

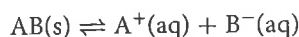
## Equilibrium of Slightly Soluble Ionic Compounds (8.4)

Answers 1.

**Solubility** is a measure of the maximum amount of a solute that will dissolve in a given quantity of solvent at a specific temperature. *Soluble ionic compounds* dissociate completely into ions. *Slightly soluble ionic compounds*, however, reach equilibrium when only a small amount of solute is dissolved or (dissociated into ions) in the solvent.

The constant value for the equilibrium established by slightly soluble ionic compounds in solution is called the **solubility-product constant,  $K_{sp}$** . The solubility-product constant expression is written using the concentration of ions at equilibrium. *As with other equilibrium constant expressions you have studied, the concentration of the undissolved solid is not included in the calculation because it is relatively constant.*

Consider the following general equation representing the dissociation of a slightly soluble ionic compound in water:

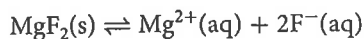


$$K_{sp} = [A^+][B^-]$$

When comparing the  $K_{sp}$  values of different ionic solids, remember the following:

- A smaller  $K_{sp}$  indicates that the solute is less soluble.
- A larger  $K_{sp}$  indicates that the solute is more soluble.

The  $K_{sp}$  expression is modified according to the ratio of ions in the ionic compound. For example, consider the expression for the dissociation of  $MgF_2$ , in which the cation and anion are present in a 1:2 molar ratio:



$$K_{sp} = [Mg^{2+}][F^-]^2$$

The ion-product expression,  $Q_{sp}$ , is calculated using the concentration of the ions involved in the dissociation reaction in the same way as  $K_{sp}$ , but the system is not necessarily at equilibrium.

1. Write the solubility equilibrium produced when each of the following dissolves in water, and write the solubility product expression for each. **K/U T/I**
  - (a) silver chloride,  $AgCl(s)$
  - (b) silver sulfide,  $Ag_2S(s)$
  - (c) magnesium carbonate,  $MgCO_3(s)$
  - (d) magnesium phosphate,  $Mg_3(PO_4)_2(s)$
2. Determine the solubility product constant,  $K_{sp}$ , for lead(II) chloride,  $PbCl_2(s)$ . The solubility of lead(II) chloride is 0.016 mol/L at 25 °C. **T/I**

3. Describe how the charge on the anions and cations of an ionic compound and their relative sizes affect the solubility of the compound. **K/U** **3C**
  
4. The  $K_{sp}$  of magnesium hydroxide,  $Mg(OH)_2$ , is  $5.6 \times 10^{-12}$  at  $25^\circ C$ . What is its molar solubility? **7/1**

### Predicting the Formation of a Precipitate (8.4)

A **precipitate** is an insoluble product formed in a reaction between two soluble ionic compounds. The formation of a precipitate can be predicted by comparing  $Q_{sp}$  and  $K_{sp}$  values for a solution containing a slightly soluble ionic compound.

#### Using $Q_{sp}$ and $K_{sp}$ to Predict Precipitation

Scenario	Outcome
$Q_{sp} < K_{sp}$	The solution is unsaturated and no precipitate forms.
$Q_{sp} = K_{sp}$	The solution is saturated and no change occurs.
$Q_{sp} > K_{sp}$	The solution is saturated and a precipitate forms.

Note that the amount (in moles) of solute in 1 L of a saturated solution is called the **molar solubility** of that solute. Because  $K_{sp}$  represents the concentrations of ions of a solution at equilibrium, you can use  $K_{sp}$  to determine molar solubility and vice versa.

#### Sample Problem: Using Molar Solubility to Determine $K_{sp}$ and Predict Precipitation

1. A student determines that the solubility of magnesium carbonate,  $MgCO_3(s)$ , in water at a certain temperature is  $2.63 \times 10^{-3}$  mol/L.
  - a. What is  $K_{sp}$  for magnesium carbonate?
  - b. The student plans to mix 250.0 mL of a 0.0035 mol/L solution of sodium carbonate,  $Na_2CO_3(s)$ , and 500.0 mL of a 0.0090 mol/L solution of magnesium chloride,  $MgCl_2(s)$ . (The temperature is the same as for the solubility experiment.) The only possible precipitate is magnesium carbonate. Will a precipitate form?

#### What Is Given?

- You know the molar solubility of  $MgCO_3(s)$ : \_\_\_\_\_
- You know the volume of  $Na_2CO_3(aq)$ : \_\_\_\_\_
- You know the concentration of  $Na_2CO_3(aq)$ : \_\_\_\_\_
- You know the volume of  $MgCl_2(s)$ : \_\_\_\_\_
- You know the concentration of  $MgCl_2(s)$ : \_\_\_\_\_

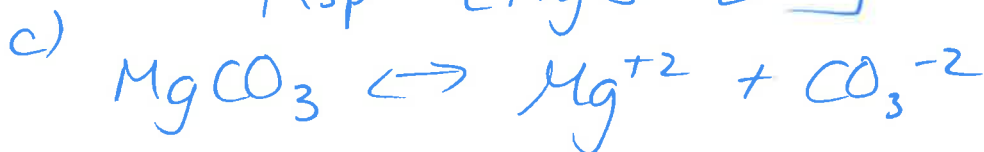
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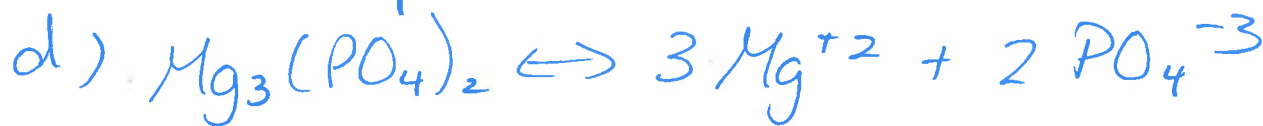
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$



$$K_{sp} = [\text{Ag}^+]^2 [\text{S}^{2-}]$$



$$K_{sp} =$$



$$K_{sp} = [\text{Mg}^{+2}]^3 [\text{PO}_4^{-3}]^2$$

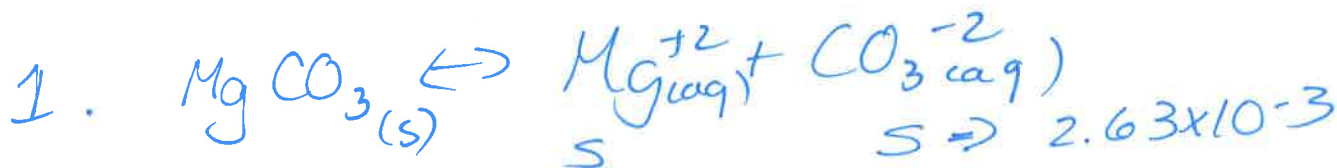
2.  $1.6 \times 10^{-5}$

8.1, 8.2, 8.4 (8.7)

# Page 2

3. Large Ions - more soluble (further apart)  
Large Charges - less soluble (closer)

4.  $1.1 \times 10^{-4} \text{ mol/L}$



$$K_{sp} = S^2 = (2.63 \times 10^{-3})^2$$

$$[\text{Mg}^{+2}] = 0.009 \text{ mol/L} \times \frac{500}{750} =$$

$$[\text{CO}_3^{-2}] = 0.0035 \times \frac{250}{750} =$$

$$Q_{sp} = [\text{Mg}][\text{CO}_3]$$

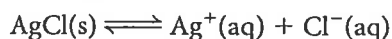
=

$Q_{sp} > < K_{sp} ?$

Solution:  $MgCO_3$

3.

2. The dissolution equilibrium system of solid silver chloride,  $AgCl(s)$ , is represented by the following balanced equation:



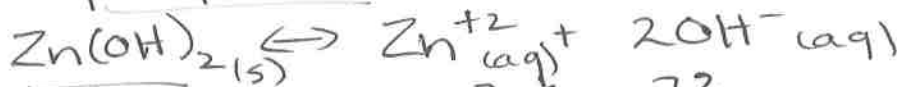
A solution containing  $Ag^+(aq)$  ions is added to a solution containing  $Cl^-(aq)$  ions. Predict what happens when the value of the trial ion product,  $Q$ , is compared to the solubility product,  $K_{sp}$ . Complete Table 1.

Table 1 Predictions Based on Relationship between  $Q$  and  $K_{sp}$

	Shift in equilibrium	Precipitation	Saturation
$Q < K_{sp}$	right	no	unsaturated
$Q = K_{sp}$	no shift	no	saturated
$Q > K_{sp}$	left	yes	saturated

3. A student mixes 100.0 mL of a  $1.2 \times 10^{-2}$  mol/L aqueous solution of zinc nitrate,  $Zn(NO_3)_2(aq)$ , with 100.0 mL of a  $6.0 \times 10^{-3}$  mol/L aqueous solution of sodium hydroxide,  $NaOH(aq)$  at 25 °C. Will solid zinc hydroxide,  $Zn(OH)_2(s)$ , precipitate? Explain your answer. The solubility product constant of zinc hydroxide at this temperature is  $7.7 \times 10^{-17}$ .

precipitate



$$Q_{sp} = [Zn^{2+}][OH^-]^2$$

$$= (0.006)(0.003)^2$$

$$= 5.4 \times 10^{-8}$$

$$[Zn^{2+}] = \frac{1.2 \times 10^{-2} \times 100}{200}$$

$$= 0.006 \frac{\text{mol}}{\text{L}}$$

$$[OH^-] = \frac{6 \times 10^{-3} \times 100}{200}$$

$$= 0.003 \frac{\text{mol}}{\text{L}}$$

$Q_{sp} > K_{sp} \therefore$  precipitate

## The Ion-Product Constant of Water, $K_w$ (8.1)

In pure water, the rate of dissociation and formation are equal. In other words, the system of water molecules, hydronium ions, and hydroxide ions is at equilibrium. At any given time, a small but constant number of hydronium and hydroxide ions are present. The equilibrium constant for water, which is called the ion-product constant of water,  $K_w$ , is shown below.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

Note that the  $K_w$  formula can be manipulated to determine the  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$ , which can then be used to determine pH or pOH, as summarized in the following table:

To solve for...	Step 1: Write the $K_w$ expression	Step 2: Manipulate the $K_w$ expression	Step 3: Substitute $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ into the pH or pOH equation
pH	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$	$[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-]$	$\text{pH} = -\log[\text{H}_3\text{O}^+]$
pOH	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$	$[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+]$	$\text{pOH} = -\log[\text{OH}^-]$

You can also work backward, using pH or pOH to determine  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$ , as follows:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

A high pH or low pOH number corresponds to a low concentration of the hydronium ion or a basic solution. A low pH or high pOH number corresponds to a high concentration of the hydronium ion or an acidic solution. Because the pH scale is logarithmic, an increase of one pH value is an increase of 10 times the ion concentration.

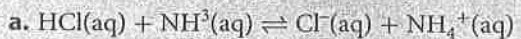
For any given system, the sum of the pH and pOH values is equal to 14.00, as illustrated in the following table:

Relationships Among pH, pOH,  $[\text{H}_3\text{O}^+]$ , and  $[\text{OH}^-]$

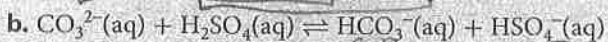
$[\text{H}_3\text{O}^+]$	$10^0$	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$	$10^{-7}$	$10^{-8}$	$10^{-9}$	$10^{-10}$	$10^{-11}$	$10^{-12}$	$10^{-13}$	$10^{-14}$
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
pOH	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
$[\text{OH}^-]$	$10^{-14}$	$10^{-13}$	$10^{-12}$	$10^{-11}$	$10^{-10}$	$10^{-9}$	$10^{-8}$	$10^{-7}$	$10^{-6}$	$10^{-5}$	$10^{-4}$	$10^{-3}$	$10^{-2}$	$10^{-1}$	$10^0$

### Learning Check

1. **K/U** Identify the conjugate acid-base pairs in the following chemical equations:



Acid Base C.B. A.C.A.



Base Acid C.A. C.B.



ACID BASE C.A. C.B.

2. **T/L** Complete the following table.

	pH	[H <sub>3</sub> O <sup>+</sup> ]	pOH	[OH <sup>-</sup> ]
a.	1.19	0.064 mol/L	12.81	1.585 × 10 <sup>-13</sup>
b.	12.46	4.4 × 10 <sup>-13</sup>	1.64	0.023 mol/L
c.	3.4	4.0 × 10 <sup>-4</sup>	10.63	2.3 × 10 <sup>-11</sup>
d.	10.00	1 × 10 <sup>-10</sup>	4.00	1 × 10 <sup>-4</sup>
e.	3.68	2.1 × 10 <sup>-4</sup> mol/L	10.32	4.8 × 10 <sup>-11</sup>

## Acid-Base Strength (8.2)

The strength of an acid is determined by the extent to which it dissociates into its composite ions when in water. A **weak acid** dissociates only slightly when dissolved in water, with most molecules staying intact. Consider the following equations for the **strong acid** hydrochloric acid, HCl(aq), and the weak acid acetic acid, CH<sub>3</sub>COOH(aq). Note that the dissociation of the strong acid is unidirectional and complete, whereas the dissociation of the weak acid is bi-directional. In other words, all of the strong acid ionizes in water, while the weak acid does not completely ionize in water—some of the ions are continually reacting to form the acid molecule. Consequently, for a weak acid, a dynamic equilibrium is established. This results in a solution that is a mixture of intact acid molecules, water molecules, hydronium ions, and the conjugate base.

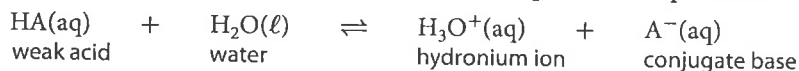
### Ionization of a Strong Acid and a Weak Acid

Acid Strength	Chemical Equation for Ionization in Water
Strong Acid	HCl(aq) + H <sub>2</sub> O(l) → H <sub>3</sub> O <sup>+</sup> (aq) + A <sup>-</sup> (aq) strong acid                      water                      hydronium ion                      conjugate base of strong acid
Weak Acid	CH <sub>3</sub> COOH(aq) + H <sub>2</sub> O(l) ⇌ H <sub>3</sub> O <sup>+</sup> (aq) + CH <sub>3</sub> COO <sup>-</sup> (aq) weak acid                      water                      hydronium ion                      conjugate base of weak acid

## The Acid-Ionization Constant, K<sub>a</sub> (8.2)

The equilibrium position for a weak acid is represented by the **acid-dissociation constant**, or **acid-ionization constant**, K<sub>a</sub>. In the case of a strong acid, an equilibrium expression is typically not written because the reaction between a strong acid and water proceeds to completion for all practical purposes.

**Monoprotic acids** yield one proton, H<sup>+</sup>, when they ionize in water. Consider the ionization of a generic monoprotic weak acid, HA, and its equilibrium expression.



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

Keep these points in mind when working with K<sub>a</sub>:

- The concentration of water does not change and is therefore not included in the value for K<sub>a</sub>.
- K<sub>a</sub>, like K<sub>eq</sub>, is temperature-dependent.
- The strength of the acid is proportional to the value of the acid-dissociation constant.

stronger acid → higher [H<sub>3</sub>O<sup>+</sup>] → larger K<sub>a</sub>

**Percent dissociation** is the fraction of acid molecules that have dissociated into ions at equilibrium compared with the initial concentration of the acid, expressed as a percent. Percent dissociation can also be used to determine acid strength, as shown below.

$$\text{Percent dissociated} = \frac{[\text{HA}]_{\text{dissociated}}}{[\text{HA}]_{\text{initial}}} \times 100\%$$

stronger acid → higher [H<sub>3</sub>O<sup>+</sup>] → higher percent dissociation of acid →  
larger K<sub>a</sub> value

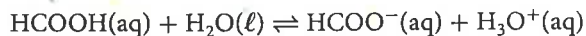
## Determining the Acid-Dissociation Constant, $K_a$ (8.2)

There are several ways to determine the equilibrium constant,  $K_a$ . In turn, the equilibrium constant can also be used to determine reactant or product concentrations at equilibrium. Use the same problem-solving skills you learned when tackling  $K_{eq}$  problems.

### Sample Problem: Determining $K_a$

#### 1. Problem

A 0.20 mol/L solution of formic acid,  $\text{HCOOH}(\text{aq})$ , has a pH of 3.38. Determine  $K_a$  for formic acid, which dissociates according to the following equation:



I	0.2 mol/L	0	0
C	-x	+x	+x
E	0.2 - x	x	x
	= 0.2 - 4.17 × 10 <sup>-4</sup>	4.17 × 10 <sup>-4</sup>	4.17 × 10 <sup>-4</sup>
	= 0.19958		

pH = 3.38  
 $[\text{H}_3\text{O}^+] = 4.17 \times 10^{-4}$

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

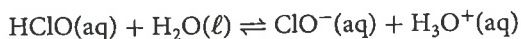
$$= \frac{(4.17 \times 10^{-4})^2}{0.19958}$$

$$= 8.71 \times 10^{-9}$$

### Sample Problem: Determining pH from $K_a$ and Initial Weak Acid Concentration

#### 2. Problem

A 0.22 mol/L solution of hypochlorous acid,  $\text{HClO}(\text{aq})$ , has  $K_a = 3.0 \times 10^{-8}$ . What is the pH of the solution at equilibrium?



I	0.22 mol/L	0	0
C	-x	+x	+x
E	0.22 - x	x	x

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

$$3.0 \times 10^{-8} = \frac{x^2}{0.22}$$

$$6 \times 10^{-9} = x^2$$

$$x = 0.00008124$$

$$= 8.124 \times 10^{-5} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(8.124 \times 10^{-5}) = 4.09$$

Check

$$\frac{0.22}{3 \times 10^{-8}} > 500$$

1. A(n) pH meter is a device that measures the acidity or alkalinity of a solution electronically and displays the result as a pH value.  
 A(n) indicator is a substance that is observed as a different colour when placed in solutions with different pH values.
2. Complete Table 3 for the pH and pOH of solutions at SATP. Use the pH or pOH to determine if the solution is acidic or basic. **171**

Table 3 pH and pOH of Solutions

Concentration	pH	pOH	Acidic or basic
$1.0 \times 10^{-8}$ mol/L $H^+(aq)$	8	6	basic
$1.0 \times 10^{-11}$ mol/L $OH^-(aq)$	3	11	acidic
$5.0 \times 10^{-4}$ mol/L $H^+(aq)$	3.30	10.70	acidic
$3.8 \times 10^{-5}$ mol/L $OH^-(aq)$	4.42	9.58	acidic

3. Calculate the  $[H^+(aq)]$  in a solution that has a pH of 5.92. **172**

$$[H^+] = 10^{-5.92} = 1.202 \times 10^{-6} \text{ mol/L}$$

4. Calculate the  $[H^+(aq)]$  and  $[OH^-(aq)]$  in a solution that has a pOH of 10.42. **173**

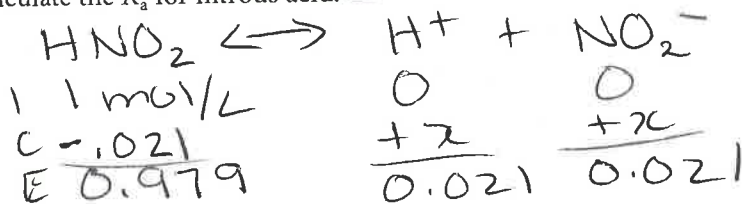
$$[OH^-] = 10^{-10.42} = 3.8 \times 10^{-11} \text{ mol/L}$$

$$pH = 3.58$$

$$[H^+] = 10^{-3.58} = 2.63 \times 10^{-4} \text{ mol/L}$$

$$[H^+][OH^-] = 1 \times 10^{-14}$$

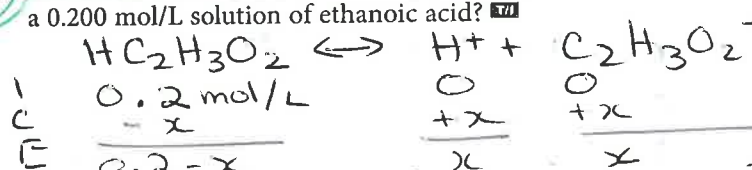
5. A 1.00 mol/L solution of nitrous acid,  $HNO_2(aq)$ , has a percentage ionization of 2.1%. Calculate the  $K_a$  for nitrous acid. **174**



$$K_a = \frac{(0.021)^2}{0.979} = 4.5 \times 10^{-4}$$

6. The  $K_a$  value for ethanoic acid,  $HC_2H_3O_2(aq)$ , is  $1.8 \times 10^{-5}$ . What is the pH of a 0.200 mol/L solution of ethanoic acid? **175**

Check  
 $\frac{0.2}{1.8 \times 10^{-5}} > 100$   
 $\therefore$  approximate



$$K_a = 1.8 \times 10^{-5}$$

$$x^2 = 0.2(1.8 \times 10^{-5}) = 0.0000036$$

$$x = 0.0018974 \text{ mol/L}$$

7. Calculate  $[H^+(aq)]$  and  $[OH^-(aq)]$  in blood, which has a pH of 7.42. (8.2) **176**

$$10^{-pH} = [H^+]$$

$$10^{-7.42} = [H^+] = 3.8 \times 10^{-8} \text{ mol/L}$$

$$pOH = 14 - 7.42 = 6.58$$

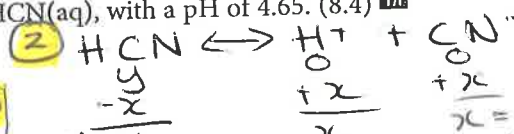
$$[OH^-] = 10^{-6.58} = 2.63 \times 10^{-7} \text{ mol/L}$$

$$pH = -\log[H^+] = -\log(3.8 \times 10^{-8}) = 7.42$$

$$pH = 4.65$$

$$[H^+] = 10^{-4.65} = 2.2387 \times 10^{-5}$$

8. Calculate the percentage ionization of 1.00 mol/L solution of hydrocyanic acid,  $HCN(aq)$ , with a pH of 4.65. (8.4) **177**



$$K_a(HCN) = 6.2 \times 10^{-10}$$

$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

$$\frac{2.2387 \times 10^{-5}}{1.00} \times 100 = 0.8084 \%$$

$$6.2 \times 10^{-10} = \frac{(2.2387 \times 10^{-5})^2}{1-y}$$

$$y = 2.2387 \times 10^{-5}$$

% Ionization = 0.02776