

## Sample Exercise 17.1 Calculating the pH When a Common Ion is Involved

What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?

### Solution

**Analyze:** We are asked to determine the pH of a solution of a weak electrolyte ( $\text{CH}_3\text{COOH}$ ) and a strong electrolyte ( $\text{CH}_3\text{COONa}$ ) that share a common ion,  $\text{CH}_3\text{COO}^-$ .

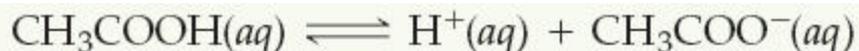
**Plan:** In any problem in which we must determine the pH of a solution containing a mixture of solutes, it is helpful to proceed by a series of logical steps:

1. Consider which solutes are strong electrolytes and which are weak electrolytes, and identify the major species in solution.
2. Identify the important equilibrium that is the source of  $\text{H}^+$  and therefore determines pH.
3. Tabulate the concentrations of ions involved in the equilibrium.
4. Use the equilibrium-constant expression to calculate  $[\text{H}^+]$  and then pH.

**Solve:** First, because  $\text{CH}_3\text{COOH}$  is a weak electrolyte and  $\text{CH}_3\text{COONa}$  is a strong electrolyte, the major species in the solution are  $\text{CH}_3\text{COOH}$  (a weak acid),  $\text{Na}^+$  (which is neither acidic nor basic and is therefore a spectator in the acid–base chemistry), and  $\text{CH}_3\text{COO}^-$  (which is the conjugate base of  $\text{CH}_3\text{COOH}$ ).

Second,  $[\text{H}^+]$  and, therefore, the pH are controlled by the dissociation equilibrium of  $\text{CH}_3\text{COOH}$ :

(We have written the equilibrium Using  $\text{H}^+(\text{aq})$  rather than  $\text{H}_3\text{O}^+(\text{aq})$  but both representations of the hydrated hydrogen ion are equally valid.)



## Sample Exercise 17.1 Calculating the pH When a Common Ion is Involved

### Solution (Continued)

Third, we tabulate the initial and equilibrium concentrations as we did in solving other equilibrium problems in Chapters 15 and 16:

	$\text{CH}_3\text{COOH}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CH}_3\text{COO}^-(aq)$
Initial	0.30 M		0		0.30 M
Change	$-x$ M		$+x$ M		$+x$ M
Equilibrium	$(0.30 - x)$ M		$x$ M		$(0.30 + x)$ M

The equilibrium concentration of  $\text{CH}_3\text{COO}^-$  (the common ion) is the initial concentration that is due to  $\text{CH}_3\text{COONa}$  (0.30 M) plus the change in concentration ( $x$ ) that is due to the ionization of  $\text{CH}_3\text{COOH}$ .

Now we can use the equilibrium-constant expression:

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

(The dissociation constant for  $\text{CH}_3\text{COOH}$  at 25 °C is from Appendix D; addition of  $\text{CH}_3\text{COONa}$  does not change the value of this constant.) Substituting the equilibrium-constant concentrations from our table into the equilibrium expression gives

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30 + x)}{0.30 - x}$$

## Sample Exercise 17.1 Calculating the pH When a Common Ion is Involved

### Solution (Continued)

Because  $K_a$  is small, we assume that  $x$  is small compared to the original concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  ( $0.30\text{ M}$  each). Thus, we can ignore the very small  $x$  relative to  $0.30\text{ M}$ , giving

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30)}{0.30}$$

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

The resulting value of  $x$  is indeed small relative to  $0.30$ , justifying the approximation made in simplifying the problem.

The resulting value of  $x$  is indeed small relative to  $0.30$ , justifying the approximation made in simplifying the problem.

Finally, we calculate the pH from the equilibrium concentration of  $\text{H}^+(\text{aq})$ :

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

**Comment:** In Section 16.6 we calculated that a  $0.30\text{ M}$  solution of  $\text{CH}_3\text{COOH}$  has a pH of 2.64, corresponding to  $[\text{H}^+] = 2.3 \times 10^{-3}\text{ M}$ . Thus, the addition of  $\text{CH}_3\text{COONa}$  has substantially decreased  $[\text{H}^+]$  as we would expect from Le Châtelier's principle.

### Practice Exercise

Calculate the pH of a solution containing  $0.085\text{ M}$  nitrous acid ( $\text{HNO}_2$ ;  $K_a = 4.5 \times 10^{-4}$ ) and  $0.10\text{ M}$  potassium nitrite ( $\text{KNO}_2$ ).

**Answer:** 3.42

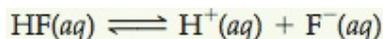
## Sample Exercise 17.2 Calculating Ion Concentrations When a Common is Involved

Calculate the fluoride ion concentration and pH of a solution that is 0.20 M in HF and 0.10 M in HCl.

### Solution

**Plan:** We can again use the four steps outlined in Sample Exercise 17.1.

**Solve:** Because HF is a weak acid and HCl is a strong acid, the major species in solution are HF, H<sup>+</sup>, and Cl<sup>-</sup>. The Cl<sup>-</sup>, which is the conjugate base of a strong acid, is merely a spectator ion in any acid–base chemistry. The problem asks for [F<sup>-</sup>], which is formed by ionization of HF. Thus, the important equilibrium is



	HF(aq)	⇌	H <sup>+</sup> (aq)	+	F <sup>-</sup> (aq)
Initial	0.20 M		0.10 M		0
Change	-x M		+x M		+x M
Equilibrium	(0.20 - x) M		(0.10 + x) M		x M

The common ion in this problem is the hydrogen (or hydronium) ion. Now we can tabulate the initial and equilibrium concentrations of each species involved in this equilibrium:

The equilibrium constant for the ionization of HF, from Appendix D, is  $6.8 \times 10^{-4}$ . Substituting the equilibrium-constant concentrations into the equilibrium expression gives

$$K_a = 6.8 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(0.10 + x)(x)}{0.20 - x}$$

$$\frac{(0.10)(x)}{0.20} = 6.8 \times 10^{-4}$$

$$x = \frac{0.20}{0.10} (6.8 \times 10^{-4}) = 1.4 \times 10^{-3} \text{ M} = [\text{F}^-]$$

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## Sample Exercise 17.2 Calculating Ion Concentrations When a Common is Involved

### Solution (Continued)

If we assume that  $x$  is small relative to 0.10 or 0.20  $M$ , this expression simplifies to

This  $F^-$  concentration is substantially smaller than it would be in a 0.20  $M$  solution of HF with no added HCl. The common ion,  $H^+$ , suppresses the ionization of HF. The concentration of  $H^+(aq)$  is

$$[H^+] = (0.10 + x) M \approx 0.10 M$$

$$pH = 1.00$$

Thus,

**Comment:** Notice that for all practical purposes,  $[H^+]$  is due entirely to the HCl; the HF makes a negligible contribution by comparison.

### Practice Exercise

Calculate the formate ion concentration and pH of a solution that is 0.050  $M$  in formic acid ( $HCOOH$ ;  $K_a = 1.8 \times 10^{-4}$ ) and 0.10  $M$  in  $HNO_3$ .

**Answer:**  $[HCOO^-] = 9.0 \times 10^{-5}$ ;  $pH = 1.00$

## 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,  $K_a = 1.4 \times 10^{-4}$ .

### Solution

**Analyze:** We are asked to calculate the pH of a buffer containing lactic acid  $\text{HC}_3\text{H}_5\text{O}_3$  and its conjugate base, the lactate ion ( $\text{C}_3\text{H}_5\text{O}_3^-$ ).

**Plan:** We will first determine the pH using the method described in Section 17.1. Because  $\text{HC}_3\text{H}_5\text{O}_3$  is a weak electrolyte and

$\text{NaC}_3\text{H}_5\text{O}_3$  is a strong electrolyte, the major species in solution are  $\text{HC}_3\text{H}_5\text{O}_3$ ,  $\text{Na}^+$ , and  $\text{C}_3\text{H}_5\text{O}_3^-$ . The  $\text{Na}^+$  ion is a spectator ion. The  $\text{HC}_3\text{H}_5\text{O}_3$ – $\text{C}_3\text{H}_5\text{O}_3^-$  conjugate acid–base pair determines  $[\text{H}^+]$  and thus pH;  $[\text{H}^+]$  can be determined using the acid dissociation equilibrium of lactic acid.

**Solve:** The initial and equilibrium concentrations of the species involved in this equilibrium are

	$\text{HC}_3\text{H}_5\text{O}_3(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{C}_3\text{H}_5\text{O}_3^-(aq)$
Initial	0.12 <i>M</i>		0		0.10 <i>M</i>
Change	– <i>x M</i>		+ <i>x M</i>		+ <i>x M</i>
Equilibrium	(0.12 – <i>x</i> ) <i>M</i>		<i>x M</i>		(0.10 + <i>x</i> ) <i>M</i>

The equilibrium concentrations are governed by the equilibrium expression:

$$K_a = 1.4 \times 10^{-4} = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{x(0.10 + x)}{(0.12 - x)}$$

## Sample Exercise 17.3 Calculating the pH of a Buffer

### Solution (Continued)

Because  $K_a$  is small and a common ion is present, we expect  $x$  to be small relative to either 0.12 or 0.10  $M$ . Thus, our equation can be simplified to give

Solving for  $x$  gives a value that justifies our approximation:

Alternatively, we could have used the Henderson–Hasselbalch equation to calculate pH directly:

$$K_a = 1.4 \times 10^{-4} = \frac{x(0.10)}{0.12}$$

$$[\text{H}^+] = x = \left(\frac{0.12}{0.10}\right)(1.4 \times 10^{-4}) = 1.7 \times 10^{-4} M$$

$$\text{pH} = -\log(1.7 \times 10^{-4}) = 3.77$$

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.85 + \log\left(\frac{0.10}{0.12}\right) \\ &= 3.85 + (-0.08) = 3.77\end{aligned}$$

### Practice Exercise

Calculate the pH of a buffer composed of 0.12  $M$  benzoic acid and 0.20  $M$  sodium benzoate. (Refer to Appendix D.)

**Answer:** 4.42

## 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.)

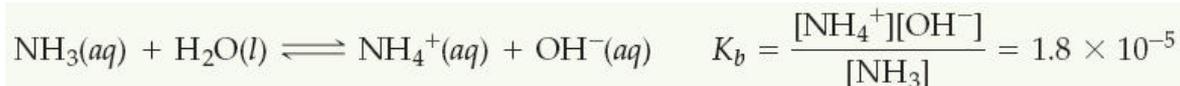
### Solution

**Analyze:** Here we are asked to determine the amount of  $\text{NH}_4^+$  ion required to prepare a buffer of a specific pH.

**Plan:** The major species in the solution will be  $\text{NH}_4^+$ ,  $\text{Cl}^-$ , and  $\text{NH}_3$ .

Of these, the ion is a spectator (it is the conjugate base of a strong acid).

Thus, the  $\text{NH}_4^+$ – $\text{NH}_3$  conjugate acid–base pair will determine the pH of the buffer solution. The equilibrium relationship between  $\text{NH}_4^+$  and  $\text{NH}_3$  is given by the basedissociation constant for  $\text{NH}_3$ :



The key to this exercise is to use this  $K_b$  expression to calculate  $[\text{NH}_4^+]$ .

**Solve:** We obtain  $[\text{OH}^-]$  from the given pH:  
and so

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.00 = 5.00$$

$$[\text{OH}^-] = 1.0 \times 10^{-5} \text{ M}$$

Because  $K_b$  is small and the common ion  $\text{NH}_4^+$  is present, the equilibrium concentration of  $\text{NH}_3$  will essentially equal its initial concentration:

$$[\text{NH}_3] = 0.10 \text{ M}$$

$$[\text{NH}_4^+] = K_b \frac{[\text{NH}_3]}{[\text{OH}^-]} = (1.8 \times 10^{-5}) \frac{(0.10 \text{ M})}{(1.0 \times 10^{-5} \text{ M})} = 0.18 \text{ M}$$

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## Sample Exercise 17.4 Preparing a Buffer

### Solution (Continued)

We now use the expression for  $K_b$  to calculate  $[\text{NH}_4^+]$ :

Thus, for the solution to have  $\text{pH} = 9.00$ ,  $[\text{NH}_4^+]$  must equal  $0.18\text{ M}$ . The number of moles of  $\text{NH}_4\text{Cl}$  needed to produce this concentration is given by the product of the volume of the solution and its molarity:

$$(2.0\text{ L})(0.18\text{ mol NH}_4\text{Cl/L}) = 0.36\text{ mol NH}_4\text{Cl}$$

**Comment:** Because  $\text{NH}_4^+$  and  $\text{NH}_3$  are a conjugate acid–base pair, we could use the Henderson–Hasselbalch equation (Equation 17.9) to solve this problem. To do so requires first using Equation 16.41 to calculate  $\text{p}K_a$  for  $\text{NH}_4^+$  from the value of  $\text{p}K_b$  for  $\text{NH}_3$ . We suggest you try this approach to convince yourself that you can use the Henderson–Hasselbalch equation for buffers for which you are given  $K_b$  for the conjugate base rather than  $K_a$  for the conjugate acid.

### Practice Exercise

Calculate the concentration of sodium benzoate that must be present in a  $0.20\text{ M}$  solution of benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) to produce a  $\text{pH}$  of  $4.00$ .

**Answer:**  $0.13\text{ M}$

## Sample Exercise 17.5 Calculating pH Changes in Buffers

A buffer is made by adding 0.300 mol  $\text{CH}_3\text{COOH}$  and 0.300 mol  $\text{CH}_3\text{COONa}$  to enough water to make 1.00 L of solution. The pH of the buffer is 4.74 (Sample Exercise 17.1). **(a)** Calculate the pH of this solution after 0.020 mol of NaOH is added. **(b)** For comparison, calculate the pH that would result if 0.020 mol of NaOH were added to 1.00 L of pure water (neglect any volume changes).

### Solution

**Analyze:** We are asked to determine the pH of a buffer after addition of a small amount of strong base and to compare the pH change to the pH that would result if we were to add the same amount of strong base to pure water.

**Plan:** **(a)** Solving this problem involves the two steps outlined in Figure 17.3. Thus, we must first do a stoichiometry calculation to determine how the added  $\text{OH}^-$  reacts with the buffer and affects its composition. Then we can use the resultant composition of the buffer and either the Henderson–Hasselbalch equation or the equilibrium constant expression for the buffer to determine the pH.

**Solve:** *Stoichiometry Calculation:* The  $\text{OH}^-$  provided by NaOH reacts with  $\text{CH}_3\text{COOH}$ , the weak acid component of the buffer. Prior to this neutralization reaction, there are 0.300 mol each of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$ . Neutralizing the 0.020 mol  $\text{OH}^-$  requires 0.020 mol of  $\text{CH}_3\text{COOH}$ . Consequently, the amount of  $\text{CH}_3\text{COOH}$  *decreases* by 0.020 mol, and the amount of the product of the neutralization,  $\text{CH}_3\text{COO}^-$ , *increases* by 0.020 mol. We can create a table to see how the composition of the buffer changes as a result of its reaction with  $\text{OH}^-$ :

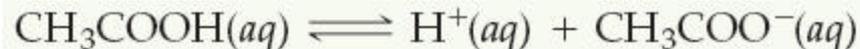
$$\text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{CH}_3\text{COO}^-(aq)$$

Buffer before addition	0.300 mol	0	—	0.300 mol
Addition	—	0.020 mol	—	—
Buffer after addition	0.280 mol	0	—	0.320 mol

## Sample Exercise 17.5 Calculating pH Changes in Buffers

### Solution (Continued)

*Equilibrium Calculation:* We now turn our attention to the equilibrium that will determine the pH of the buffer, namely the ionization of acetic acid.



Using the quantities of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  remaining in the buffer, we can determine the pH using the Henderson–Hasselbalch equation.

$$\text{pH} = 4.74 + \log \frac{0.320 \text{ mol}/1.00 \text{ L}}{0.280 \text{ mol}/1.00 \text{ L}} = 4.80$$

**Comment** Notice that we could have used mole amounts in place of concentrations in the Henderson–Hasselbalch equation and gotten the same result. The volumes of the acid and base are equal and cancel. If 0.020 mol of  $\text{H}^+$  was added to the buffer, we would proceed in a similar way to calculate the resulting pH of the buffer. In this case the pH decreases by 0.06 units, giving  $\text{pH} = 4.68$ , as shown in the figure in the margin.

**(b)** To determine the pH of a solution made by adding 0.020 mol of NaOH to 1.00 L of pure water, we can first determine pOH using Equation 16.18 and subtracting from 14.

$$\text{pH} = 14 - (-\log 0.020) = 12.30$$

Note that although the small amount of NaOH changes the pH of water significantly, the pH of the buffer changes very little.

### Practice Exercise

Determine **(a)** the pH of the original buffer described in Sample Exercise 17.5 after the addition of 0.020 mol HCl and **(b)** the pH of the solution that would result from the addition of 0.020 mol HCl to 1.00 L of pure water

**Answers:** (a) 4.68. (b) 1.70

## Sample Exercise 17.6 Calculating pH for a Strong Acid-Strong Base Titration

Calculate the pH when the following quantities of 0.100 M NaOH solution have been added to 50.0 mL of 0.100 M HCl solution: (a) 49.0 mL, (b) 51.0 mL.

### Solution

**Analyze:** We are asked to calculate the pH at two points in the titration of a strong acid with a strong base. The first point is just before the equivalence point, so we expect the pH to be determined by the small amount of strong acid that has not yet been neutralized. The second point is just after the equivalence point, so we expect this pH to be determined by the small amount of excess strong base.

**Plan:** (a) As the NaOH solution is added to the HCl solution,  $\text{H}^+(\text{aq})$  reacts with  $\text{OH}^-(\text{aq})$  to form  $\text{H}_2\text{O}$ . Both  $\text{Na}^+$  and  $\text{Cl}^-$  are spectator ions, having negligible effect on the pH. To determine the pH of the solution, we must first determine how many moles of  $\text{H}^+$  were originally present and how many moles of  $\text{OH}^-$  were added. We can then calculate how many moles of each ion remain after the neutralization reaction. To calculate  $[\text{H}^+]$ , and hence pH, we must also remember that the volume of the solution increases as we add titrant, thus diluting the concentration of all solutes present.

**Solve:** The number of moles of  $\text{H}^+$  in the original HCl solution is given by the product of the volume of the solution (50.0 mL = 0.0500 L) and its molarity (0.100 M):

$$(0.0500 \text{ L soln}) \left( \frac{0.100 \text{ mol H}^+}{1 \text{ L soln}} \right) = 5.00 \times 10^{-3} \text{ mol H}^+$$

Likewise, the number of moles of  $\text{OH}^-$  in 49.0 mL of 0.100 M NaOH is

$$(0.0490 \text{ L soln}) \left( \frac{0.100 \text{ mol OH}^-}{1 \text{ L soln}} \right) = 4.90 \times 10^{-3} \text{ mol OH}^-$$

## Sample Exercise 17.6 Calculating pH for a Strong Acid-Strong Base Titration

### Solution (Continued)

Because we have not yet reached the equivalence point, there are more moles of  $\text{H}^+$  present than  $\text{OH}^-$ . Each mole of  $\text{OH}^-$  will react with one mole of  $\text{H}^+$ . Using the convention introduced in Sample Exercise 17.5,

During the course of the titration, the volume of the reaction mixture increases as the NaOH solution is added to the HCl solution. Thus, at this point in the titration, the total volume of the solutions is

(We assume that the total volume is the sum of the volumes of the acid and base solutions.) Thus, the concentration of  $\text{H}^+(aq)$  is

The corresponding pH equals

**Plan: (b)** We proceed in the same way as we did in part (a), except we are now past the equivalence point and have more  $\text{OH}^-$  in the solution than  $\text{H}^+$ . As before, the initial number of moles of each reactant is determined from their volumes and concentrations. The reactant present in smaller stoichiometric amount (the limiting reactant) is consumed completely, leaving an excess of hydroxide ion.

	$\text{H}^+(aq)$	+	$\text{OH}^-(aq)$	$\longrightarrow$	$\text{H}_2\text{O}(l)$
Before addition	$5.00 \times 10^{-3} \text{ mol}$		0		—
Addition			$4.90 \times 10^{-3} \text{ mol}$		
After addition	$0.10 \times 10^{-3} \text{ mol}$		0		—

$$50.0 \text{ mL} + 49.0 \text{ mL} = 99.0 \text{ mL} = 0.0990 \text{ L}$$

$$[\text{H}^+] = \frac{\text{moles } \text{H}^+(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3} \text{ mol}}{0.09900 \text{ L}} = 1.0 \times 10^{-3} \text{ M}$$

$$-\log(1.0 \times 10^{-3}) = 3.00$$

## Sample Exercise 17.6 Calculating pH for a Strong Acid-Strong Base Titration

### Solution (Continued)

Solve:

	$\text{H}^+(aq)$	+	$\text{OH}^-(aq)$	$\longrightarrow$	$\text{H}_2\text{O}(l)$
Before addition	$5.00 \times 10^{-3} \text{ mol}$		0		—
Addition			$5.10 \times 10^{-3} \text{ mol}$		
After addition	0		$0.10 \times 10^{-3} \text{ mol}$		—

In this case the total volume of the solution is

$$50.0 \text{ mL} + 51.0 \text{ mL} = 101.0 \text{ mL} = 0.1010 \text{ L}$$

Hence, the concentration of  $\text{OH}^-(aq)$  in the solution is

$$[\text{OH}^-] = \frac{\text{moles OH}^-(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3} \text{ mol}}{0.1010 \text{ L}} = 1.0 \times 10^{-3} \text{ M}$$

Thus, the pOH of the solution equals

$$\text{pOH} = -\log(1.0 \times 10^{-3}) = 3.00$$

and the pH equals

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.00 = 11.00$$

### Practice Exercise

Calculate the pH when the following quantities of  $0.100 \text{ M HNO}_3$  have been added to  $25.0 \text{ mL}$  of  $0.100 \text{ M KOH}$  solution: (a)  $24.9 \text{ mL}$ , (b)  $25.1 \text{ mL}$ .

**Answers:** (a) 10.30, (b) 3.70

## Sample Exercise 17.7 Calculating pH for a Weak Acid-Strong Base Titration

Calculate the pH of the solution formed when 45.0 mL of 0.100 M NaOH is added to 50.0 mL of 0.100 M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.8 \times 10^{-5}$ ).

### Solution

**Analyze:** We are asked to calculate the pH before the equivalence point of the titration of a weak acid with a strong base.

**Plan:** We first must determine the number of moles of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  that are present after the neutralization reaction. We then calculate pH using  $K_a$  together with  $[\text{CH}_3\text{COOH}]$  and  $[\text{CH}_3\text{COO}^-]$ .

**Solve:** *Stoichiometry Calculation:* The product of the volume and concentration of each solution gives the number of moles of each reactant present before the neutralization:

$$(0.0500 \text{ L soln}) \left( \frac{0.100 \text{ mol CH}_3\text{COOH}}{1 \text{ L soln}} \right) = 5.00 \times 10^{-3} \text{ mol CH}_3\text{COOH}$$
$$(0.0450 \text{ L soln}) \left( \frac{0.100 \text{ mol NaOH}}{1 \text{ L soln}} \right) = 4.50 \times 10^{-3} \text{ mol NaOH}$$

The  $4.50 \times 10^{-3}$  mol of NaOH consumes  $4.50 \times 10^{-3}$  mol of  $\text{CH}_3\text{COOH}$ :

	$\text{CH}_3\text{COOH}(aq)$	$+$	$\text{OH}^-(aq)$	$\longrightarrow$	$\text{CH}_3\text{COO}^-(aq)$	$+$	$\text{H}_2\text{O}(l)$
Before addition	$5.00 \times 10^{-3} \text{ mol}$		0		0		—
Addition			$4.50 \times 10^{-3} \text{ mol}$				
After addition	$0.50 \times 10^{-3} \text{ mol}$		0		$4.50 \times 10^{-3} \text{ mol}$		—

The total volume of the solution is

$$45.0 \text{ mL} + 50.0 \text{ mL} = 95.0 \text{ mL} = 0.0950 \text{ L}$$

The resulting molarities of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  after the reaction are therefore

$$[\text{CH}_3\text{COOH}] = \frac{0.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0053 \text{ M}$$
$$[\text{CH}_3\text{COO}^-] = \frac{4.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0474 \text{ M}$$

## Sample Exercise 17.7 Calculating pH for a Weak Acid-Strong Base Titration

### Solution (Continued)

*Equilibrium Calculation:* The equilibrium between  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  must obey the equilibrium-constant expression for  $\text{CH}_3\text{COOH}$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = (1.8 \times 10^{-5}) \times \left( \frac{0.0053}{0.0474} \right) = 2.0 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log(2.0 \times 10^{-6}) = 5.70$$

Solving for  $[\text{H}^+]$  gives

**Comment:** We could have solved for pH equally well using the Henderson–Hasselbalch equation.

### Practice Exercise

(a) Calculate the pH in the solution formed by adding 10.0 mL of 0.050 M NaOH to 40.0 mL of 0.0250 M benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ,  $K_a = 6.3 \times 10^{-5}$ ). (b) Calculate the pH in the solution formed by adding 10.0 mL of 0.100 M HCl to 20.0 mL of 0.100 M  $\text{NH}_3$ .

**Answers:** (a) 4.20, (b) 9.26

## Sample Exercise 17.8 Calculating the pH at the Equivalence Point

Calculate the pH at the equivalence point in the titration of 50.0 mL of 0.100 *M* CH<sub>3</sub>COOH with 0.100 *M* NaOH.

### Solution

**Analyze:** We are asked to determine the pH at the equivalence point of the titration of a weak acid with a strong base. Because the neutralization of a weak acid produces its anion, which is a weak base, we expect the pH at the equivalence point to be greater than 7.

**Plan:** The initial number of moles of acetic acid will equal the number of moles of acetate ion at the equivalence point. We use the volume of the solution at the equivalence point to calculate the concentration of acetate ion. Because the acetate ion is a weak base, we can calculate the pH using  $K_b$  and [CH<sub>3</sub>COO<sup>-</sup>].

**Solve:** The number of moles of acetic acid in the initial solution is obtained from the volume and molarity of the solution:

$$\text{Moles} = M \times L = (0.100 \text{ mol/L})(0.0500 \text{ L}) = 5.00 \times 10^{-3} \text{ mol CH}_3\text{COOH}$$

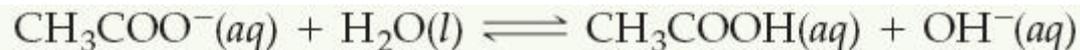
Hence  $5.00 \times 10^{-3}$  mol of CH<sub>3</sub>COO<sup>-</sup> is formed. It will take 50.0 mL of NaOH to reach the equivalence point (Figure 17.9). The volume of this salt solution at the equivalence point is the sum of the volumes of the acid and base, 50.0 mL + 50.0 mL = 100.0 mL = 0.1000 L. Thus, the concentration of CH<sub>3</sub>COO<sup>-</sup> is

$$[\text{CH}_3\text{COO}^-] = \frac{5.00 \times 10^{-3} \text{ mol}}{0.1000 \text{ L}} = 0.0500 \text{ M}$$

## Sample Exercise 17.8 Calculating the pH at the Equivalence Point

### Solution (Continued)

The  $\text{CH}_3\text{COO}^-$  ion is a weak base.



The  $K_b$  for  $\text{CH}_3\text{COO}^-$  can be calculated from the  $K_a$  value of its conjugate acid,  $K_b = K_w/K_a = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$ . Using the  $K_b$  expression, we have

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{(x)(x)}{0.0500 - x} = 5.6 \times 10^{-10}$$

Making the approximation that  $0.0500 - x \approx 0.0500$ , and then solving for  $x$ , we have  $x = [\text{OH}^-] = 5.3 \times 10^{-6} M$ , which gives  $\text{pOH} = 5.28$   $\text{pH} = 8.72$

**Check:** The pH is above 7, as expected for the salt of a weak acid and strong base.

### Practice Exercise

Calculate the pH at the equivalence point when (a) 40.0 mL of 0.025 M benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ,  $K_a = 6.3 \times 10^{-5}$ ) is titrated with 0.050 M NaOH; (b) 40.0 mL of 0.100 M  $\text{NH}_3$  is titrated with 0.100 M HCl.

**Answers:** (a) 8.21, (b) 5.28

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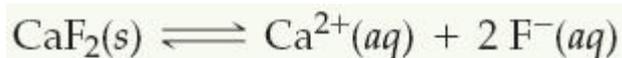
## Sample Exercise 17.9 Writing Solubility-Product ( $K_{sp}$ ) Expressions

Write the expression for the solubility-product constant for  $\text{CaF}_2$ , and look up the corresponding  $K_{sp}$  value in Appendix D.

### Solution

**Analyze:** We are asked to write an equilibrium-constant expression for the process by which  $\text{CaF}_2$  dissolves in water.

**Plan:** We apply the same rules for writing any equilibrium-constant expression, excluding the solid reactant from the expression. We assume that the compound dissociates completely into its component ions.



**Solve:** Following the italicized rule stated previously, the expression for  $K_{sp}$  is

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

In Appendix D we see that this  $K_{sp}$  has a value of  $3.9 \times 10^{-11}$ .

### Practice Exercise

Give the solubility-product-constant expressions and the values of the solubility-product constants (from Appendix D) for the following compounds: **(a)** barium carbonate, **(b)** silver sulfate.

*Answers:* **(a)**  $K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}] = 5.0 \times 10^{-9}$ ; **(b)**  $K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = 1.5 \times 10^{-5}$

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## Sample Exercise 17.10 Calculating $K_{sp}$ from Solubility

Solid silver chromate is added to pure water at 25 °C. Some of the solid remains undissolved at the bottom of the flask. The mixture is stirred for several days to ensure that equilibrium is achieved between the undissolved  $\text{Ag}_2\text{CrO}_4(s)$  and the solution. Analysis of the equilibrated solution shows that its silver ion concentration is  $1.3 \times 10^{-4} M$ . Assuming that  $\text{Ag}_2\text{CrO}_4$  dissociates completely in water and that there are no other important equilibria involving the  $\text{Ag}^+$  or  $\text{CrO}_4^{2-}$  ions in the solution, calculate  $K_{sp}$  for this compound.

### Solution

**Analyze:** We are given the equilibrium concentration of  $\text{Ag}^+$  in a saturated solution of  $\text{Ag}_2\text{CrO}_4$ . From this information, we are asked to determine the value of the solubility product constant,  $K_{sp}$ , for  $\text{Ag}_2\text{CrO}_4$ .

**Plan:** The equilibrium equation and the expression for  $K_{sp}$  are



To calculate  $K_{sp}$ , we need the equilibrium concentrations of  $\text{Ag}^+$  and  $\text{CrO}_4^{2-}$ . We know that at equilibrium  $[\text{Ag}^+] = 1.3 \times 10^{-4} M$ . All the  $\text{Ag}^+$  and  $\text{CrO}_4^{2-}$  ions in the solution come from the  $\text{Ag}_2\text{CrO}_4$  that dissolves. Thus, we can use  $[\text{Ag}^+]$  to calculate  $[\text{CrO}_4^{2-}]$ .

**Solve:** From the chemical formula of silver chromate, we know that there must be 2  $\text{Ag}^+$  ions in solution for each  $\text{CrO}_4^{2-}$  ion in solution. Consequently, the concentration of  $\text{CrO}_4^{2-}$  is half the concentration of  $\text{Ag}^+$ :

$$[\text{CrO}_4^{2-}] = \left( \frac{1.3 \times 10^{-4} \text{ mol Ag}^+}{\text{L}} \right) \left( \frac{1 \text{ mol CrO}_4^{2-}}{2 \text{ mol Ag}^+} \right) = 6.5 \times 10^{-5} M$$

We can now calculate the value of  $K_{sp}$ .

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (1.3 \times 10^{-4})^2(6.5 \times 10^{-5}) = 1.1 \times 10^{-12}$$

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## Sample Exercise 17.10 Calculating $K_{sp}$ from Solubility

### Solution (Continued)

**Check:** We obtain a small value, as expected for a slightly soluble salt. Furthermore, the calculated value agrees well with the one given in Appendix D,  $1.2 \times 10^{-12}$ .

### Practice Exercise

A saturated solution of  $\text{Mg}(\text{OH})_2$  in contact with undissolved solid is prepared at  $25\text{ }^\circ\text{C}$ . The pH of the solution is found to be 10.17. Assuming that  $\text{Mg}(\text{OH})_2$  dissociates completely in water and that there are no other simultaneous equilibria involving the  $\text{Mg}^{2+}$  or  $\text{OH}^-$  ions in the solution, calculate  $K_{sp}$  for this compound.

**Answer:**  $1.6 \times 10^{-12}$

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## Sample Exercise 17.11 Calculating Solubility from $K_{sp}$

The  $K_{sp}$  for  $\text{CaF}_2$  is  $3.9 \times 10^{-11}$  at  $25^\circ\text{C}$ . Assuming that  $\text{CaF}_2$  dissociates completely upon dissolving and that there are no other important equilibria affecting its solubility, calculate the solubility of  $\text{CaF}_2$  in grams per liter.

### Solution

**Analyze:** We are given  $K_{sp}$  for  $\text{CaF}_2$  and are asked to determine solubility. Recall that the *solubility* of a substance is the quantity that can dissolve in solvent, whereas the *solubility-product constant*,  $K_{sp}$ , is an equilibrium constant.

**Plan:** We can approach this problem by using our standard techniques for solving equilibrium problems. We write the chemical equation for the dissolution process and set up a table of the initial and equilibrium concentrations. We then use the equilibrium constant expression. In this case we know  $K_{sp}$ , and so we solve for the concentrations of the ions in solution.

**Solve:** Assume initially that none of the salt has dissolved, and then allow  $x$  moles/liter of  $\text{CaF}_2$  to dissociate completely when equilibrium is achieved.

The stoichiometry of the equilibrium dictates that  $2x$  moles/liter of  $\text{F}^-$  are produced for each  $x$  moles/liter of  $\text{CaF}_2$  that dissolve. We now use the expression for  $K_{sp}$  and substitute the equilibrium concentrations to solve for the value of  $x$ :

	$\text{CaF}_2(s)$	$\rightleftharpoons$	$\text{Ca}^{2+}$	+	$2\text{F}^-(aq)$
Initial	—		0		0
Change	—		$+x\text{ M}$		$+2x\text{ M}$
Equilibrium	—		$x\text{ M}$		$2x\text{ M}$

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = (x)(2x)^2 = 4x^3 = 3.9 \times 10^{-11}$$

$$x = \sqrt[3]{\frac{3.9 \times 10^{-11}}{4}} = 2.1 \times 10^{-4}\text{ M}$$

## Sample Exercise 17.11 Calculating Solubility from $K_{sp}$

### Solution

(Remember that  $\sqrt[3]{y} = y^{1/3}$  to calculate the cube root of a number, you can use the  $yx$  function on your calculator, with  $x = \frac{1}{3}$ .) Thus, the molar solubility of  $\text{CaF}_2$  is  $2.1 \times 10^{-4}$  mol/L. The mass of  $\text{CaF}_2$  that dissolves in water to form a liter of solution is

$$\left(\frac{2.1 \times 10^{-4} \text{ mol CaF}_2}{1 \text{ L soln}}\right)\left(\frac{78.1 \text{ g CaF}_2}{1 \text{ mol CaF}_2}\right) = 1.6 \times 10^{-2} \text{ g CaF}_2/\text{L soln}$$

**Check:** We expect a small number for the solubility of a slightly soluble salt. If we reverse the calculation, we should be able to recalculate the solubility product:  $K_{sp} = (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 = 3.7 \times 10^{-11}$ , close to the starting value for  $K_{sp}$ ,  $3.9 \times 10^{-11}$ ,

**Comment:** Because  $\text{F}^-$  is the anion of a weak acid, you might expect that the hydrolysis of the ion would affect the solubility of  $\text{CaF}_2$ . The basicity of  $\text{F}^-$  is so small ( $K_b = 1.5 \times 10^{-11}$ ), however, that the hydrolysis occurs to only a slight extent and does not significantly influence the solubility. The reported solubility is 0.017 g/L at 25 °C, in good agreement with our calculation

### Practice Exercise

The  $K_{sp}$  for  $\text{LaF}_3$  is  $2 \times 10^{-19}$ . What is the solubility of  $\text{LaF}_3$  in water in moles per liter?

**Answer:**  $9 \times 10^{-6}$  mol/L

## Sample Exercise 17.12 Calculating the Effect of a Common Ion on Solubility

Calculate the molar solubility of  $\text{CaF}_2$  at  $25^\circ\text{C}$  in a solution that is (a)  $0.010\text{ M}$  in  $\text{Ca}(\text{NO}_3)_2$ , (b)  $0.010\text{ M}$  in  $\text{NaF}$ .

### Solution

**Analyze:** We are asked to determine the solubility of  $\text{CaF}_2$  in the presence of two strong electrolytes, each of which contains an ion common to  $\text{CaF}_2$ . In (a) the common ion is  $\text{Ca}^{2+}$ , and  $\text{NO}_3^-$  is a spectator ion. In (b) the common ion is  $\text{F}^-$ , and  $\text{Na}^+$  is a spectator ion.

**Plan:** Because the slightly soluble compound is  $\text{CaF}_2$ , we need to use the  $K_{sp}$  for this compound, which is available in Appendix D:

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = 3.9 \times 10^{-11}$$

The value of  $K_{sp}$  is unchanged by the presence of additional solutes. Because of the common-ion effect, however, the solubility of the salt will decrease in the presence of common ions. We can again use our standard equilibrium techniques of starting with the equation for  $\text{CaF}_2$  dissolution, setting up a table of initial and equilibrium concentrations, and using the  $K_{sp}$  expression to determine the concentration of the ion that comes only from  $\text{CaF}_2$ .

**Solve:** (a) In this instance the initial concentration of  $\text{Ca}^{2+}$  is  $0.010\text{ M}$  because of the dissolved  $\text{Ca}(\text{NO}_3)_2$ :

	$\text{CaF}_2(\text{s})$	$\rightleftharpoons$	$\text{Ca}^{2+}(\text{aq})$	+	$2\text{F}^{-}(\text{aq})$
Initial	—		$0.010\text{ M}$		0
Change	—		$+x\text{ M}$		$+2x\text{ M}$
Equilibrium	—		$(0.010 + x)\text{ M}$		$2x\text{ M}$

Substituting into the solubility-product expression gives

$$K_{sp} = 3.9 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2 = (0.010 + x)(2x)^2$$

## Sample Exercise 17.12 Calculating the Effect of a Common Ion on Solubility

### Solution (Continued)

This would be a messy problem to solve exactly, but fortunately it is possible to simplify matters greatly. Even without the common-ion effect, the solubility of  $\text{CaF}_2$  is very small ( $2.1 \times 10^{-4} \text{ M}$ ). Thus, we assume that the  $0.010 \text{ M}$  concentration of  $\text{Ca}^{2+}$  from  $\text{Ca}(\text{NO}_3)_2$  is very much greater than the small additional concentration resulting from the solubility of  $\text{CaF}_2$ ; that is,  $x$  is small compared to  $0.010 \text{ M}$ , and  $0.010 + x \approx 0.010$ .

We then have

$$\begin{aligned} 3.9 \times 10^{-11} &= (0.010)(2x)^2 \\ x^2 &= \frac{3.9 \times 10^{-11}}{4(0.010)} = 9.8 \times 10^{-10} \\ x &= \sqrt{9.8 \times 10^{-10}} = 3.1 \times 10^{-5} \text{ M} \end{aligned}$$

The very small value for  $x$  validates the simplifying assumption we have made. Our calculation indicates that  $3.1 \times 10^{-5} \text{ mol}$  of solid  $\text{CaF}_2$  dissolves per liter of the  $0.010 \text{ M}$   $\text{Ca}(\text{NO}_3)_2$  solution.

(b) In this case the common ion is  $\text{F}^-$ , and at equilibrium we have

$$[\text{Ca}^{2+}] = x \quad \text{and} \quad [\text{F}^-] = 0.010 + 2x$$

Assuming that  $2x$  is small compared to  $0.010 \text{ M}$  (that is,  $0.010 + 2x \approx 0.010$ ), we have

$$\begin{aligned} 3.9 \times 10^{-11} &= x(0.010)^2 \\ x &= \frac{3.9 \times 10^{-11}}{(0.010)^2} = 3.9 \times 10^{-7} \text{ M} \end{aligned}$$

Thus,  $3.9 \times 10^{-7} \text{ mol}$  of solid  $\text{CaF}_2$  should dissolve per liter of  $0.010 \text{ M}$   $\text{NaF}$  solution.

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## Sample Exercise 17.12 Calculating the Effect of a Common Ion on Solubility

### Solution (Continued)

**Comment:** The molar solubility of  $\text{CaF}_2$  in pure water is  $2.1 \times 10^{-4} M$  (Sample Exercise 17.11). By comparison, our calculations above show that the solubility of  $\text{CaF}_2$  in the presence of  $0.010 M \text{Ca}^{2+}$  is  $3.1 \times 10^{-5} M$ , and in the presence of  $0.010 M \text{F}^-$  ion it is  $3.9 \times 10^{-7} M$ . Thus, the addition of either  $\text{Ca}^{2+}$  or  $\text{F}^-$  to a solution of  $\text{CaF}_2$  decreases the solubility. However, the effect of  $\text{F}^-$  on the solubility is more pronounced than that of  $\text{Ca}^{2+}$  because  $[\text{F}^-]$  appears to the second power in the  $K_{sp}$  expression for  $\text{CaF}_2$ , whereas  $\text{Ca}^{2+}$  appears to the first power.

### Practice Exercise

The value for  $K_{sp}$  for manganese(II) hydroxide,  $\text{Mn}(\text{OH})_2$ , is  $1.6 \times 10^{-13}$ . Calculate the molar solubility of  $\text{Mn}(\text{OH})_2$  in a solution that contains  $0.020 M \text{NaOH}$ .

**Answer:**  $4.0 \times 10^{-10} M$

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## Sample Exercise 17.13 Predicting the Effect of Acid on Solubility

Which of the following substances will be more soluble in acidic solution than in basic solution:

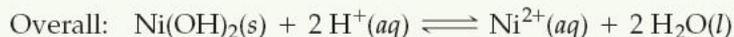
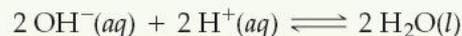
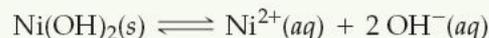
(a)  $\text{Ni}(\text{OH})_2(\text{s})$ , (b)  $\text{CaCO}_3(\text{s})$ , (c)  $\text{BaF}_2(\text{s})$ , (d)  $\text{AgCl}(\text{s})$ ?

### Solution

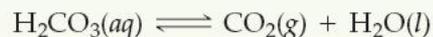
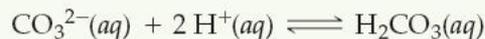
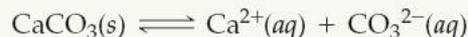
**Analyze:** The problem lists four sparingly soluble salts, and we are asked to determine which will be more soluble at low pH than at high pH.

**Plan:** Ionic compounds that dissociate to produce a basic anion will be more soluble in acid solution.

(a)  $\text{Ni}(\text{OH})_2(\text{s})$  will be more soluble in acidic solution because of the basicity of  $\text{OH}^-$ ; the  $\text{H}^+$  ion reacts with the  $\text{OH}^-$  ion, forming water.

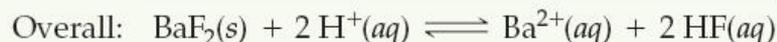
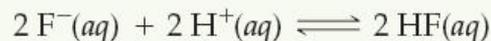
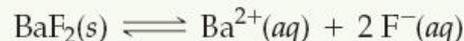


(b) Similarly,  $\text{CaCO}_3(\text{s})$  dissolves in acid solutions because  $\text{CO}_3^{2-}$  is a basic anion.



The reaction between  $\text{CO}_3^{2-}$  and  $\text{H}^+$  occurs in a stepwise fashion, first forming  $\text{HCO}_3^-$ .  $\text{H}_2\text{CO}_3$  forms in appreciable amounts only when the concentration of  $\text{H}^+$  is sufficiently high.

(c) The solubility of  $\text{BaF}_2$  is also enhanced by lowering the pH, because  $\text{F}^-$  is a basic anion.



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## Sample Exercise 17.13 Predicting the Effect of Acid on Solubility

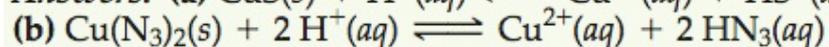
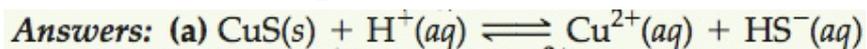
### Solution

(d) The solubility of AgCl is unaffected by changes in pH because Cl<sup>-</sup> is the anion of a strong acid and therefore has negligible basicity.

### Practice Exercise

Write the net ionic equation for the reaction of the following copper(II) compounds with acid:

(a) CuS, (b) Cu(N<sub>3</sub>)<sub>2</sub>.



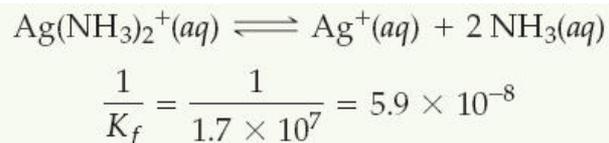
## Sample Exercise 17.14 Evaluating an Equilibrium Involving a Complex Ion

Calculate the concentration of  $\text{Ag}^+$  present in solution at equilibrium when concentrated ammonia is added to a  $0.010\text{ M}$  solution of  $\text{AgNO}_3$  to give an equilibrium concentration of  $[\text{NH}_3] = 0.20\text{ M}$ . Neglect the small volume change that occurs when  $\text{NH}_3$  is added.

### Solution

**Analyze:** When  $\text{NH}_3(\text{aq})$  is added to  $\text{Ag}^+(\text{aq})$ , a reaction occurs forming  $\text{Ag}(\text{NH}_3)_2^+$  as shown in Equation 17.22. We are asked to determine what concentration of  $\text{Ag}^+(\text{aq})$  will remain uncombined when the  $\text{NH}_3$  concentration is brought to  $0.20\text{ M}$  in a solution originally  $0.010\text{ M}$  in  $\text{AgNO}_3$ .

**Plan:** We first assume that the  $\text{AgNO}_3$  is completely dissociated, giving  $0.010\text{ M}$   $\text{Ag}^+$ . Because  $K_f$  for the formation of  $\text{Ag}(\text{NH}_3)_2^+$  is quite large, we assume that essentially all the  $\text{Ag}^+$  is then converted to  $\text{Ag}(\text{NH}_3)_2^+$  and approach the problem as though we are concerned with the *dissociation* of  $\text{Ag}(\text{NH}_3)_2^+$  rather than its *formation*. To facilitate this approach, we will need to reverse the equation to represent the formation of  $\text{Ag}^+$  and  $\text{NH}_3$  from  $\text{Ag}(\text{NH}_3)_2^+$  and also make the corresponding change to the equilibrium constant.



**Solve:** If  $[\text{Ag}^+]$  is  $0.010\text{ M}$  initially, then  $[\text{Ag}(\text{NH}_3)_2^+]$  will be  $0.010\text{ M}$  following addition of the  $\text{NH}_3$ . We now construct a table to solve this equilibrium problem. Note that the  $\text{NH}_3$  concentration given in the problem is an *equilibrium* concentration rather than an initial concentration.

	$\text{Ag}(\text{NH}_3)_2^+(\text{aq})$	$\rightleftharpoons$	$\text{Ag}^+(\text{aq})$	+	$2\text{NH}_3(\text{aq})$
Initial	$0.010\text{ M}$		$0\text{ M}$		
Change	$-x\text{ M}$		$+x\text{ M}$		
Equilibrium	$0.010 - x\text{ M}$		$x\text{ M}$		$0.20\text{ M}$

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## Sample Exercise 17.14 Evaluating an Equilibrium Involving a Complex Ion

### Solution (Continued)

Because the concentration of  $\text{Ag}^+$  is very small, we can ignore  $x$  in comparison with 0.010. Thus,  $0.010 - x \approx 0.010 \text{ M}$ . Substituting these values into the equilibrium constant expression for the dissociation of  $\text{Ag}(\text{NH}_3)_2^+$ , we obtain

$$\frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = \frac{(x)(0.20)^2}{0.010} = 5.9 \times 10^{-8}$$

Solving for  $x$ , we obtain  $x = 1.5 \times 10^{-8} \text{ M} = [\text{Ag}^+]$ . Thus, formation of the  $\text{Ag}(\text{NH}_3)_2^+$  complex drastically reduces the concentration of free  $\text{Ag}^+$  ion in solution.

### Practice Exercise

Calculate  $[\text{Cr}^{3+}]$  in equilibrium with  $\text{Cr}(\text{OH})_4^-$  when 0.010 mol of  $\text{Cr}(\text{NO}_3)_3$  is dissolved in a liter of solution buffered at pH 10.0.

**Answer:**  $1 \times 10^{-16} \text{ M}$

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## Sample Exercise 17.15 Predicting Whether a Precipitate Will Form

Will a precipitate form when 0.10 L of  $8.0 \times 10^{-3} \text{ M Pb(NO}_3)_2$  is added to 0.40 L of  $5.0 \times 10^{-3} \text{ M Na}_2\text{SO}_4$ ?

### Solution

**Analyze:** The problem asks us to determine whether a precipitate will form when two salt solutions are combined.

**Plan:** We should determine the concentrations of all ions immediately upon mixing of the solutions and compare the value of the

reaction quotient,  $Q$ , to the solubility-product constant,  $K_{sp}$ , for any potentially insoluble product. The possible metathesis products are  $\text{PbSO}_4$  and  $\text{NaNO}_3$ . Sodium salts are quite soluble;  $\text{PbSO}_4$  has a  $K_{sp}$  of  $6.3 \times 10^{-7}$  (Appendix D), however, and will precipitate if the  $\text{Pb}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations are high enough for  $Q$  to exceed  $K_{sp}$  for the salt.

**Solve:** When the two solutions are mixed, the total volume becomes  $0.10 \text{ L} + 0.40 \text{ L} = 0.50 \text{ L}$ . The number of moles of  $\text{Pb}^{2+}$  in 0.10 L of  $8.0 \times 10^{-3} \text{ M Pb(NO}_3)_2$  is

$$(0.10 \text{ L}) \left( 8.0 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) = 8.0 \times 10^{-4} \text{ mol}$$

$$[\text{Pb}^{2+}] = \frac{8.0 \times 10^{-4} \text{ mol}}{0.50 \text{ L}} = 1.6 \times 10^{-3} \text{ M}$$

The concentration of  $\text{Pb}^{2+}$  in the 0.50-L mixture is therefore  
The number of moles of  $\text{SO}_4^{2-}$  in 0.40 L of  $5.0 \times 10^{-3} \text{ M Na}_2\text{SO}_4$  is

$$(0.40 \text{ L}) \left( 5.0 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right) = 2.0 \times 10^{-3} \text{ mol}$$

$$[\text{SO}_4^{2-}] = \frac{2.0 \times 10^{-3} \text{ mol}}{0.50 \text{ L}} = 4.0 \times 10^{-3} \text{ M}$$

Therefore,  $[\text{SO}_4^{2-}]$  in the 0.50-L mixture is

We then have

$$Q = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (1.6 \times 10^{-3})(4.0 \times 10^{-3}) = 6.4 \times 10^{-6}$$

Because  $Q > K_{sp}$ ,  $\text{PbSO}_4$  will precipitate.

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## Sample Exercise 17.15 Predicting Whether a Precipitate Will Form

### Practice Exercise

Will a precipitate form when 0.050 L of  $2.0 \times 10^{-2} M$  NaF is mixed with 0.010 L of  $1.0 \times 10^{-2} M$   $\text{Ca}(\text{NO}_3)_2$ ?

**Answer:** Yes,  $\text{CaF}_2$  precipitates because  $Q = 4.6 \times 10^{-8}$  is larger than  $K_{sp} = 3.9 \times 10^{-11}$

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## Sample Exercise 17.16 Calculating Ion Concentrations for Precipitation

A solution contains  $1.0 \times 10^{-2} M$   $\text{Ag}^+$  and  $2.0 \times 10^{-2} M$   $\text{Pb}^{2+}$ . When  $\text{Cl}^-$  is added to the solution, both  $\text{AgCl}$  ( $K_{sp} = 1.8 \times 10^{-10}$ ) and  $\text{PbCl}_2$  ( $K_{sp} = 1.7 \times 10^{-5}$ ) precipitate from the solution. What concentration of  $\text{Cl}^-$  is necessary to begin the precipitation of each salt? Which salt precipitates first?

### Solution

**Analyze:** We are asked to determine the concentration of  $\text{Cl}^-$  necessary to begin the precipitation from a solution containing  $\text{Ag}^+$  and  $\text{Pb}^{2+}$ , and to predict which metal chloride will begin to precipitate first.

**Plan:** We are given  $K_{sp}$  values for the two possible precipitates. Using these and the metal ion concentrations, we can calculate what concentration of  $\text{Cl}^-$  ion would be necessary to begin precipitation of each. The salt requiring the lower  $\text{Cl}^-$  ion concentration will precipitate first.

**Solve:** For  $\text{AgCl}$  we have

Because  $[\text{Ag}^+] = 1.0 \times 10^{-2} M$ , the greatest concentration of  $\text{Cl}^-$  that can be present without causing precipitation of  $\text{AgCl}$  can be calculated from the  $K_{sp}$  expression

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$K_{sp} = [1.0 \times 10^{-2}][\text{Cl}^-] = 1.8 \times 10^{-10}$$
$$[\text{Cl}^-] = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.8 \times 10^{-8} M$$

Any  $\text{Cl}^-$  in excess of this very small concentration will cause  $\text{AgCl}$  to precipitate from solution. Proceeding similarly for  $\text{PbCl}_2$ , we have

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}$$
$$[2.0 \times 10^{-2}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}$$
$$[\text{Cl}^-]^2 = \frac{1.7 \times 10^{-5}}{2.0 \times 10^{-2}} = 8.5 \times 10^{-4}$$
$$[\text{Cl}^-] = \sqrt{8.5 \times 10^{-4}} = 2.9 \times 10^{-2} M$$

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## Sample Exercise 17.16 Calculating Ion Concentrations for Precipitation

### Solution (Continued)

Thus, a concentration of  $\text{Cl}^-$  in excess of  $2.9 \times 10^{-2} M$  will cause  $\text{PbCl}_2$  to precipitate.

Comparing the concentrations of  $\text{Cl}^-$  required to precipitate each salt, we see that as  $\text{Cl}^-$  is added to the solution,  $\text{AgCl}$  will precipitate first because it requires a much smaller concentration of  $\text{Cl}^-$ . Thus,  $\text{Ag}^+$  can be separated from by slowly adding  $\text{Cl}^-$  so  $[\text{Cl}^-]$  is between  $1.8 \times 10^{-8} M$  and  $2.9 \times 10^{-2} M$ .

### Practice Exercise

A solution consists of  $0.050 M \text{Mg}^{2+}$  and  $0.020 M \text{Cu}^{2+}$ . Which ion will precipitate first as  $\text{OH}^-$  is added to the solution? What concentration of  $\text{OH}^-$  is necessary to begin the precipitation of each cation? [ $K_{sp} = 1.8 \times 10^{-11}$  for  $\text{Mg}(\text{OH})_2$ , and  $K_{sp} = 4.8 \times 10^{-20}$  for  $\text{Cu}(\text{OH})_2$ .]

**Answer:**  $\text{Cu}(\text{OH})_2$  precipitates first.  $\text{Cu}(\text{OH})_2$  begins to precipitate when  $[\text{OH}^-]$  exceeds  $1.5 \times 10^{-9} M$ ;  $\text{Mg}(\text{OH})_2$  begins to precipitate when  $[\text{OH}^-]$  exceeds  $1.9 \times 10^{-5} M$ .

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## Sample Integrative Exercise Putting Concepts Together

A sample of 1.25 L of HCl gas at 21 °C and 0.950 atm is bubbled through 0.500 L of 0.150 M NH<sub>3</sub> solution. Calculate the pH of the resulting solution assuming that all the HCl dissolves and that the volume of the solution remains 0.500 L.

### Solution

The number of moles of HCl gas is calculated from the ideal-gas law.

$$n = \frac{PV}{RT} = \frac{(0.950 \text{ atm})(1.25 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(294 \text{ K})} = 0.0492 \text{ mol HCl}$$

The number of moles of NH<sub>3</sub> in the solution is given by the product of the volume of the solution and its concentration.

$$\text{Moles NH}_3 = (0.500 \text{ L})(0.150 \text{ mol NH}_3/\text{L}) = 0.0750 \text{ mol NH}_3$$

The acid HCl and base NH<sub>3</sub> react, transferring a proton from HCl to NH<sub>3</sub>, producing NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> ions.



To determine the pH of the solution, we first calculate the amount of each reactant and each product present at the completion of the reaction.

	HCl(g)	+ NH <sub>3</sub> (aq)	→ NH <sub>4</sub> <sup>+</sup> (aq)	+ Cl <sup>-</sup> (aq)
Before addition	0.0492 mol	0 mol	0 mol	0 mol
Addition		0.0750 mol		
After addition	0 mol	0.0258 mol	0.0492 mol	0.0492 mol

## Sample Integrative Exercise Putting Concepts Together

### Solution (Continued)

Thus, the reaction produces a solution containing a mixture of  $\text{NH}_3$ ,  $\text{NH}_4^+$ , and  $\text{Cl}^-$ . The  $\text{NH}_3$  is a weak base ( $K_b = 1.8 \times 10^{-5}$ ),  $\text{NH}_4^+$  is its conjugate acid, and  $\text{Cl}^-$  is neither acidic nor basic. Consequently, the pH depends on  $[\text{NH}_3]$  and  $[\text{NH}_4^+]$ .

$$[\text{NH}_3] = \frac{0.0258 \text{ mol NH}_3}{0.500 \text{ L soln}} = 0.0516 \text{ M}$$
$$[\text{NH}_4^+] = \frac{0.0492 \text{ mol NH}_4^+}{0.500 \text{ L soln}} = 0.0984 \text{ M}$$

We can calculate the pH using either  $K_b$  for  $\text{NH}_3$  or  $K_a$  for  $\text{NH}_4^+$ . Using the  $K_b$  expression, we have



Initial	0.0516 M	—	0.0984 M	0
Change	$-x \text{ M}$	—	$+x \text{ M}$	$+x \text{ M}$
Equilibrium	$(0.0516 - x) \text{ M}$	—	$(0.0984 + x) \text{ M}$	$x \text{ M}$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.0984 + x)(x)}{(0.0516 - x)} \approx \frac{(0.0984)x}{0.0516} = 1.8 \times 10^{-5}$$

$$x = [\text{OH}^-] = \frac{(0.0516)(1.8 \times 10^{-5})}{0.0984} = 9.4 \times 10^{-6} \text{ M}$$

Hence,  $\text{pOH} = -\log(9.4 \times 10^{-6}) = 5.03$  and  $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.03 = 8.97$ .

Hence,  $\text{pOH} = -\log(9.4 \times 10^{-6}) = 5.03$  and  $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.03 = 8.97$ .