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Chapter 16

Acid-Base Equilibria and Solubility Equilibria

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1

Common Ion Effect

The ***common ion effect*** is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

The presence of a common ion **suppresses** the ionization of a weak acid or a weak base.

Consider mixture of CH_3COONa (strong electrolyte) and CH_3COOH (weak acid).
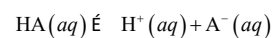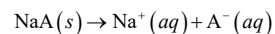
$$CH_3COONa(s) \rightarrow Na^+(aq) + CH_3COO^-(aq)$$

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$
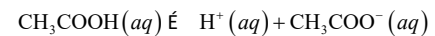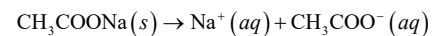
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Henderson-Hasselbalch Equation

Consider mixture of salt NaA and weak acid HA.

$$NaA(s) \rightarrow Na^+(aq) + A^-(aq)$$
$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

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

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

Henderson-Hasselbalch equation

$$-\log[H^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$-\log[H^+] = -\log K_a + \log\frac{[A^-]}{[HA]}$$

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

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \qquad pK_a = -\log K_a$$

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Example 16.1 [1]

(a) Calculate the pH of a 0.20 M CH₃COOH solution.

(b) What is the pH of a solution containing both 0.20 M CH₃COOH and 0.30 M CH₃COONa? The K_a of CH₃COOH is 1.8×10^{-5}.

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Example 16.1 [2]

Strategy

a) We calculate $[H^+]$ and hence the pH of the solution by following the procedure in Example 15.8.

b) CH_3COOH is a weak acid $(CH_3COOH \leftrightarrow CH_3COO^- + H^+)$, and CH_3COONa is a soluble salt that is completely dissociated in solution $(CH_3COONa \rightarrow Na^+ + CH_3COO^-)$.

The common ion here is the acetate ion, CH_3COO^-. At equilibrium, the major species in solution are CH_3COOH, CH_3COO^-, Na^+, H^+, and H_2O. The Na^+ ion has no acid or base properties and we ignore the ionization of water. Because K_a is an equilibrium constant, its value is the same whether we have just the acid or a mixture of the acid and its salt in solution. Therefore, we can calculate $[H^+]$ at equilibrium and hence pH if we know both CH_3COOH and $[CH_3COO^-]$ at equilibrium.

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Example 16.1 [3]

Solution

a) In this case, the changes are

$$CH_3COOH(aq) \leftrightarrow H^+(aq) + CH_3COO^-(aq)$$

	CH_3COOH	H^+	CH_3COO^-
Initial (*M*):	0.20	0	0
Change (*M*):	–*x*	+*x*	+*x*
Equilibrium (*M*):	0.20 – *x*	*x*	*x*

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

$$1.8\times10^{-5} = \frac{x^2}{0.20 - x}$$

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Example 16.1 [4]

Assuming $0.20 - x \approx 0.20$, we obtain

$$1.8 \times 10^{-5} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

or

$$x = \left[H^+ \right] = 1.9 \times 10^{-3}\ M$$

Thus,

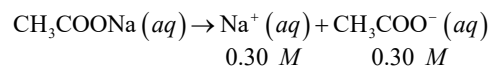$$pH = -\log\left(1.9 \times 10^{-3}\right) = \mathbf{2.72}$$

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Example 16.1 [5]

Sodium acetate is a strong electrolyte, so it dissociates completely in solution:

$$CH_3COONa\left(aq\right) \rightarrow Na^+\left(aq\right) + CH_3COO^-\left(aq\right)$$
$$0.30\ M \qquad 0.30\ M$$

The initial concentrations, changes, and final concentrations of the species involved in the equilibrium are

$$CH_3COOH\left(aq\right) \leftrightarrow H^+\left(aq\right) + CH_3COO^-\left(aq\right)$$
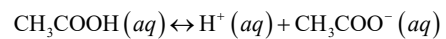
	CH_3COOH	H^+	CH_3COO^-
Initial (M):	0.20	0	0.30
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$0.20 - x$	x	$0.30 + x$

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Example 16.1 ₆

From Equation (16.1),

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

$$1.8 \times 10^{-5} = \frac{(x)(0.30+x)}{0.20-x}$$

Assuming that $0.30 + x \approx 0.30$ and $0.20 - x \approx 0.20,$ we obtain

$$1.8 \times 10^{-5} = \frac{(x)(0.30+x)}{0.20-x} \approx \frac{(x)(0.30)}{0.20}$$

or

$$x = \left[H^+\right] = 1.2 \times 10^{-5}\ M$$

Thus,

$$pH = -\log\left[H^+\right]$$

$$= -\log(1.2 \times 10^{-5}) = \mathbf{4.92}$$

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Example 16.1 ₇

Check

Comparing the results in (a) and (b), we see that when the common ion (CH_3COO^-) is present, according to Le Châtelier's principle, the equilibrium shifts from right to left. This action decreases the extent of ionization of the weak acid.

Consequently, fewer H^+ ions are produced in (b) and the pH of the solution is higher than that in (a). As always, you should check the validity of the assumptions.

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Buffers

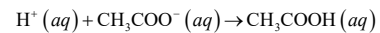A *buffer solution* is a solution of:

1. A weak acid or a weak base **and**

2. The salt of the weak acid or weak base

Both must be present!

A buffer solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base. Consider an equal molar mixture of CH_3COOH and CH_3COONa

Add strong acid

$$H^+(aq) + CH_3COO^-(aq) \rightarrow CH_3COOH(aq)$$

Add strong base

$$OH^-(aq) + CH_3COOH(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

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Example 16.2 [1]

Which of the following solutions can be classified as buffer systems?

(*a*) KH_2PO_4/H_3PO_4

(*b*) $NaClO_4/HClO_4$

(*c*) C_5H_5N/C_5H_5NHCl (C_5H_5N is pyridine; its K_b is given in table 15.4)

Explain your answer.

12

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Example 16.2 ₂

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?

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Example 16.2 ₃

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) H_3PO_4 is a weak acid, and its conjugate base, $H_2PO_4^-$ is a weak base (see Table 15.5). Therefore, this is a buffer system.

b) Because $HClO_4$ is a strong acid, its conjugate base, ClO_4^- is an extremely weak base. This means that the ClO_4^- ion will not combine with a H^+ ion in solution to form $HClO_4$. Thus, the system cannot act as a buffer system.

c) As Table 15.4 shows, C_5H_5N is a weak base and its conjugate acid, $C_5H_5NH^+$ (the cation of the salt C_5H_5NHCl), is a weak acid. Therefore, this is a buffer system.

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Example 16.3 1

a) Calculate the pH of a buffer system containing 1.0 M CH_3COOH and 1.0 M CH_3COONa.

b) What is the pH of the buffer system after the addition of 0.10 mole of gaseous HCl to 1.0 L of the solution? Assume that the volume of the solution does not change when the HCl is added.

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Example 16.3 2

Strategy

a) The pH of the buffer system before the addition of HCl can be calculated with the procedure described in Example 16.1, because it is similar to the common ion problem. The K_a of CH_3COOH is 1.8×10^{-5} (see Table 15.3).

b) The reaction describing the buffer action, in this case, is $CH_3COOH^- + H^+ \rightarrow CH_3COOH$.

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Example 16.3 [3]

Solution

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

$$CH_3COOH(aq) \leftrightarrow H^+(aq) + CH_3COO^-(aq)$$

	$CH_3COOH(aq) \leftrightarrow H^+(aq) + CH_3COO^-(aq)$		
Initial (*M*):	1.0	0	1.0
Change (*M*):	–*x*	+*x*	+*x*
Equilibrium (*M*):	1.0 – *x*	*x*	1.0 + *x*

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

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

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Example 16.3 [4]

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

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

Thus,

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

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Example 16.3 [5]

b) When HCl is added to the solution, the initial changes are

	$HCl(aq)$	$\rightarrow$	$H^+(aq)$	$Cl^-(aq)$
Initial (mol):	0.10		0	0
Change (mol):	−0.10		+0.10	+0.10
Final (mol):	0		0.10	0.10

The Cl^- ion is a spectator ion in solution because it is the conjugate base of a strong acid. The H^+ ions provided by the strong acid HCl react completely with the conjugate base of the buffer, which is CH_3COO^-. 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.

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Example 16.3 [6]

The neutralization reaction is summarized next:

	$CH_3COO^-(aq)$	$+ H^+(aq)$	$\rightarrow CH_3COOH(aq)$
Initial (mol):	1.0	0.10	1.0
Change (mol):	−0.10	−0.10	+0.10
Final (mol):	0.9	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.

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Example 16.3 [7]

$$CH_3COOH\,(aq) \leftrightarrow H^+\,(aq) + CH_3COO^-\,(aq)$$

	CH_3COOH	H^+	CH_3COO^-
Initial (M):	1.1	0	0.90
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$1.1 - x$	x	$0.90 + x$

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

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

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Example 16.3 [8]

Assuming $0.90 + x \approx 0.09$ 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,

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

Check

The pH decreases by only a small amount upon the addition of HCl. This is consistent with the action of a buffer solution.

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Addition of a Strong Acid to a Buffer
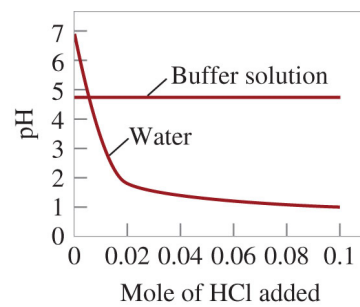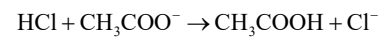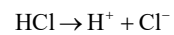
$$HCl \rightarrow H^+ + Cl^-$$

$$HCl + CH_3COO^- \rightarrow CH_3COOH + Cl^-$$

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Example 16.4 [1]

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

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Example 16.4 2

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 ≈ pK_a,

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

or

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

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Example 16.4 3

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).

$$H_3PO_4\,(aq) \rightleftharpoons H^+\,(aq) + H_2PO_4^-\,(aq)\quad K_{a_1} = 7.5 \times 10^{-3};\, pK_{a_1} = 2.21$$

$$H_2PO_4^-\,(aq) \rightleftharpoons H^+\,(aq) + HPO_4^{2-}\,(aq)\quad K_{a_2} = 6.2 \times 10^{-8};\, pK_{a_2} = 7.21$$

$$HPO_4^{2-}\,(aq) \rightleftharpoons H^+\,(aq) + PO_4^{3-}\,(aq)\quad K_{a_3} = 4.8 \times 10^{-13};\, pK_{a_3} = 12.32$$
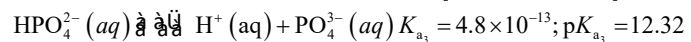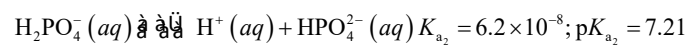
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Example 16.4 4

The most suitable of the three buffer systems is $HPO_4^{2-}/H_2PO_4^-$, because the pK_a of the acid $H_2PO_4^-$ is closest to the desired pH.

From the Henderson-Hasselbalch equation we write

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

$$7.40 = 7.21 + \log \frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]}$$

$$\log \frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = 0.19$$

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Example 16.4 5

Taking the antilog, we obtain

$$\frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = 10^{0.19} = 1.5$$

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

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Titrations (Review)

In a ***titration***, a solution of accurately known concentration is gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

Equivalence point *– the point at which the reaction is complete*

Indicator *– substance that changes color at (or near) the equivalence point*

Slowly add base
to unknown acid
UNTIL
the indicator
changes color
(**pink**)

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Alternative Method of Equivalence Point Detection

monitor pH

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Strong Acid-Strong Base Titrations

$$NaOH(aq) + HCl(aq) \rightarrow H_2O(l) + NaCl(aq)$$

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Equivalence point
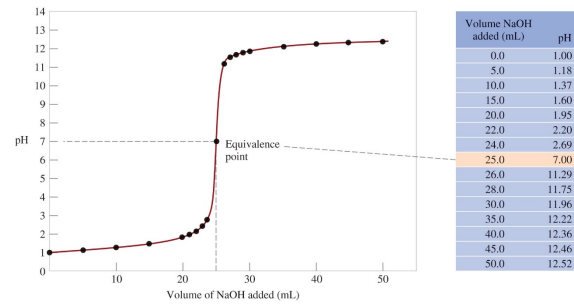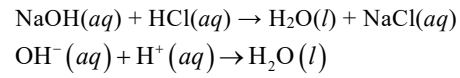
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Chemistry In Action: Maintaining the pH of Blood

Red blood cells in a capillary

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Weak Acid-Strong Base Titrations

$$CH_3COOH\,(aq) + NaOH\,(aq) \rightarrow CH_3COONa\,(aq) + H_2O\,(l)$$

$$CH_3COOH\,(aq) + OH^-\,(aq) \rightarrow CH_3COO^-\,(aq) + H_2O\,(l)$$

At equivalence point (pH > 7):
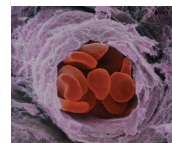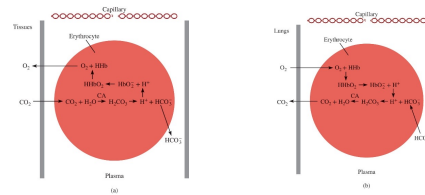
$$CH_3COO^-\,(aq) + H_2O\,(l) \leftrightarrow OH^-\,(aq) + CH_3COOH\,(aq)$$

Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

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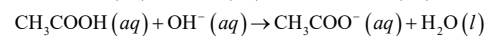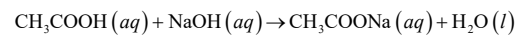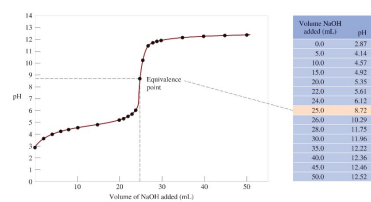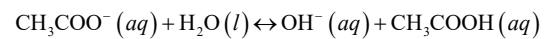
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Example 16.5 [1]

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid by sodium hydroxide after the addition to the acid solution of

a) 10.0 mL of 0.100 M NaOH

b) 25.0 mL of 0.100 M NaOH

c) 35.0 mL of 0.100 M NaOH

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Example 16.5 ₂

Strategy

The reaction between CH_3COOH and NaOH is

$$CH_3COOH\ (aq) + NaOH\ (aq) \rightarrow CH_3COONa\ (aq) + H_2O\ (l)$$
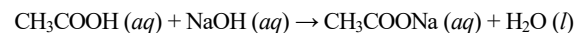
We see that 1 mol CH_3COOH = 1 mol NaOH. Therefore, at every stage of the titration we can calculate the number of moles of base reacting with the acid, and the pH of the

solution is determined by the excess acid or base left over. At the equivalence point, however, the neutralization is complete and the pH of the solution will depend on the extent of the hydrolysis of the salt formed, which is CH_3COONa.

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Example 16.5 ₃

Solution

a) The number of moles of NaOH in 10.0 mL is

$$10.0\ mL \times \frac{0.100\ mol\ NaOH}{1L\ NaOH\ soln} \times \frac{1L}{1000\ mL} = 1.00 \times 10^{-3}\ mol$$

The number of moles of CH_3COOH originally present in 25.0 mL of solution is

$$25.0\ mL \times \frac{0.100\ mol\ CH_3COOH}{1\ L\ CH_3COOH\ soln} \times \frac{1\ L}{1000\ mL} = 2.50 \times 10^{-3}\ mol$$

We work with moles at this point because when two solutions are mixed, the solution volume increases. As the volume increases, molarity will change but the number of moles will remain the same.

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Example 16.5 [4]

The changes in number of moles are summarized next:

$$CH_3COOH\ (aq) + NaOH\ (aq) \rightarrow CH_3COONa\ (aq) + H_2O\ (l)$$
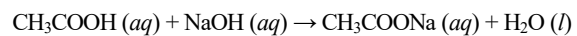
Initial (mol):	2.50×10^{-3}	1.00×10^{-3}	0
Change (mol):	-1.00×10^{-3}	-1.00×10^{-3}	$+1.00 \times 10^{-3}$
Final (mol):	1.50×10^{-3}	0	1.00×10^{-3}

At this stage we have a buffer system made up of CH_3COOH and CH_3COO^- (from the salt, CH_3COONa)

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Example 16.5 [5]

To calculate the pH of the solution, we write

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

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

$$= \frac{(1.50 \times 10^{-3})(1.8 \times 10^{-5})}{1.00 \times 10^{-3}} = 2.7 \times 10^{-5}\ M$$

Therefore,

$$pH = -\log(2.7 \times 10^{-5}) = \textbf{4.57}$$

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Example 16.5 [6]

b) These quantities (that is, 25.0 mL of 0.100 M NaOH reacting with 25.0 mL of 0.100 M CH$_3$COOH) correspond to the equivalence point. The number of moles of NaOH in 25.0 mL of the solution is

$$25.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.50 \times 10^{-3} \text{ mol}$$

The changes in number of moles are summarized next:
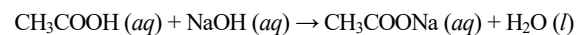
$$CH_3COOH \ (aq) + NaOH \ (aq) \rightarrow CH_3COONa \ (aq) + H_2O \ (l)$$

	CH$_3$COOH	NaOH	CH$_3$COONa
Initial (mol):	2.50×10^{-3}	2.50×10^{-3}	0
Change (mol):	-2.50×10^{-3}	-2.50×10^{-3}	$+2.50 \times 10^{-3}$
Final (mol):	0	0	2.50×10^{-3}

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Example 16.5 [7]

At the equivalence point, the concentrations of both the acid and the base are zero. The total volume is (25.0 + 25.0) mL or 50.0 mL, so the concentration of the salt is

$$[CH_3COONa] = \frac{2.50 \times 10^{-3} \text{ mol}}{50.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

$$= 0.0500 \text{ mol/L} = 0.0500 \ M$$

The next step is to calculate the pH of the solution that results from the hydrolysis of the CH$_3$COO$^-$ ions.

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Example 16.5 [8]

Following the procedure described in Example 15.13 and looking up the base ionization constant (K_b) for CH_3COO^- in Table 15.3, we write

$$K_b = 5.6 \times 10^{-10} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{x^2}{0.0500 - x}$$

$$x = [OH^-] = 5.3 \times 10^{-6} \, M, \, pH = \mathbf{8.72}$$

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Example 16.5 [9]

c) After the addition of 35.0 mL of NaOH, the solution is well past the equivalence point. The number of moles of NaOH originally present is

$$35.0 \, mL \times \frac{0.100 \, mol \, NaOH}{1 \, L \, NaOH \, soln} \times \frac{1 \, L}{1000 \, mL} = 3.50 \times 10^{-3} \, mol$$

The changes in number of moles are summarized next:

$$CH_3COOH \, (aq) + NaOH \, (aq) \rightarrow CH_3COONa \, (aq) + H_2O \, (l)$$
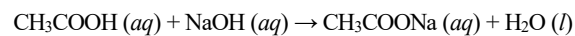
	CH_3COOH	$NaOH$	CH_3COONa
Initial (mol):	2.50×10^{-3}	3.50×10^{-3}	0
Change (mol):	-2.50×10^{-3}	-2.50×10^{-3}	$+2.50 \times 10^{-3}$
Final (mol):	0	1.00×10^{-3}	2.50×10^{-3}

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Example 16.5 [10]

At this stage we have two species in solution that are responsible for making the solution basic: OH^- and CH_3COO^- (from CH_3COONa). However, because OH^- is a much stronger base than CH_3COO^-, we can safely neglect the hydrolysis of the CH_3COO^- ions and calculate the pH of the solution using only the concentration of the OH^- ions. The total volume of the combined solutions is (25.0 + 35.0) mL or 60.0 mL, so we calculate OH^- concentration as follows:

$$\left[OH^-\right] = \frac{1.00 \times 10^{-3} \text{ mol}}{60.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

$$= 0.0167 \text{ mol/L} = 0.0167 \, M$$

$$pOH = -\log\left[OH^-\right] = -\log 0.0167 = 1.78$$

$$pH = 14.00 - 1.78 = \mathbf{12.22}$$

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Strong Acid-Weak Base Titrations
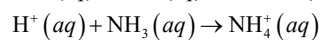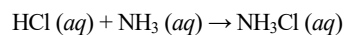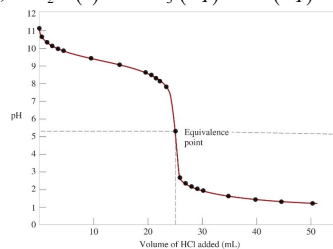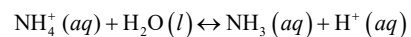
$$HCl \, (aq) + NH_3 \, (aq) \rightarrow NH_3Cl \, (aq)$$

$$H^+ \left(aq\right) + NH_3 \left(aq\right) \rightarrow NH_4^+ \left(aq\right)$$

At equivalence point (pH > 7):

$$NH_4^+ \left(aq\right) + H_2O \left(l\right) \leftrightarrow NH_3 \left(aq\right) + H^+ \left(aq\right)$$

Volume HCl added (mL)	pH
0.0	11.13
5.0	9.86
10.0	9.44
15.0	9.08
20.0	8.66
22.0	8.39
24.0	7.88
25.0	5.28
26.0	2.70
28.0	2.22
30.0	2.00
35.0	1.70
40.0	1.52
45.0	1.40
50.0	1.30

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Example 16.6 [1]

Calculate the pH at the equivalence point when 25.0 mL of 0.100 M NH$_3$ is titrated by a 0.100 M HCl solution.

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Example 16.6 [2]

Strategy

The reaction between NH$_3$ and HCl is

$$NH_3 \, (aq) + HCl \, (aq) \rightarrow NH_4Cl \, (aq)$$
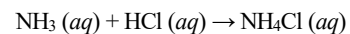
We see that 1 mol NH$_3$ = 1 mol HCl. At the equivalence point, the major species in solution are the salt NH$_4$Cl (dissociated into NH$_4^+$ and Cl$^-$ ions) and H$_2$O. First, we determine the concentration of NH$_4$Cl formed. Then we calculate the pH as a result of the NH$_4^+$ ion hydrolysis. The Cl$^-$ ion, being the conjugate base of a strong acid HCl, does not react with water. As usual, we ignore the ionization of water.

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Example 16.6 ₃

Solution

The number of moles of NH_3 in 25.0 mL of 0.100 M solution is

$$25.0\,\text{mL} \times \frac{0.100\,\text{mol NH}_3}{1\,\text{L NH}_3} \times \frac{1\,\text{L}}{1000\,\text{mL}} = 2.50 \times 10^{-3}\,\text{mol}$$

At the equivalence point the number of moles of HCl added equals the number of moles of NH_3 . The changes in number of moles are summarized below:

$$NH_3\,(aq) + HCl\,(aq) \rightarrow NH_4Cl\,(aq)$$

	NH_3	HCl	NH_4Cl
Initial (mol):	2.50×10^{-3}	2.50×10^{-3}	0
Change (mol):	-2.50×10^{-3}	-2.50×10^{-3}	$+2.50 \times 10^{-3}$
Final (mol):	0	0	2.50×10^{-3}

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Example 16.6 ₄

At the equivalence point, the concentrations of both the acid and the base are zero. The total volume is (25.0 + 25.0) mL, or 50.0 mL, so the concentration of the salt is

$$[NH_4Cl] = \frac{2.50 \times 10^{-3}\,\text{mol}}{50.0\,\text{mL}} \times \frac{1000\,\text{mL}}{1\,\text{L}}$$
$$= 0.0500\,\text{mol/L} = 0.0500\,M$$

The pH of the solution at the equivalence point is determined by the hydrolysis of NH_4^+ ions.

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Example 16.6 [5]

Step 1: We represent the hydrolysis of the cation NH_4^+
and let x be the equilibrium concentration of NH_3 and
H^+ ions in mol/L:

$$NH_4^+ (aq) \leftrightarrow NH_3 (aq) + H^+ (aq)$$

	$NH_4^+ (aq)$	$NH_3 (aq)$	$H^+ (aq)$
Initial (mol):	0.0500	0.000	0.000
Change (mol):	$-x$	$+x$	$+x$
Equilibrium (mol):	$(0.0500 - x)$	x	x

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Example 16.6 [6]

Step 2: From Table 15.4 we obtain the K_a for NH_4^+:

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.0500 - x}$$

Applying the approximation $0.0500 - x \approx 0.0500$, we get

$$5.6 \times 10^{-10} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}$$

$$x = 5.3 \times 10^{-6} \ M$$

Thus, the pH is given by

$$pH = -\log(5.3 \times 10^{-6})$$

$$= \mathbf{5.28}$$

50

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Example 16.6 [7]

Check

Note that the pH of the solution is acidic. This is what we would expect from the hydrolysis of the ammonium ion.

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Acid-Base Indicators

$$\frac{[\text{Hln}]}{[\text{ln}^-]} \geq 10$$

$$\frac{[\text{Hln}]}{[\text{ln}^-]} \leq 10$$

$$\text{Hln}(aq) \leftrightarrow \text{H}^+(aq) + \text{ln}^-(aq)$$
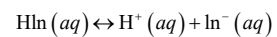
Color of acid (Hln) predominates

Color of conjugate base (ln^-) predominates

Table 16.1 Some Common Acid-Base Indicators

Indicator	In Acid *Color*	In Base *Color*	pH Range*
Thymol blue	Red	yellow	1.2–2.8
Bromophenol blue	Yellow	Blueish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
phenolphthalein	Colorless	Reddish pink	8.3–10.0

*The pH range is defined as the range over which the indicator changes from the acid color to the base color

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Solutions of Red Cabbage Extract

— pH →

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The Titration Curve of a Strong Acid with a Strong Base
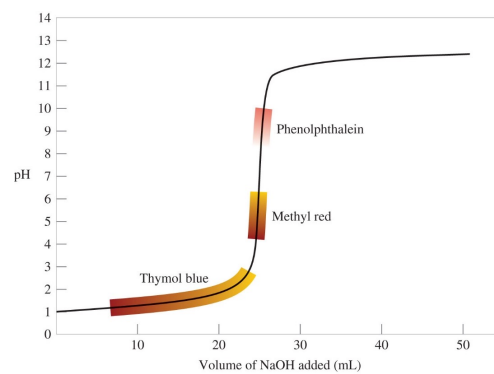
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Example 16.7 [1]

Which indicator or indicators listed in Table 16.1 would you use for the acid-base titrations shown in

a) Figure 16.4?

Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

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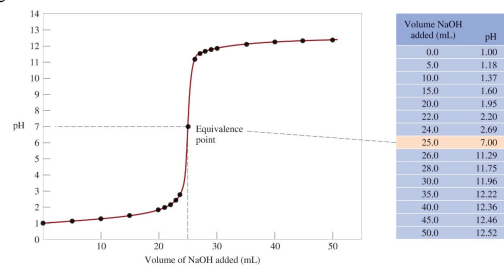
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Example 16.7 [2]

b) Figure 16.5

Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

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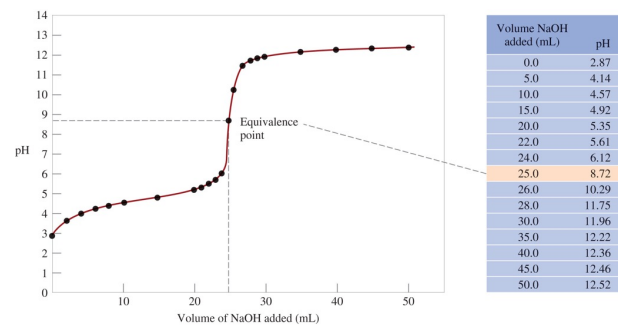
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Example 16.7 3

c) Figure 16.6?

Volume HCl added (mL)	pH
0.0	11.13
5.0	9.86
10.0	9.44
15.0	9.08
20.0	8.66
22.0	8.39
24.0	7.88
25.0	5.28
26.0	2.70
28.0	2.22
30.0	2.00
35.0	1.70
40.0	1.52
45.0	1.40
50.0	1.30
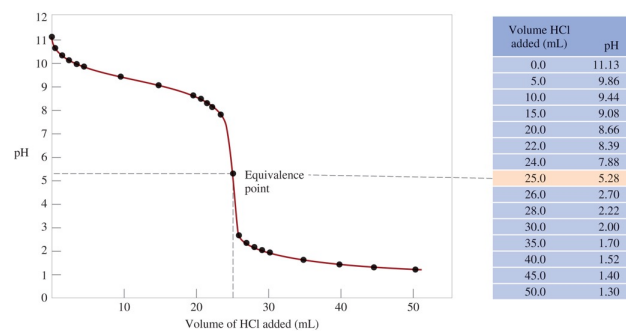
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Example 16.7 4

Strategy

The choice of an indicator for a particular titration is based on the fact that its pH range for color change must overlap the steep portion of the titration curve. Otherwise we cannot use the color change to locate the equivalence point.

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Example 16.7 5

Solution

a) Near the equivalence point, the pH of the solution changes abruptly from 4 to 10. Therefore, all the indicators except thymol blue, bromophenol blue, and methyl orange are suitable for use in the titration.

b) Here the steep portion covers the pH range between 7 and 10; therefore, the suitable indicators are cresol red and phenolphthalein.

c) Here the steep portion of the pH curve covers the pH range between 3 and 7; therefore, the suitable indicators are bromophenol blue, methyl orange, methyl red, and chlorophenol blue.

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Solubility Equilibria

$$AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$$
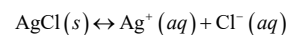
$$K_{sp} = \left[Ag^+ \right]\left[Cl^- \right] \qquad K_{sp} \text{ is the } \textit{solubility product constant}$$

$$MgF_2(s) \leftrightarrow Mg^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = \left[Mg^{2+} \right]\left[F^- \right]^2$$

$$Ag_2CO_3(s) \leftrightarrow 2Ag^+(aq) + CO_3^{2-}(aq) \qquad K_{sp} = \left[Ag^+ \right]^2 \left[CO_3^{2-} \right]$$

$$Ca_3(PO_4)_2(s) \leftrightarrow 3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \qquad K_{sp} = \left[Ca^{2+} \right]^3 \left[PO_4^{3-} \right]^2$$
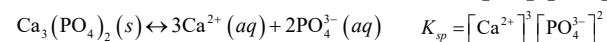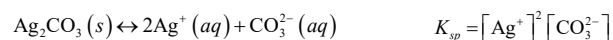
Dissolution of an ionic solid in aqueous solution:

$Q < K_{sp}$ Unsaturated solution   No precipitate

$Q = K_{sp}$ Saturated solution

$Q > K_{sp}$ Supersaturated solution   Precipitate will form

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Solubility Products

Table 16.2 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [Al(OH)$_3$]	1.8×10^{-33}	Lead(II) chromate (PbCrO$_4$)	2.0×10^{-14}
Barium carbonate (BaCO$_3$)	8.1×10^{-9}	Lead(II) fluoride (PbF$_2$)	4.1×10^{-8}
Barium fluoride (BaF$_2$)	1.7×10^{-6}	Lead(II) iodide (PbI$_2$)	1.4×10^{-8}
Barium sulfate (BaSO$_4$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi$_2$S$_3$)	1.6×10^{-72}	Magnesium carbonate (MgCO$_3$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [Mg(OH)$_2$]	1.2×10^{-11}
Calcium carbonate (CaCO$_3$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF$_2$)	4.0×10^{-11}	Mercury(I) chloride (Hg$_2$Cl$_2$)	3.5×10^{-18}
Calcium hydroxide [Ca(OH)$_2$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [Ca$_3$(PO$_4$)$_2$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [Cr(OH)$_3$]	3.0×10^{-29}	Silver bromide (AgBr)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag$_2$CO$_3$)	8.1×10^{-12}
Copper(I) bromide (CuBr)	4.2×10^{-8}	Silver chloride (AgCl)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [Cu(OH)$_2$]	2.2×10^{-20}	Silver sulfate (Ag$_2$SO$_4$)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag$_2$S)	6.0×10^{-51}
Iron(II) hydroxide [Fe(OH)$_2$]	1.6×10^{-14}	Strontium carbonate (SrCO$_3$)	1.6×10^{-9}
Iron(III) hydroxide [Fe(OH)$_3$]	1.1×10^{-36}	Strontium sulfate (SrSO$_4$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate (PbCO$_3$)	3.3×10^{-14}	Zinc hydroxide [Zn(OH)$_2$]	1.8×10^{-14}
Lead(II) chloride (PbCl$_2$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

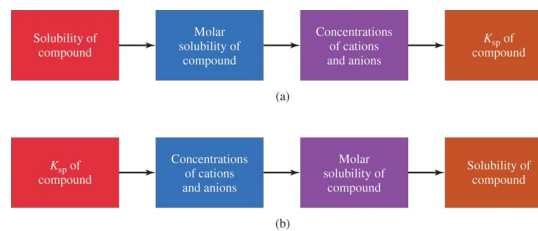Access the text alternative for slide images.

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Solubility

Molar solubility (mol/L) is the number of moles of solute dissolved in 1 L of a saturated solution.

Solubility (g/L) is the number of grams of solute dissolved in 1 L of a saturated solution.

(a)

(b)

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Example 16.8 [1]

The solubility of calcium sulfate ($CaSO_4$) is found to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulfate.

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Example 16.8 [2]

Strategy

We are given the solubility of $CaSO_4$ and asked to calculate its K_{sp}. The sequence of conversion steps, according to Figure 16.9(a), is

$$\text{solubility of } CaSO_4 \text{ in g/L} \rightarrow \text{molar solubility of } CaSO_4 \rightarrow \left[Ca^{2+}\right] \text{ and } \left[SO_4^{2-}\right] \rightarrow K_{sp} \text{ of } CaSO_4$$

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Example 16.8 3

Consider the dissociation of $CaSO_4$ in water. Let s be the molar solubility (in mol/L) of $CaSO_4$.

$$CaSO_4(s) \leftrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$$

Initial (M):		0	0
Change (M):	$-s$	$+s$	$+s$
Equilibrium (M):		s	s

The solubility product for $CaSO_4$ is

$$K_{sp} = \left[Ca^{2+}\right]\left[SO_4^{2-}\right] = s^2$$

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65

Example 16.8 4

First, we calculate the number of moles of $CaSO_4$ dissolved in 1L of solution:

$$\frac{0.67 \text{ g } CaSO_4}{1 \text{ L soln}} \times \frac{1 \text{ mol } CaSO_4}{136.2 \text{ g } CaSO_4} = 4.9 \times 10^{-3} \text{ mol/L} = s$$

From the solubility equilibrium we see that for every mole of $CaSO_4$ that dissolves, 1 mole of Ca^{2+} and 1 mole of SO_4^{2-} are produced. Thus, at equilibrium,

$$\left[Ca^{2+}\right] = 4.9 \times 10^{-3} \ M \text{ and } \left[SO_4^{2-}\right] = 4.9 \times 10^{-3} \ M$$

66

66

Example 16.8 [5]

Now we can calculate K_{sp} :

$$K_{sp} = \left[Ca^{2+} \right]\left[SO_4^{2-} \right]$$
$$= \left(4.9 \times 10^{-3} \right)\left(4.9 \times 10^{-3} \right)$$
$$= 2.4 \times 10^{-5}$$

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Example 16.9 [1]

Using the data in Table 16.2, calculate the solubility of copper(II) hydroxide, $Cu(OH)_2$, in g/L.

Table 16.2 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [$Al(OH)_3$]	1.8×10^{-33}	Lead(II) chromate ($PbCrO_4$)	2.0×10^{-14}
Barium carbonate ($BaCO_3$)	8.1×10^{-9}	Lead(II) fluoride (PbF_2)	4.1×10^{-8}
Barium fluoride (BaF_2)	1.7×10^{-6}	Lead(II) iodide (PbI_2)	1.4×10^{-8}
Barium sulfate ($BaSO_4$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi_2S_3)	1.6×10^{-72}	Magnesium carbonate ($MgCO_3$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [$Mg(OH)_2$]	1.2×10^{-11}
Calcium carbonate ($CaCO_3$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF_2)	4.0×10^{-11}	Mercury(I) chloride (Hg_2Cl_2)	3.5×10^{-18}
Calcium hydroxide [$Ca(OH)_2$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [$Ca_3(PO_4)_2$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [$Cr(OH)_3$]	3.0×10^{-29}	Silver bromide ($AgBr$)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag_2CO_3)	8.1×10^{-12}
Copper(I) bromide ($CuBr$)	4.2×10^{-8}	Silver chloride ($AgCl$)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [$Cu(OH)_2$]	2.2×10^{-20}	Silver sulfate (Ag_2SO_4)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag_2S)	6.0×10^{-51}
Iron(II) hydroxide [$Fe(OH)_2$]	1.6×10^{-14}	Strontium carbonate ($SrCO_3$)	1.6×10^{-9}
Iron(III) hydroxide [$Fe(OH)_3$]	1.1×10^{-36}	Strontium sulfate ($SrSO_4$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate ($PbCO_3$)	3.3×10^{-14}	Zinc hydroxide [$Zn(OH)_2$]	1.8×10^{-14}
Lead(II) chloride ($PbCl_2$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

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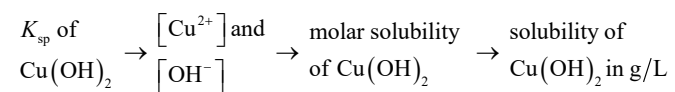## Example 16.9 ₂

Strategy

We are given the K_{sp} of Cu(OH)₂ and asked to calculate its solubility in g/L. The sequence of conversion steps, according to Figure 16.9(b), is
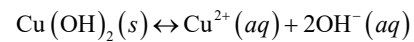
$$K_{sp} \text{ of } \\ Cu(OH)_2 \rightarrow \begin{bmatrix} Cu^{2+} \end{bmatrix} \text{ and } \\ \begin{bmatrix} OH^- \end{bmatrix} \rightarrow \text{molar solubility} \\ \text{of } Cu(OH)_2 \rightarrow \text{solubility of} \\ Cu(OH)_2 \text{ in g/L}$$

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Example 16.9 ₃

Consider the dissociation of Cu(OH)₂ in water:

$$Cu(OH)_2(s) \leftrightarrow Cu^{2+}(aq) + 2OH^-(aq)$$

	Cu(OH)₂(s)	Cu²⁺(aq)	2OH⁻(aq)
Initial (*M*):		0	0
Change (*M*):	−s	+s	+2s
Equilibrium (*M*):		s	2s

Note that the molar concentration of OH⁻ is twice that of Cu²⁺. The solubility product of Cu(OH)₂ is

$$K_{sp} = \begin{bmatrix} Cu^{2+} \end{bmatrix} \begin{bmatrix} OH^- \end{bmatrix}^2$$
$$= (s)(2s)^2 = 4s^3$$

70

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Example 16.9 [4]

From the K_{sp} value in Table 16.2, we solve for the molar solubility of Cu(OH)$_2$ as follows:

$$2.2 \times 10^{-20} = 4s^3$$

$$s^3 = \frac{2.2 \times 10^{-20}}{4} = 5.5 \times 10^{-21}$$

Hence $\qquad s = 1.8 \times 10^{-7} \, M$

Finally, from the molar mass of Cu(OH)$_2$ and its molar solubility, we calculate the solubility in g/L:

$$\text{solubility of Cu(OH)}_2 = \frac{1.8 \times 10^{-7} \, \text{mol Cu(OH)}_2}{1 \, \text{L soln}} \times \frac{97.57 \, \text{g Cu(OH)}_2}{1 \, \text{mol Cu(OH)}_2}$$

$$= \mathbf{1.8 \times 10^{-5} \, g/L}$$

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Relationship of K$_{sp}$ and Molar Solubility

Table 16.3 Relationship Between K$_{sp}$ and Molar Solubility (s)

Compound	K_{sp} Expression	Cation	Anion	Relation Between K_{sp} and s
AgCl	$\left[\text{Ag}^+\right]\left[\text{Cl}^-\right]$	S	S	$K_{sp} = s^2; s = \left(K_{sp}\right)^{\frac{1}{2}}$
BaSO$_4$	$\left[\text{Ba}^{2+}\right]\left[\text{SO}_4^{2-}\right]$	S	S	$K_{sp} = s^2; s = \left(K_{sp}\right)^{\frac{1}{2}}$
Ag$_2$CO$_3$	$\left[\text{Ag}^+\right]^2\left[\text{CO}_3^{2-}\right]$	$2s$	S	$K_{sp} = 4s^3; s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
PbF$_2$	$\left[\text{Pb}^{2+}\right]\left[\text{F}^-\right]^2$	S	$2s$	$K_{sp} = 4s^3; s = \left(\frac{K_{sp}}{4}\right)^{\frac{2}{3}}$
Al(OH)$_3$	$\left[\text{Al}^{3+}\right]\left[\text{OH}^-\right]^3$	S	$3s$	$K_{sp} = 27s^4; s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
Ca$_3$(PO$_4$)$_2$	$\left[\text{Ca}^{2+}\right]^3\left[\text{PO}_4^{3-}\right]^2$	$3s$	$2s$	$K_{sp} = 108s^5; s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

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Example 16.10 [1]

Exactly 200 mL of 0.0040 M BaCl$_2$ are mixed with exactly 600 mL of 0.0080 M K$_2$SO$_4$. Will a precipitate form?

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Example 16.10 [2]

Strategy

Under what condition will an ionic compound precipitate from solution? The ions in solution are $Ba^{2+}, Cl^-, K^+,$ and SO_4^{2-}. According to the solubility rules listed in Table 4.2 (p. 125), the only precipitate that can form is BaSO$_4$. From the information given, we can calculate $\left[Ba^{2+}\right]$ and $\left[SO_4^{2-}\right]$ because we know the number of moles of moles of the ions in the original solutions and the volume of the combined solution. Next, we calculate the ion product Q $\left(Q = \left[Ba^{2+}\right]_0 \left[SO_4^{2-}\right]_0\right)$ and compare the value of Q with K_{sp} of BaSO$_4$ to see if a precipitate will form, that is, if the solution is supersaturated.

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Example 16.10 [4]

Solution

The number of moles of Ba^{2+} present in the original 200 mL of solution is

$$200 \text{ mL} \times \frac{0.0040 \text{ mol } Ba^{2+}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 8.0 \times 10^{-4} \text{ mol } Ba^{2+}$$

The total volume after combining the two solutions is 800 mL.
The concentration of Ba^{2+} in the 800 mL volume is

$$\left[Ba^{2+} \right] = \frac{8.0 \times 10^{-4} \text{ mol}}{800 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}}$$
$$= 1.0 \times 10^{-3} \text{ } M$$

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Example 16.10 [5]

The number of moles of SO_4^{2-} in the original 600 mL solution is

$$600 \text{ mL} \times \frac{0.0080 \text{ mol } SO_4^{2-}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 4.8 \times 10^{-3} \text{ mol } SO_4^{2-}$$

The concentration of SO_4^{2-} in the 800 mL of the combined solution is

$$\left[SO_4^{2-} \right] = \frac{4.8 \times 10^{-3} \text{ mol}}{800 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L soln}}$$
$$= 6.0 \times 10^{-3} \text{ } M$$

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Example 16.10 [6]

Now we must compare Q and K_{sp}. From Table 16.2,

$$BaSO_4\,(s) \leftrightarrow Ba^{2+}\,(aq) + SO_4^{2-}\,(aq) \qquad K_{sp} = 1.1 \times 10^{-10}$$
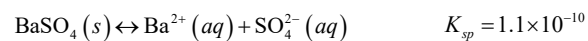
As for Q,

$$Q = \left[Ba^{2+}\right]_0 \left[SO_4^{2-}\right]_0 = \left(1.0 \times 10^{-3}\right)\left(6.0 \times 10^{-3}\right)$$
$$= 6.0 \times 10^{-6}$$

Therefore, $Q > K_{sp}$

The solution is supersaturated because the value of Q indicates that the concentrations of the ions are too large. Thus, some of the $BaSO_4$ will precipitate out of solution until

$$\left[Ba^{2+}\right]\left[SO_4^{2-}\right] = 1.1 \times 10^{-10}$$

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Example 16.11 [1]

A solution contains 0.020 M Cl$^-$ ions and 0.020 M Br$^-$ ions. To separate the Cl$^-$ ions from the Br$^-$ ions, solid $AgNO_3$ is slowly added to the solution without changing the volume. What concentration of Ag$^+$ ions (in mol/L) is needed to precipitate as much AgBr as possible without precipitating AgCl?

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Example 16.11 ₂

Strategy

In solution, $AgNO_3$ dissociates into Ag^+ and NO_3^- ions. The Ag^+ ions then combine with the Cl^- and Br^- ions to form AgCl and AgBr precipitates. Because AgBr is less soluble (it has a smaller K_{sp} than that of AgCl), it will precipitate first. Therefore, this is a fractional precipitation problem. Knowing the concentrations of Cl^- and Br^- ions, we can calculate $[Ag^+]$ from the K_{sp} values. Keep in mind that K_{sp} refers to a saturated solution. To initiate precipitation, $[Ag^+]$ must exceed concentration in the saturated solution in each case.

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Example 16.11 ₃

Solution

The solubility equilibrium for AgBr is

$$AgBr(s) \leftrightarrow Ag^+(aq) + Br^-(aq) \quad K_{sp} = [Ag^+][Br^-]$$
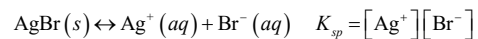
Because $[Br^-] = 0.020\,M$, the concentration of Ag^+ that must be exceeded to initiate the precipitation of AgBr is

$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{7.7 \times 10^{-13}}{0.020}$$

$$= 3.9 \times 10^{-11}\,M$$

Thus, $[Ag^+] > 3.9 \times 10^{-11}$ M is required to start the precipitation of AgBr.

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Example 16.11 [4]

The solubility equilibrium for AgCl is

$$AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = \left[Ag^+\right]\left[Cl^-\right]$$
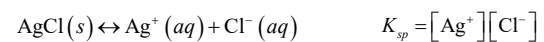
so that

$$\left[Ag^+\right] = \frac{K_{sp}}{\left[Cl^-\right]} = \frac{1.6 \times 10^{-10}}{0.020}$$

$$= 8.0 \times 10^{-9} \, M$$

Therefore $\left[Ag^+\right] > 8.0 \times 10^{-9} M$
is needed to initiate the precipitation of AgCl. To precipitate the Br^- ions
as AgBr without precipitating the $_{Cl^-}$ ions as AgCl, then, $\left[Ag^+\right]$
must be greater than $3.9 \times 10^{-11} M$ and lower than $8.0 \times 10^{-9} M$.

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The Common Ion Effect and Solubility

The presence of a common ion **decreases** the solubility of
the salt.

82

Example 16.12 1

Calculate the solubility of silver chloride (in g/L) in a $6.5 \times 10^{-3} M$ silver nitrate solution.

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Example 16.12 2

Strategy

This is a common-ion problem. The common ion here is Ag^+, which is supplied by both AgCl and AgNO3. Remember that the presence of the common ion will affect only the solubility of AgCl (in g/L), but not the K_{sp} value because it is an equilibrium constant.

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Example 16.12 ₃

Solution

Step 1: The relevant species in solution are Ag^+ ions (from both AgCl and $AgNO_3$) and Cl^- ions. The NO_3^- ions are spectator ions.

Step 2: Because $AgNO_3$ is a soluble strong electrolyte, it dissociates completely:

$$AgNO_3\,(s) \xrightarrow{\;H_2O\;} Ag^+\,(aq) + NO_3^-\,(aq)$$
$$6.5\times10^{-3}\,M \qquad 6.5\times10^{-3}\,M$$
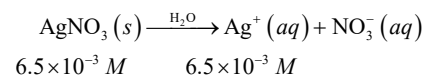
Example 16.12 ₄

Let *s* be the molar solubility of AgCl in $AgNO_3$ solution. We summarize the changes in concentrations as follows:

$$AgCl(s) \leftrightarrow Ag^+\,(aq) + Cl^-\,(aq)$$

		Ag^+	Cl^-
Initial (*M*):		6.5×10^{-3}	0
Change (*M*):	$-s$	$+s$	$+s$
Equilibrium (*M*):		$6.5 \times 10^{-3} + s$	s

Step 3:

$$K_{sp} = \left[Ag^+\right]\left[Cl^-\right]$$
$$1.6\times10^{-10} = \left(6.5\times10^{-3} + s\right)(s)$$

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Example 16.12 [5]

Because AgCl is quite insoluble and the presence of Ag^+ ions from $AgNO_3$ further lowers the solubility of AgCl, s must be very small compared with 6.5×10^{-3}. Therefore, applying the approximation $6.5 \times 10^{-3} + s \approx 6.5 \times 10^{-3}$, we obtain

$$1.6 \times 10^{-10} = \left(6.5 \times 10^{-3}\right) s$$

$$s = 2.5 \times 10^{-8} \, M$$

Step 4: At equilibrium

$$\left[Ag^+\right] = \left(6.5 \times 10^{-3} + 2.5 \times 10^{-8}\right) M \approx 6.5 \times 10^{-3} \, M$$

$$\left[Cl^-\right] = 2.5 \times 10^{-8} \, M$$

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Example 16.12 [6]

and so our approximation was justified in step 3. Because all the Cl^- ions must come from AgCl, the amount of AgCl dissolved in $AgNO_3$ solution also is 2.5×10^{-8}. Then, knowing the molar mass of AgCl (143.4 g), we can calculate the solubility of AgCl as follows:

$$\text{solubility of AgCl in AgNO}_3 \text{ solution} = \frac{2.5 \times 10^{-8} \, \text{mol AgCl}}{1 \, \text{L soln}} \times \frac{143.4 \, \text{g AgCl}}{1 \, \text{mol AgCl}}$$

$$= \mathbf{3.6 \times 10^{-6} \, g/L}$$

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Example 16.12 [7]

Check

The solubility of AgCl in pure water is 1.9×10^{-3} g/L (see the Practice Exercise in Example 16.9). Therefore, the lower solubility (3.6×10^{-6} g/L) in the presence of AgNO$_3$ is reasonable. You should also be able to predict the lower solubility using LeChâtelier's principle. Adding Ag$^+$ ions shifts the equilibrium to the left, thus decreasing the solubility of AgCl.

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pH and Solubility

The presence of a common ion **decreases** the solubility.

Insoluble bases dissolve in acidic solutions

Insoluble acids dissolve in basic solutions

$$Mg(OH)_2 (s) \leftrightarrow Mg^{2+} (aq) + 2OH^- (aq)$$

$K_{sp} = \left[Mg^{2+} \right] \left[OH^- \right]^2 = 1.2 \times 10^{-11}$

$K_{sp} = (s)(2s)^2 = 4s^3$

$4s^3 = 1.2 \times 10^{-11}$
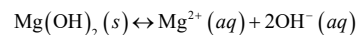
$s = 1.4 \times 10^{-4} M$

$\left[OH^- \right] = 2s = 2.8 \times 10^{-4} M$

$pOH = 3.55 \quad pH = 10.45$

At pH less than 10.45

Lower [OH$^-$]

$$OH^- (aq) + H^+ (aq) \rightarrow H_2O (l)$$
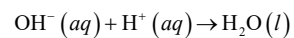
Increase solubility of Mg(OH)$_2$

At pH greater than 10.45

Raise [OH$^-$]

Decrease solubility of Mg(OH)$_2$

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45

Example 16.13 [1]

Which of the following compounds will be more soluble in acidic solution than in water:

a) CuS

b) AgCl

c) $PbSO_4$

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Example 16.13 [2]

Strategy

In each case, write the dissociation reaction of the salt into its cation and anion. The cation will not interact with the H^+ ion because they both bear positive charges. The anion will act as a proton acceptor only if it is the conjugate base of a weak acid. How would the removal of the anion affect the solubility of the salt?

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Example 16.13 ₃

Solution

a) The solubility equilibrium for CuS is

$$CuS(s) \leftrightarrow Cu^{2+}(aq) + S^{2-}(aq)$$
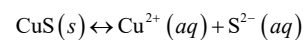
The sulfide ion is the conjugate base of the weak acid HS^-. Therefore, the S^{2-} ion reacts with the H^+ ion as follows:

$$S^{2-}(aq) + H^+(aq) \rightarrow HS^-(aq)$$
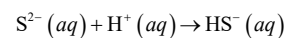
This reaction removes the S^{2-} ions from solution. According to Le Châtelier's principle, the equilibrium will shift to the right to replace some of the S^{2-} ions that were removed, thereby increasing the solubility of CuS.

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Example 16.13 ₄

b) The solubility equilibrium is

$$AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$$
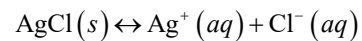
Because Cl^- is the conjugate base of a strong acid (HCl), the solubility of AgCl is not affected by an acid solution.

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Example 16.13 [5]

c) The solubility equilibrium for $PbSO_4$ is

$$PbSO_4\,(s) \leftrightarrow Pb^{2+}\,(aq) + SO_4^{2-}\,(aq)$$
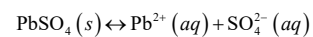
The sulfate ion is a weak base because it is the conjugate base
of the weak acid HSO_4^-.
Therefore, the ion reacts with the H^+ ion as follows:

$$SO_4^{2-}\,(aq) + H^+\,(aq) \rightarrow HSO_4^-\,(aq)$$
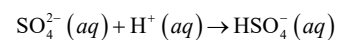
This reaction removes the SO_4^{2-} ions from solution.
According to Le Châtelier's principle, the equilibrium will shift to
the right to replace some of the SO_4^{2-} ions that were removed,
thereby increasing the solubility of $PbSO_4$.

Example 16.14 [1]

Calculate the concentration of aqueous ammonia
necessary to initiate the precipitation of iron(II) hydroxide
from a 0.0030 M solution of $FeCl_2$.

Example 16.14 2

Strategy

For iron(II) hydroxide to precipitate from solution, the product $\left[Fe^{2+}\right]\left[OH^-\right]^2$ must be greater than its K_{sp}. First, we calculate $\left[OH^-\right]$ from the known $\left[Fe^{2+}\right]$ and the K_{sp}

value listed in Table 16.2. This is the concentration of OH^- in a saturated solution of $Fe(OH)_2$. Next, we calculate the concentration of NH_3 that will supply this concentration of OH^- ions. Finally, any NH_3 concentration greater than the calculated value will initiate the precipitation of $Fe(OH)_2$ because the solution will become supersaturated.

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Example 16.14 3

Solution

Ammonia reacts with water to produce OH^- ions, which then react with Fe^{2+} to form $Fe(OH)_2$. The equilibria of interest are

$$NH_3\left(aq\right) + H_2O\left(l\right) \leftrightarrow NH_4^+\left(aq\right) + OH^-\left(aq\right)$$
$$Fe^{2+}\left(aq\right) + 2OH^-\left(aq\right) \leftrightarrow Fe\left(OH\right)_2\left(s\right)$$
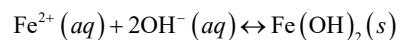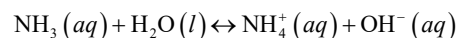
First we find the OH^- concentration above which $Fe(OH)_2$ begins to precipitate. We write

$$K_{sp} = \left[Fe^{2+}\right]\left[OH^-\right]^2 = 1.6\times10^{-14}$$

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Example 16.14 [4]

Because FeCl$_2$ is a strong electrolyte, $\left[Fe^{2-} \right] = 0.0030\ M$ and

$$\left[OH^- \right]^2 = \frac{1.6 \times 10^{-14}}{0.0030} = 5.3 \times 10^{-12}$$

$$\left[OH^- \right] = 2.3 \times 10^{-6}\ M$$

Next, we calculate the concentration of NH$_3$ that will supply $2.3 \times 10^{-6}\ M$ OH$^-$ ions. Let x be the initial concentration of NH$_3$ in mol/L.
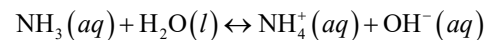
99

Example 16.14 [5]

We summarize the changes in concentrations resulting from the ionization of NH$_3$ as follows.

$$NH_3\left(aq\right) + H_2O\left(l\right) \leftrightarrow NH_4^+\left(aq\right) + OH^-\left(aq\right)$$

	NH$_3$	NH$_4^+$	OH$^-$
Initial (M):	x	0.00	0.00
Change (M):	-2.3×10^{-6}	$+2.3 \times 10^{-6}$	$+2.3 \times 10^{-6}$
Equilibrium (M)	$\left(x - 2.3 \times 10^{-6}\right)$	2.3×10^{-6}	2.3×10^{-6}

Substituting the equilibrium concentrations in the expression for the ionization constant (see Table 15.4),

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Example 16.14 [6]

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}$$

$$1.8 \times 10^{-5} = \frac{\left(2.3 \times 10^{-6}\right)\left(2.3 \times 10^{-6}\right)}{\left(x - 2.3 \times 10^{-6}\right)}$$

Solving for x, we obtain

$$x = 2.6 \times 10^{-6} \, M$$

Therefore, the concentration of NH_3 must be slightly greater than 2.6×10^{-6} M to initiate the precipitation of $Fe(OH)_2$.
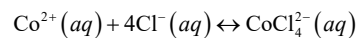
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Complex Ion Equilibria and Solubility

A *complex ion* is an ion containing a central metal cation bonded to one or more molecules or ions.

$$Co^{2+}(aq) + 4Cl^-(aq) \leftrightarrow CoCl_4^{2-}(aq)$$

The **formation constant or stability constant** (K_f) is the equilibrium constant for the complex ion formation.

$Co(H_2O)_6^{2+}$ $CoCl_4^{2-}$ $K_f = \dfrac{\left[CoCl_4^{2-}\right]}{\left[Co^{2+}\right]\left[Cl^-\right]^4}$

$K_f \uparrow$ stability of complex $\uparrow$

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Formation Constants

Table 16.4 Formation Constants of Selected Complex Ions in Water at 25°C

Complex Ion	Equilibrium Expression	Formation Constant (K_f)
$Ag(NH_3)_2^+$	$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$	1.5×10^7
$Ag(CN)_2^-$	$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$	1.0×10^{21}
$Cu(CN)_4^{2-}$	$Cu^{2+} + 4CN^- \rightleftharpoons Cu(CN)_4^{2-}$	1.0×10^{25}
$Cu(NH_3)_4^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$	5.0×10^{13}
$Cd(CN)_4^{2-}$	$Cd^{2+} + 4CN^- \rightleftharpoons Cd(CN)_4^{2-}$	7.1×10^{16}
CdI_4^{2-}	$Cd^{2+} + 4I^- \rightleftharpoons CdI_4^{2-}$	2.0×10^6
$HgCl_4^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-}$	1.7×10^{16}
HgI_4^{2-}	$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	2.0×10^{30}
$Hg(CN)_4^{2-}$	$Hg^{2+} + 4CN^- \rightleftharpoons Hg(CN)_4^{2-}$	2.5×10^{41}
$Co(NH_3)_6^{3+}$	$Co^{3+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$	5.0×10^{31}
$Zn(NH_3)_4^{2+}$	$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$	2.9×10^9

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Example 16.15 [1]

A 0.20 – mole quantity of $CuSO_4$ is added to a liter of 1.20 M NH_3 solution. What is the concentration of Cu^{2+} ions at equilibrium?
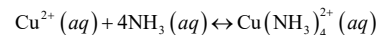
Example 16.15 ₂

Strategy

The addition of $CuSO_4$ to the NH_3 solution results in complex ion formation

$$Cu^{2+}(aq) + 4NH_3(aq) \leftrightarrow Cu(NH_3)_4^{2+}(aq)$$

From Table 16.4 we see that the formation constant (K_f) for this reaction is very large; therefore, the reaction lies mostly to the right. At equilibrium, the concentration of Cu^{2+} will be very small. As a good approximation, we can assume that essentially all the dissolved Cu^{2+} ions end up as $Cu(NH_3)_4^{2+}$ ions.

How many moles of NH_3 will react with 0.20 mole of Cu^{2+}? How many moles of $Cu(NH_3)_4^{2+}$ will be produced? A very small amount of Cu^{2+} will be present at equilibrium. Set up the K_f expression for the preceding equilibrium to solve for $[Cu^{2+}]$.

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Example 16.15 ₃

Solution

The amount of NH_3 consumed in forming the complex ion is 4 × 0.20 mol, or 0.80 mol. (Note that 0.20 mol Cu^{2+} is initially present in solution and four NH_3 molecules are needed to form a complex ion with one Cu^{2+} ion.) The concentration of NH_3 at equilibrium is therefore (1.20 – 0.80) mol/L soln or 0.40 *M*, and that of $Cu(NH_3)_4^{2+}$ is 0.20 mol/L soln or 0.20 *M*. is the same as the initial concentration of Cu^{2+} [There is a 1:1 mole ratio between Cu^{2+} and $Cu(NH_3)_4^{2+}$]. Because $Cu(NH_3)_4^{2+}$ does dissociate to a slight extent, we call the concentration of Cu^{2+} at equilibrium x and write

$$K_f = \frac{\left[Cu(NH_3)_4^{2+}\right]}{\left[Cu^{2+}\right]\left[NH_3\right]^4}$$

$$5.0 \times 10^{13} = \frac{0.20}{x(0.40)^4}$$

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Example 16.15 [4]

Solving for x and keeping in mind that the volume of the solution is 1 L, we obtain

$$x = \left[Cu^{2+}\right] = 1.6 \times 10^{-13} \ M$$

Check

The small value of $\left[Cu^{2+}\right]$ at equilibrium, compared with 0.20 M, certainly justifies our approximation

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Example 16.16 [1]

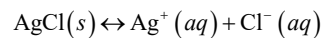Calculate the molar solubility of AgCl in a 1.0 M NH$_3$ solution.

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Example 16.16 ₂

Strategy

AgCl is only slightly soluble in water

$$\text{AgCl}(s) \leftrightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

The Ag^+ ions form a complex ion with NH_3 (see Table 16.4)

$$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \leftrightarrow \text{Ag}(\text{NH}_3)_2^+$$
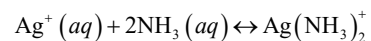
Combining these two equilibria will give the overall equilibrium for the process.

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Example 16.16 ₃

Solution

Step 1: Initially, the species in solution are Ag^+ and Cl^- ions and NH_3. The reaction between Ag^+ and NH_3 produces the complex ion $\text{Ag}(\text{NH}_3)_2^+$

Step 2: The equilibrium reactions are
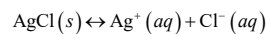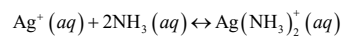
$$\text{AgCl}(s) \leftrightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$$
$$K_{sp} = \left[\text{Ag}^+\right]\left[\text{Cl}^-\right] = 1.6 \times 10^{-10}$$
$$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \leftrightarrow \text{Ag}(\text{NH}_3)_2^+(aq)$$
$$K_f = \frac{\left[\text{Ag}(\text{NH}_3)_2^+\right]}{\left[\text{Ag}^+\right]\left[\text{NH}_3\right]^2} = 1.5 \times 10^7$$

$$\text{Overall}: \text{AgCl}(s) + 2\text{NH}_3(aq) \leftrightarrow \text{Ag}(\text{NH}_3)_2^+(aq) + \text{Cl}^-(aq)$$
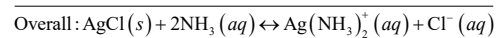
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Example 16.16 4

The equilibrium constant for the overall reaction is the product of the equilibrium constants of the individual reactions (see Section 14.2):

$$K = K_{sp}K_f = \frac{\left[Ag\left(NH_3\right)_2^+\right]\left[Cl^-\right]}{\left[NH_3\right]^2}$$

$$= \left(1.6\times10^{-10}\right)\left(1.5\times10^7\right)$$

$$= 2.4\times10^{-3}$$

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Example 16.16 5

Let s be the molar solubility of AgCl (mol/L). We summarize the changes in concentrations that result from formation of the complex ion as follows:

$$AgCl(s) + 2NH_3(aq) \leftrightarrow Ag\left(NH_3\right)_2^+(aq) + Cl^-(aq)$$
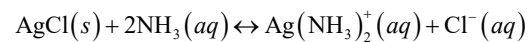
Initial (*M*):		1.0	0.0	0.0
Change (*M*):	−*s*	−2*s*	+*s*	+*s*
Equilibrium (*M*):		(1.0 − 2*s*)	*s*	*s*

The formation constant for $Ag\left(NH_3\right)_2^+$ is quite large, so most of the silver ions exist in the complexed form. In the absence of ammonia we have, at equilibrium, $\left[Ag^+\right]=\left[Cl^-\right]$
As a result of complex ion formation, however, we can write $\left[Ag\left(NH_3\right)_2^+\right]=\left[Cl^-\right]$

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Example 16.16 [6]

Step 3:

$$K = \frac{(s)(s)}{(1.0 - 2s)^2}$$

$$2.4 \times 10^{-3} = \frac{s^2}{(1.0 - 2s)^2}$$

Taking the square root of both sides, we obtain

$$0.049 = \frac{s}{1.0 - 2s}$$

$$s = \mathbf{0.045 \ M}$$

Step 4: At equilibrium, 0.045 mole of AgCl dissolves in 1 L of 1.0 M
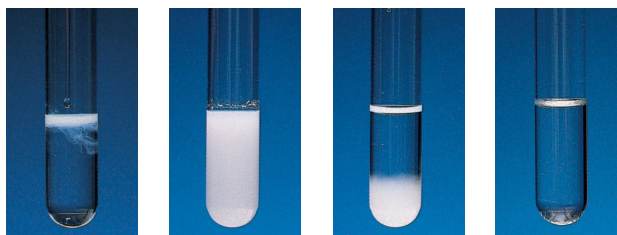   NH$_3$ solution.

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Example 16.16 [7]

Check

The molar solubility of AgCl in pure water is $1.3 \times 10^{-5} \ M$.
Thus, the formation of the complex ion $Ag(NH_3)_2^+$
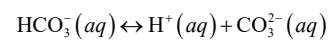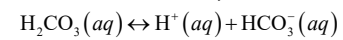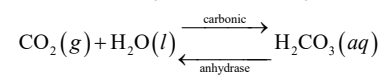enhances the solubility of AgCl (Figure 16.12).

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Chemistry In Action: How an Eggshell is Formed

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightarrow CaCO_3(s)$$

$$CO_2(g) + H_2O(l) \underset{\text{anhydrase}}{\overset{\text{carbonic}}{\rightleftarrows}} H_2CO_3(aq)$$

$$H_2CO_3(aq) \leftrightarrow H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \leftrightarrow H^+(aq) + CO_3^{2-}(aq)$$
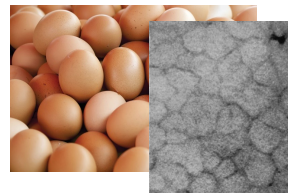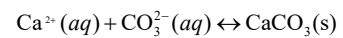
(Left image): muratart/Shutterstock; (Right image): Courtesy of A. Raymond Terepka   115

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Effect of Complexation on Solubility

AgCl

Ken Karp/McGraw-Hill   116

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Precipitation Reactions with Various Cations

Table 16.5 Separation of Cations into Groups According to Their Precipitation Reactions with Various Reagents

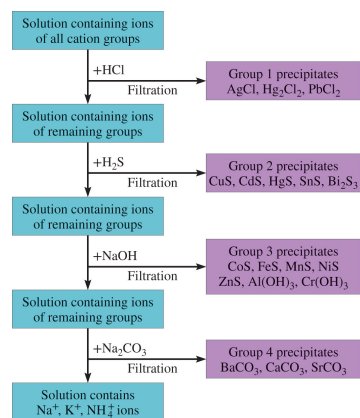| Group	Cation	Precipitating Reagents	Insoluble Compound	K_{sp}
1	Ag^+	HCl	AgCl	1.6×10^{-10}
	Hg_2^{2+}		Hg_2Cl_2	3.5×10^{-18}
	Pb^{2+}		$PbCl_2$	2.4×10^{-4}
2	Bi^{3+}	H_2S	Bi_2S_3	1.6×10^{-72}
	Cd^{2+}	in acidic	CdS	8.0×10^{-28}
	Cu^{2+}	solutions	CuS	6.0×10^{-37}
	Hg^{2+}		HgS	4.0×10^{-54}
	Sn^{2+}		SnS	1.0×10^{-26}
3	Al^{3+}	H_2S	$Al(OH)_3$	1.8×10^{-33}
	Co^{2+}	in basic	CoS	4.0×10^{-21}
	Cr^{3+}	solutions	$Cr(OH)_3$	3.0×10^{-29}
	Fe^{2+}		FeS	6.0×10^{-19}
	Mn^{2+}		MnS	3.0×10^{-14}
	Ni^{2+}		NiS	1.4×10^{-24}
	Zn^{2+}		ZnS	3.0×10^{-23}
4	Ba^{2+}	Na_2CO_3	$BaCO_3$	8.1×10^{-9}
	Ca^{2+}		$CaCO_3$	8.7×10^{-9}
	Sr^{2+}		$SrCO_3$	1.6×10^{-9}
5	K^+	No precipitating	None	
	Na^+	reagent	None	
	NH_4^+		None	

Access the text alternative for slide images.

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Qualitative Analysis of Cations

Solution containing ions of all cation groups

+HCl → Filtration → Group 1 precipitates AgCl, Hg_2Cl_2, $PbCl_2$

Solution containing ions of remaining groups

+H_2S → Filtration → Group 2 precipitates CuS, CdS, HgS, SnS, Bi_2S_3

Solution containing ions of remaining groups

+NaOH → Filtration → Group 3 precipitates CoS, FeS, MnS, NiS ZnS, $Al(OH)_3$, $Cr(OH)_3$

Solution containing ions of remaining groups

+Na_2CO_3 → Filtration → Group 4 precipitates $BaCO_3$, $CaCO_3$, $SrCO_3$

Solution contains Na^+, K^+, NH_4^+ ions

Access the text alternative link, if needed.

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Flame Test for Cations

lithium   sodium   potassium   copper

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