Lewis theory and Brønsted-Lowry theory.  
 H<sub>3</sub>O<sup>+</sup>    BF<sub>3</sub>    H<sub>2</sub>SO<sub>4</sub>    H<sub>2</sub>O    NH<sub>4</sub><sup>+</sup>    CH<sub>3</sub>NH<sub>2</sub>

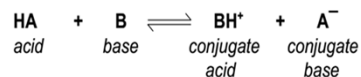
### Concept of the conjugate acid-base

- The conjugate base of a Brønsted acid is the species that remains when one proton has been removed from the acid. Conversely, a conjugate acid results from the addition of a proton to a Brønsted base

Acids are related to bases    ACID  $\rightleftharpoons$  PROTON + CONJUGATE BASE

Bases are related to acids    BASE + PROTON  $\rightleftharpoons$  CONJUGATE ACID

For an acid to behave as an acid, it must have a base present to accept a proton...



### Conjugate acid-base pairs have the following properties:

- If an acid is strong, its conjugate base has no measurable strength.
- **H<sub>3</sub>O<sup>+</sup> is the strongest acid** that can exist in aqueous solution. **Acids stronger than H<sub>3</sub>O<sup>+</sup>** react with water to produce H<sub>3</sub>O<sup>+</sup> and their conjugate bases
- **Acids weaker than H<sub>3</sub>O<sup>+</sup>** react with water to a much smaller extent, producing H<sub>3</sub>O<sup>+</sup> and their conjugate bases

- The **OH<sup>-</sup> ion is the strongest base** that can exist in aqueous solution. Bases stronger than OH<sup>-</sup> react with water to produce OH<sup>-</sup> and their conjugate acids

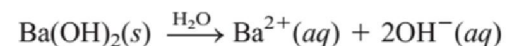
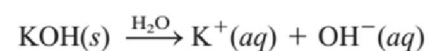
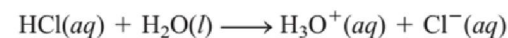
- For any conjugate acid-base pair it is always true that

$$K_a = \frac{K_w}{K_b} \quad K_b = \frac{K_w}{K_a}$$

- Thus, the stronger the acid (the larger  $K_a$ ), the weaker its conjugate base (the smaller  $K_b$ ), and vice versa

### The strength of acids and bases

- Acids and bases that are strong electrolytes (**completely ionized in solution**) are strong acids and strong bases

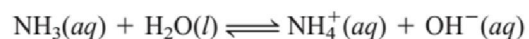


- At equilibrium, solutions of strong acids and bases will not contain any non-ionized acid molecules

- Those that are weak electrolytes (**partly ionized**) are weak acids and weak bases



- At equilibrium, aqueous solutions of weak acids contain a mixture of non-ionized acid molecules, H<sub>3</sub>O<sup>+</sup> ions, and the conjugate base



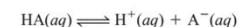
- At equilibrium, aqueous solutions of weak bases contain a mixture of non-ionized base molecules, OH<sup>-</sup> ions, and the conjugate acid

### Weak acids and acid ionization constants

- Consider a weak monoprotic acid, HA. Its ionization in water is represented by



or simply



The equilibrium expression for this ionization is

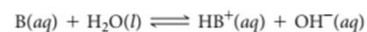
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

where  $K_a$ , the acid ionization constant, is the equilibrium constant for the ionization of an acid

- At a given temperature, the strength of the acid HA is measured quantitatively by the magnitude of  $K_a$ . The larger  $K_a$ , the stronger the acid

#### Weak bases and base ionization constants

Consider a weak base, B. Its ionization in water is represented by



The equilibrium-constant expression for this reaction can be written as

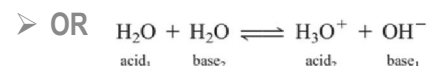
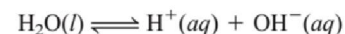
$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

where  $K_b$ , the base ionization constant, is the equilibrium constant for the ionization of a base

- At a given temperature, the strength of the base B is measured quantitatively by the magnitude of  $K_b$ . The larger  $K_b$ , the stronger the base

#### Acid-base properties of water

- Water is a very weak electrolyte and therefore a poor conductor of electricity, but it does undergo ionization to a small extent:



- This reaction is sometimes called the **autoionization** of water

- The equilibrium constant for the autoionization of water, according to the above equation, is

$$K_c = [H_3O^+][OH^-] \quad \text{OR} \quad K_c = [H^+][OH^-]$$

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

where  $K_w$  is called the **ion-product constant**

In pure water at 25°C, the concentrations of  $H^+$  and  $OH^-$  ions are equal and found to be  $[H^+] = 1.0 \times 10^{-7} M$  and  $[OH^-] = 1.0 \times 10^{-7} M$ . Thus, from Equation (16.3), at 25°C

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- Whether we have pure water or an aqueous solution of dissolved species, the following relation always holds at 25°C:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

- Whenever  $[H^+] = [OH^-]$  the aqueous solution is said to be **neutral**.
- In an **acidic solution**, there is an excess of  $H^+$  ions and  $[H^+] > [OH^-]$
- In a **basic solution**, there is an excess of hydroxide ions, so  $[H^+] < [OH^-]$

**pH—A measure of acidity**

- The pH of a solution is defined as the negative logarithm of the hydrogen ion concentration (in mol/L):

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \quad \text{or} \quad \text{pH} = -\log[\text{H}^+]$$

- A pOH scale analogous to the pH scale can be devised using the negative logarithm of the hydroxide ion concentration of a solution. Thus, we define pOH as

$$\text{pOH} = -\log[\text{OH}^-]$$

- The pH and pOH of a solution is a dimensionless quantity

- From the definitions of pH and pOH we obtain

$$\text{pH} + \text{pOH} = 14.00$$

Because pH is simply a way to express hydrogen ion concentration, acidic and basic solutions at 25°C can be distinguished by their pH values, as follows:

Acidic solutions:  $[\text{H}^+] > 1.0 \times 10^{-7} \text{ M}$ ,  $\text{pH} < 7.00$

Basic solutions:  $[\text{H}^+] < 1.0 \times 10^{-7} \text{ M}$ ,  $\text{pH} > 7.00$

Neutral solutions:  $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$ ,  $\text{pH} = 7.00$

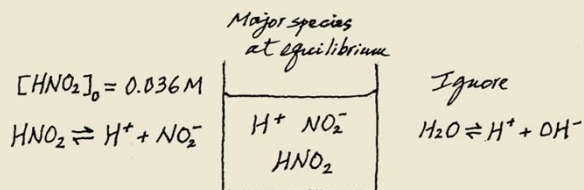
Notice that pH increases as  $[\text{H}^+]$  decreases.

**Calculating the pH of weak acids and weak bases****Example 16.8**

Calculate the pH of a 0.036 M nitrous acid ( $\text{HNO}_2$ ) solution:



**Strategy** Recall that a weak acid only partially ionizes in water. We are given the initial concentration of a weak acid and asked to calculate the pH of the solution at equilibrium. It is helpful to make a sketch to keep track of the pertinent species.



As in Example 16.6, we ignore the ionization of  $\text{H}_2\text{O}$  so the major source of  $\text{H}^+$  ions is the acid. The concentration of  $\text{OH}^-$  ions is very small as we would expect from an acidic solution so it is present as a minor species.

**Solution** We follow the procedure already outlined.

**Step 1:** The species that can affect the pH of the solution are  $\text{HNO}_2$ ,  $\text{H}^+$ , and the conjugate base  $\text{NO}_2^-$ . We ignore water's contribution to  $[\text{H}^+]$ .

**Step 2:** Letting  $x$  be the equilibrium concentration of  $\text{H}^+$  and  $\text{NO}_2^-$  ions in mol/L, we summarize:

	$\text{HNO}_2(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	+	$\text{NO}_2^-(\text{aq})$
Initial (M):	0.036		0.00		0.00
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$0.036 - x$		$x$		$x$

**Step 3:** From Table 16.3 we write

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

$$4.5 \times 10^{-4} = \frac{x^2}{0.036 - x}$$

Applying the approximation  $0.036 - x \approx 0.036$ , we obtain

$$4.5 \times 10^{-4} = \frac{x^2}{0.036 - x} \approx \frac{x^2}{0.036}$$

$$x^2 = 1.62 \times 10^{-5}$$

$$x = 4.0 \times 10^{-3} \text{ M}$$

To test the approximation,

$$\frac{4.0 \times 10^{-3} M}{0.036 M} \times 100\% = 11\%$$

Because this is greater than 5%, our approximation is not valid and we must solve the quadratic equation, as follows:

$$\begin{aligned} x^2 + 4.5 \times 10^{-4}x - 1.62 \times 10^{-5} &= 0 \\ x &= \frac{-4.5 \times 10^{-4} \pm \sqrt{(4.5 \times 10^{-4})^2 - 4(1)(-1.62 \times 10^{-5})}}{2(1)} \\ &= 3.8 \times 10^{-3} M \quad \text{or} \quad -4.3 \times 10^{-3} M \end{aligned}$$

The second solution is physically impossible, because the concentration of ions produced as a result of ionization cannot be negative. Therefore, the solution is given by the positive root,  $x = 3.8 \times 10^{-3} M$ .

Step 4: At equilibrium,

$$\begin{aligned} [\text{H}^+] &= 3.8 \times 10^{-3} M \\ \text{pH} &= -\log(3.8 \times 10^{-3}) \\ &= 2.42 \end{aligned}$$

**Check** Note that the calculated pH indicates that the solution is acidic, which is what we would expect for a weak acid solution. Also, compare the calculated pH with that of a 0.036 M strong acid solution such as HCl to convince yourself of the difference between a strong acid and a weak acid.

**Practice Exercise** What is the pH of a 0.122 M monoprotic acid whose  $K_a$  is  $5.7 \times 10^{-4}$ ?

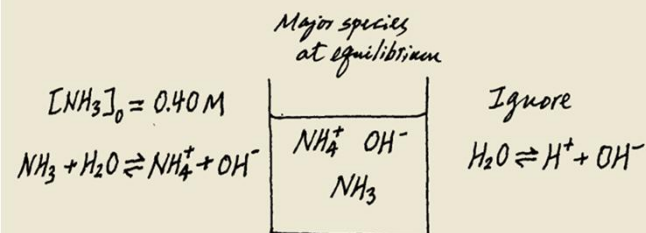
**Practice Exercise** The pH of a 0.060 M weak monoprotic acid is 3.44. Calculate the  $K_a$  of the acid.

A student prepared a 0.10 M solution of formic acid (HCOOH) and found its pH at 25 °C to be 2.38. Calculate  $K_a$  for formic acid at this temperature.

### Example 16.11

What is the pH of a 0.40 M ammonia solution?

**Strategy** The procedure here is similar to the one used for a weak acid (see Example 16.8). From the ionization of ammonia, we see that the major species in solution at equilibrium are  $\text{NH}_3$ ,  $\text{NH}_4^+$ , and  $\text{OH}^-$ . The hydrogen ion concentration is very small as we would expect from a basic solution, so it is present as a minor species. As before, we ignore the ionization of water. We make a sketch to keep track of the pertinent species as follows:



**Solution** We proceed according to the following steps:

**Step 1:** The major species in an ammonia solution are  $\text{NH}_3$ ,  $\text{NH}_4^+$ , and  $\text{OH}^-$ . We ignore the very small contribution to  $\text{OH}^-$  concentration by water.

**Step 2:** Letting  $x$  be the equilibrium concentration of  $\text{NH}_4^+$  and  $\text{OH}^-$  ions in mol/L, we summarize:

	$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$		
Initial (M):	0.40	0.00	0.00
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$0.40 - x$	$x$	$x$

**Step 3:** Table 16.5 gives us  $K_b$ :

$$\begin{aligned} K_b &= \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \\ 1.8 \times 10^{-5} &= \frac{x^2}{0.40 - x} \end{aligned}$$

Applying the approximation  $0.40 - x \approx 0.40$ , we obtain

$$1.8 \times 10^{-5} = \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40}$$

$$x^2 = 7.2 \times 10^{-6}$$

$$x = 2.7 \times 10^{-3} M$$

To test the approximation, we write

$$\frac{2.7 \times 10^{-3} M}{0.40 M} \times 100\% = 0.68\%$$

Therefore, the approximation is valid.

Step 4: At equilibrium,  $[\text{OH}^-] = 2.7 \times 10^{-3} M$ . Thus,

$$\text{pOH} = -\log(2.7 \times 10^{-3})$$

$$= 2.57$$

From Equation (16.9)

$$\text{pH} = 14.00 - 2.57$$

$$= 11.43$$

**Check** Note that the pH calculated is basic, which is what we would expect from a weak base solution. Compare the calculated pH with that of a  $0.40 M$  strong base solution, such as KOH, to convince yourself of the difference between a strong base and a weak base.

**Practice Exercise** Calculate the pH of a  $0.26 M$  methylamine solution (see Table 16.5).

Calculate the pH for a  $15.0 M$  solution of  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ).

Calculate the pH of a  $1.0 M$  solution of methylamine ( $K_b = 4.38 \times 10^{-4}$ ).

Lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ) is a waste product that accumulates in muscle tissue during exertion, leading to pain and a feeling of fatigue. In a  $0.100 M$  aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of  $K_a$  for this acid.

## Percent dissociation

➤ It is often useful to specify the amount of weak acid or weak base that has dissociated in achieving equilibrium in an aqueous solution. It is another measure of the strength of an acid, which is defined as

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100\%$$

Referring to Example 16.8, we see that the percent ionization of a  $0.036 M$   $\text{HNO}_2$  solution is

$$\text{percent ionization} = \frac{3.8 \times 10^{-3} M}{0.036 M} \times 100\% = 11\%$$

## PRACTICE EXERCISE

A  $0.020 M$  solution of niacin has a pH of 3.26. Calculate the percent ionization of the niacin.

**Answer:** 2.7%

## PRACTICE EXERCISE

The  $K_a$  for niacin (Practice Exercise 16.10) is  $1.5 \times 10^{-5}$ . What is the pH of a  $0.010 M$  solution of niacin?

**Answer:** 3.41

Calculate the percent dissociation of acetic acid ( $K_a = 1.8 \times 10^{-5}$ ) in each of the following solutions.

- $1.00 M \text{HC}_2\text{H}_3\text{O}_2$
- $0.100 M \text{HC}_2\text{H}_3\text{O}_2$

➤ In general, for a given weak acid, the percent dissociation increases as the acid becomes more dilute



### Buffer solutions

- As many reactions depend greatly upon the concentration of hydrogen ions in the solutions being used, it is important to control the pH. This is usually achieved by using a solution which has a pH that is accurately known and that resists any change in pH as solvent for the experiment. Such solutions are called buffers.

A buffer solution is defined as a solution of:

- ☐ A weak acid and its conjugate base (the salt of the weak acid) or
- ☐ A weak base and its conjugate acid (the salt of the weak base)

- ☐ Salts of a dibasic (or tribasic) acid such as phosphoric acid,  $\text{H}_3\text{PO}_4$ . For example, potassium dihydrogen phosphate,  $\text{KH}_2\text{PO}_4$ , and disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ .

### Buffer Capacity

- This is the amount of acid (or alkali) that, when added to 1 liter of buffer, will change its pH by 1 unit. The more concentrated the buffer, the greater will be its buffer capacity.
- A buffer solution containing equal concentration of a weak acid and its salt or a weak base and its salt has a maximum buffer capacity and is known as a **Half-neutralized solution**.

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### Example 16.2

Which of the following solutions can be classified as buffer systems? (a)  $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ , (b)  $\text{NaClO}_4/\text{HClO}_4$ , (c)  $\text{C}_5\text{H}_5\text{N}/\text{C}_5\text{H}_5\text{NHCl}$  ( $\text{C}_5\text{H}_5\text{N}$  is pyridine; its  $K_b$  is given in Table 15.4). Explain your answer.

**Strategy** What constitutes a buffer system? Which of the preceding solutions contains a weak acid and its salt (containing the weak conjugate base)? Which of the preceding solutions contains a weak base and its salt (containing the weak conjugate acid)? Why is the conjugate base of a strong acid not able to neutralize an added acid?

**Solution** The criteria for a buffer system is that we must have a weak acid and its salt (containing the weak conjugate base) or a weak base and its salt (containing the weak conjugate acid).

(a)  $\text{H}_3\text{PO}_4$  is a weak acid, and its conjugate base,  $\text{H}_2\text{PO}_4^-$ , is a weak base (see Table 15.5). Therefore, this is a buffer system.

(b) Because  $\text{HClO}_4$  is a strong acid, its conjugate base,  $\text{ClO}_4^-$ , is an extremely weak base. This means that the  $\text{ClO}_4^-$  ion will not combine with a  $\text{H}^+$  ion in solution to form  $\text{HClO}_4$ . Thus the system cannot act as a buffer system.

(c) As Table 15.4 shows,  $\text{C}_5\text{H}_5\text{N}$  is a weak base and its conjugate acid,  $\text{C}_5\text{H}_5\text{NH}^+$  (the cation of the salt  $\text{C}_5\text{H}_5\text{NHCl}$ ), is a weak acid. Therefore, this is a buffer system.

**Practice Exercise** Which of the following are buffer systems? (a)  $\text{KF}/\text{HF}$ , (b)  $\text{KBr}/\text{HBr}$ , (c)  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ .

### Calculation of the pH of a buffer solution

- For a buffer composed of a weak acid and its salt,

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

Or

$$\text{pH} = \text{pK}_a + \log \left( \frac{[\text{salt}]}{[\text{acid}]}\right)$$

- This equation is known as Henderson Hasselbalch equation.

**For example:** Calculate the pH of a solution which is 1.0 M in  $\text{CH}_3\text{COOH}$  and 1.0 M in  $\text{CH}_3\text{COONa}$ .

#### SAMPLE EXERCISE 17.3 Calculating the pH of a Buffer

What is the pH of a buffer that is 0.12 M in lactic acid [ $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , or  $\text{HC}_3\text{H}_5\text{O}_3$ ] and 0.10 M in sodium lactate [ $\text{CH}_3\text{CH}(\text{OH})\text{COONa}$ , or  $\text{NaC}_3\text{H}_5\text{O}_3$ ]? For lactic acid,  $K_a = 1.4 \times 10^{-4}$ .

- Similarly for a buffer composed of a weak base and its salt,

$$\text{pOH} = \text{pK}_b + \log \left( \frac{[\text{salt}]}{[\text{base}]}\right)$$

And then,  $\text{pH} = 14 - \text{pOH}$

**For example:** Calculate the pH of a solution which is 1.0 M in  $\text{NH}_3$  and 0.1 M in  $\text{NH}_4\text{Cl}$ .

### Practice exercise

A buffered solution contains 0.25 M  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ) and 0.40 M  $\text{NH}_4\text{Cl}$ . Calculate the pH of this solution.

#### SAMPLE EXERCISE 17.4 Preparing a Buffer

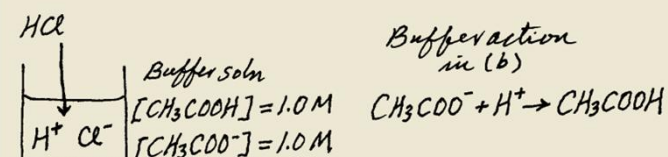
How many moles of  $\text{NH}_4\text{Cl}$  must be added to 2.0 L of 0.10 M  $\text{NH}_3$  to form a buffer whose pH is 9.00? (Assume that the addition of  $\text{NH}_4\text{Cl}$  does not change the volume of the solution.)

## Calculating the pH of a Buffer

### Example 17.2

(a) Calculate the pH of a buffer system containing 1.0 M  $\text{CH}_3\text{COOH}$  and 1.0 M  $\text{CH}_3\text{COONa}$ . (b) What is the pH of the buffer system after the addition of 0.10 mole of gaseous  $\text{HCl}$  to 1.0 L of the solution? Assume that the volume of the solution does not change when the  $\text{HCl}$  is added.

**Strategy** (a) The pH of the buffer solution before the addition of  $\text{HCl}$  can be calculated from the ionization of  $\text{CH}_3\text{COOH}$ . Note that because both the acid and the sodium salt of the acid are present, the initial concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  (from  $\text{CH}_3\text{COONa}$ ) are both 1.0 M. The  $K_a$  of  $\text{CH}_3\text{COOH}$  is  $1.8 \times 10^{-5}$  (see Table 16.3). (b) It is helpful to make a sketch of the changes that occur in this case.



**Solution** (a) We summarize the concentrations of the species at equilibrium as follows:

	$\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$		
Initial (M):	1.0	0	1.0
Change (M):	-x	+x	+x
Equilibrium (M):	1.0 - x	x	1.0 + x

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

$$1.8 \times 10^{-5} = \frac{(x)(1.0 + x)}{(1.0 - x)}$$

Assuming  $1.0 + x \approx 1.0$  and  $1.0 - x \approx 1.0$ , we obtain

$$1.8 \times 10^{-5} = \frac{(x)(1.0 + x)}{(1.0 - x)} \approx \frac{x(1.0)}{1.0}$$

or  $x = [\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$

Thus,  $\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$

(b) When  $\text{HCl}$  is added to the solution, the initial changes are

	$\text{HCl}(aq) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$		
Initial (mol):	0.10	0	0
Change (mol):	-0.10	+0.10	+0.10
Final (mol):	0	0.10	0.10

The  $\text{Cl}^-$  ion is a spectator ion in solution because it is the conjugate base of a strong acid.

The  $\text{H}^+$  ions provided by the strong acid  $\text{HCl}$  react completely with the conjugate base of the buffer, which is  $\text{CH}_3\text{COO}^-$ . At this point it is more convenient to work with moles rather than molarity. The reason is that in some cases the volume of the solution may change when a substance is added. A change in volume will change the molarity, but not the number of moles. The neutralization reaction is summarized next:

	$\text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq) \longrightarrow \text{CH}_3\text{COOH}(aq)$		
Initial (mol):	1.0	0.10	1.0
Change (mol):	-0.10	-0.10	+0.10
Final (mol):	0.90	0	1.1

Finally, to calculate the pH of the buffer after neutralization of the acid, we convert back to molarity by dividing moles by 1.0 L of solution.

	$\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$		
Initial (M):	1.1	0	0.90
Change (M):	-x	+x	+x
Equilibrium (M):	1.1 - x	x	0.90 + x



$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{(x)(0.90 + x)}{1.1 - x}$$

Assuming  $0.90 + x \approx 0.90$  and  $1.1 - x \approx 1.1$ , we obtain

$$1.8 \times 10^{-5} = \frac{(x)(0.90 + x)}{1.1 - x} \approx \frac{x(0.90)}{1.1}$$

or  $x = [H^+] = 2.2 \times 10^{-5} M$

Thus,  $pH = -\log(2.2 \times 10^{-5}) = 4.66$

**Practice Exercise** Calculate the pH of the 0.30 M  $NH_3$ /0.36 M  $NH_4Cl$  buffer system. What is the pH after the addition of 20.0 mL of 0.050 M NaOH to 80.0 mL of the buffer solution?

### Buffering action: How does it work?

#### What if some acid ( $H^+$ ) is added?

- If  $H^+$  ions are added, they react with the base component of the buffer:



- This reaction causes  $[HA]$  to increase and  $[A^-]$  to decrease. But, as long as some  $A^-$  remains, the system is still a mixture of  $HA$  and  $A^-$ , and it is still a buffer solution

#### What if some base ( $OH^-$ ) is added instead?

- The added base ( $OH^-$ ) will neutralize some of the acid  $HA$  and produce more of the conjugate base,  $A^-$



- This reaction causes  $[HA]$  to decrease and  $[A^-]$  to increase. But, as long as some  $HA$  remains, the system is still a mixture of  $HA$  and  $A^-$ , and it is still a buffer solution

**For example:** Look at example 17.2 b.

#### Practice exercise

Calculate the change in pH that occurs when 0.010 mol gaseous HCl is added to 1.0 L of each of the following solutions:

Solution A: 5.00 M  $HCl_2H_3O_2$  and 5.00 M  $NaC_2H_3O_2$

Solution B: 0.050 M  $HCl_2H_3O_2$  and 0.050 M  $NaC_2H_3O_2$

For acetic acid,  $K_a = 1.8 \times 10^{-5}$ .

#### Sample exercise 15.5

A buffered solution contains 0.25 M  $NH_3$  ( $K_b = 1.8 \times 10^{-5}$ ) and 0.40 M  $NH_4Cl$ . Calculate the pH of this solution.

Calculate the pH of the solution that results when 0.10 mol gaseous HCl is added to 1.0 L of the buffered solution from Sample Exercise 15.5.

### Preparing a buffer solution with a specific pH

- Choose a weak acid whose  $pK_a$  is close to the desired pH
- Substitute  $pK_a$  and pH values into the Henderson-Hasselbalch Equation. This will give a ratio of [conjugate Base]/[Acid]
- Convert ratio to molar quantities

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#### Example 16.4

Describe how you would prepare a "phosphate buffer" with a pH of about 7.40.

**Strategy** For a buffer to function effectively, the concentrations of the acid component must be roughly equal to the conjugate base component. According to Equation (16.4), when the desired pH is close to the  $pK_a$  of the acid, that is, when  $pH \approx pK_a$ ,

(Continued)

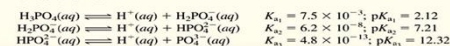
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$$\log \frac{[\text{conjugate base}]}{[\text{acid}]} \approx 0$$

or

$$\frac{[\text{conjugate base}]}{[\text{acid}]} \approx 1$$

**Solution** Because phosphoric acid is a triprotic acid, we write the three stages of ionization as follows. The  $K_a$  values are obtained from Table 15.5 and the  $pK_a$  values are found by applying Equation (16.3).



The most suitable of the three buffer systems is  $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ , because the  $pK_a$  of the acid  $\text{H}_2\text{PO}_4^-$  is closest to the desired pH. From the Henderson-Hasselbalch equation we write

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$7.40 = 7.21 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$\log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 0.19$$

Taking the antilog, we obtain

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{0.19} = 1.5$$

Thus, one way to prepare a phosphate buffer with a pH of 7.40 is to dissolve disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) and sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) in a mole ratio of 1.5:1.0 in water. For example, we could dissolve 1.5 moles of  $\text{Na}_2\text{HPO}_4$  and 1.0 mole of  $\text{NaH}_2\text{PO}_4$  in enough water to make up a 1-L solution.

**Practice Exercise** How would you prepare a liter of "carbonate buffer" at a pH of 10.10? You are provided with carbonic acid ( $\text{H}_2\text{CO}_3$ ), sodium hydrogen carbonate ( $\text{NaHCO}_3$ ), and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). See Table 15.5 for  $K_a$  values.

### Acid-base properties of salt solutions

- A salt is an ionic compound formed by the reaction between an acid and a base
- Salts are strong electrolytes that completely dissociate in water and in some cases react with water
- The term salt hydrolysis describes the reaction of an anion or a cation of a salt, or both, with water
- Salt hydrolysis usually affects **the pH of a solution**. Thus, the pH of an aqueous salt solution can be predicted qualitatively by considering the salt's cations and anions

### Salts that produce neutral solutions

- Salts that consist of the cations of strong bases and the anions of strong acids have no effect on  $[\text{H}^+]$  when dissolved in water. This means that aqueous solutions of salts such as KCl, NaCl,  $\text{NaNO}_3$ , and  $\text{KNO}_3$  are neutral

### Salts that produce basic solutions

- In general, for any salt whose cation has neutral properties (such as  $\text{Na}^+$  or  $\text{K}^+$ ) and whose anion is the conjugate base of a weak acid, the aqueous solution will be basic. This means that aqueous solutions of salts such as  $\text{NaClO}$ ,  $\text{RbF}$ ,  $\text{BaSO}_3$  are basic

### Salts that produce acidic solutions

- In general, salts in which the anion is not a base and the cation is the conjugate acid of a weak base produce acidic solutions. This means that aqueous solutions of salts such as  $\text{NH}_4\text{NO}_3$ ,  $\text{AlCl}_3$ ,  $\text{Fe}(\text{NO}_3)_3$  are acidic.

#### The Acid–Base Properties of Salts

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral.

- a.  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$     b.  $\text{NH}_4\text{CN}$     c.  $\text{Al}_2(\text{SO}_4)_3$

#### PRACTICE EXERCISE

Indicate which salt in each of the following pairs forms the more acidic (or less basic) 0.010 M solution: (a)  $\text{NaNO}_3$  or  $\text{Fe}(\text{NO}_3)_3$ , (b)  $\text{KBr}$  or  $\text{KBrO}_3$ , (c)  $\text{CH}_3\text{NH}_3\text{Cl}$  or  $\text{BaCl}_2$ , (d)  $\text{NH}_4\text{NO}_2$  or  $\text{NH}_4\text{NO}_3$ .

**Answers:** (a)  $\text{Fe}(\text{NO}_3)_3$ , (b)  $\text{KBr}$ , (c)  $\text{CH}_3\text{NH}_3\text{Cl}$ , (d)  $\text{NH}_4\text{NO}_3$

#### SAMPLE EXERCISE 16.18 Determining Whether Salt Solutions Are Acidic, Basic, or Neutral

Determine whether aqueous solutions of each of these salts are acidic, basic, or neutral: (a)  $\text{Ba}(\text{CH}_3\text{COO})_2$ , (b)  $\text{NH}_4\text{Cl}$ , (c)  $\text{CH}_3\text{NH}_3\text{Br}$ , (d)  $\text{KNO}_3$ , (e)  $\text{Al}(\text{ClO}_4)_3$ .

### Solving salt hydrolysis problems

- Follow the same procedure we used for the determination of the pH of a weak acids and a weak

#### Salts as Weak Bases

Calculate the pH of a 0.30 M NaF solution. The  $K_a$  value for HF is  $7.2 \times 10^{-4}$ .

#### Salts as Weak Acids I

Calculate the pH of a 0.10 M  $\text{NH}_4\text{Cl}$  solution. The  $K_b$  value for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .

#### Salts as Weak Acids II

Calculate the pH of a 0.010 M  $\text{AlCl}_3$  solution. The  $K_a$  value for  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  is  $1.4 \times 10^{-5}$ .

### Example 16.13

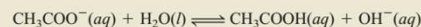
Calculate the pH of a 0.15 M solution of sodium acetate ( $\text{CH}_3\text{COONa}$ ). What is the percent hydrolysis?

#### Solution

*Step 1:* Because we started with a 0.15 M sodium acetate solution, the concentrations of the ions are also equal to 0.15 M after dissociation:

	$\text{CH}_3\text{COONa}(aq) \longrightarrow \text{Na}^+(aq) + \text{CH}_3\text{COO}^-(aq)$		
Initial (M):	0.15	0	0
Change (M):	-0.15	+0.15	+0.15
Final (M):	0	0.15	0.15

Of these ions, only the acetate ion will react with water



At equilibrium, the major species in solution are  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{OH}^-$ . The concentration of the  $\text{H}^+$  ion is very small as we would expect for a basic solution, so it is treated as a minor species. We ignore the ionization of water.

*Step 2:* Let  $x$  be the equilibrium concentration of  $\text{CH}_3\text{COOH}$  and  $\text{OH}^-$  ions in mol/L, we summarize:

	$\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq)$		
Initial (M):	0.15	0.00	0.00
Change (M):	-x	+x	+x
Equilibrium (M):	0.15 - x	x	x

*Step 3:* From the preceding discussion and Table 16.3 we write the equilibrium constant of hydrolysis, or the base ionization constant, as

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

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x}$$

Because  $K_b$  is very small and the initial concentration of the base is large, we can apply the approximation  $0.15 - x \approx 0.15$ :

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$x = 9.2 \times 10^{-6} \text{ M}$$

Step 4: At equilibrium:

$$\begin{aligned}[\text{OH}^-] &= 9.2 \times 10^{-6} \text{ M} \\ \text{pOH} &= -\log(9.2 \times 10^{-6}) \\ &= 5.04 \\ \text{pH} &= 14.00 - 5.04 \\ &= 8.96\end{aligned}$$

Thus the solution is basic, as we would expect. The percent hydrolysis is given by

$$\begin{aligned}\% \text{ hydrolysis} &= \frac{[\text{CH}_3\text{COO}^-]_{\text{hydrolyzed}}}{[\text{CH}_3\text{COO}^-]_{\text{initial}}} \\ &= \frac{9.2 \times 10^{-6} \text{ M}}{0.15 \text{ M}} \times 100\% \\ &= 0.0061\%\end{aligned}$$

**Check** The result shows that only a very small amount of the anion undergoes hydrolysis. Note that the calculation of percent hydrolysis takes the same form as the test for the approximation, which is valid in this case.

**Practice Exercise** Calculate the pH of a 0.24 M sodium formate solution ( $\text{HCOONa}$ ).

### Salts in which both the cation and the anion hydrolyze

- If the salt contains an anion and a cation both capable of reacting with water, both hydroxide ions and hydronium ions are produced. Examples:  $\text{NH}_4\text{ClO}_4$ ,  $\text{Al}(\text{CH}_3\text{COO})_3$ ,  $\text{CrF}_3$
- To predict whether the solution will be basic, acidic, or neutral, it depends on the  $K_a$  value for the acidic ion and the  $K_b$  value for the basic ion
- If the  $K_a$  value for the acidic ion is **larger than the  $K_b$  value** for the basic ion, the solution will be acidic
- If the  $K_b$  value is **larger than the  $K_a$  value**, the solution will be basic

- **Equal  $K_a$  and  $K_b$  values mean a neutral solution**
- The acid–base properties of aqueous solutions of various salts are summarized in Table 14.6

TABLE 14.6 Acid–Base Properties of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	$\text{KCl}$ , $\text{KNO}_3$ , $\text{NaCl}$ , $\text{NaNO}_3$	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	$\text{NaC}_2\text{H}_3\text{O}_2$ , $\text{KCN}$ , $\text{NaF}$	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	$\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{NO}_3$	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , $\text{NH}_4\text{CN}$	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$ , basic if $K_b > K_a$ , neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	$\text{Al}(\text{NO}_3)_3$ , $\text{FeCl}_3$	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

# THANK YOU

