Solubility Equilibria

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, Ksp, of the solid. For a heterogeneous equilibrium involving the slightly soluble solid MpXq and its ions M^{m+} and $X^{n-}: MpXq(s) \Rightarrow pM^{m+}(aq)+qX^{n-}(aq)$ the solubility product expression is: $Ksp=[M^{m+}]P[X^{n-}]q$ The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its Ksp, provided the only significant reaction that occurs when the solid dissolves is the formation of its ions. A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product.

30.1 Precipitation and Dissolution

Learning Objectives

By the end of this section, you will be able to:

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

Solubility equilibria are established when the dissolution and precipitation of a solute species occur at equal rates. These equilibria underlie many natural and technological processes, ranging from tooth decay to water purification. An understanding of the factors affecting compound solubility is, therefore, essential to the effective management of these processes. This section applies previously introduced equilibrium concepts and tools to systems involving dissolution and precipitation.

30.1.1 The Solubility Product

Recall from the chapter on solutions that the solubility of a substance can vary from essentially zero (*insoluble* or *sparingly soluble*) to infinity (*miscible*). A solute with finite solubility can yield a *saturated* solution when it is added to a solvent in an amount exceeding its solubility, resulting in a heterogeneous mixture of the saturated solution and the excess, undissolved solute. For example, a saturated solution of silver chloride is one in which the equilibrium shown below has been established.

30

AgCl(s)
$$\underset{\text{precipitation}}{\overset{\text{dissolution}}{\longrightarrow}} \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

In this solution, an excess of solid AgCl dissolves and dissociates to produce aqueous Ag^+ and Cl^- ions at the same rate that these aqueous ions combine and precipitate to form solid AgCl (<u>Figure 30.1</u>). Because silver chloride is a sparingly soluble salt, the equilibrium concentration of its dissolved ions in the solution is relatively low.

Figure 30.1

Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.



The equilibrium constant for solubility equilibria such as this one is called the **solubility product constant**, *K*_{sp}, in this case

$$\operatorname{AgCl}(s) \rightleftharpoons \operatorname{Ag}^+(aq) + \operatorname{Cl}^-(aq) \qquad K_{sp} = [\operatorname{Ag}^+(aq)][\operatorname{Cl}^-(aq)]$$

Recall that only gases and solutes are represented in equilibrium constant expressions, so the K_{sp} does not include a term for the undissolved AgCl. A listing of solubility product constants for several sparingly soluble compounds is provided in <u>Appendix J</u>.

Writing Equations and Solubility Products

Write the dissolution equation and the solubility product expression for each of the following slightly soluble ionic compounds:

(a) AgI, silver iodide, a solid with antiseptic properties

(b) CaCO₃, calcium carbonate, the active ingredient in many over-the-counter chewable antacids

(c) Mg(OH)₂, magnesium hydroxide, the active ingredient in Milk of Magnesia

(d) $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium

(e) Ca₅(PO₄)₃OH, the mineral apatite, a source of phosphate for fertilizers

Solution

(a) $\operatorname{AgI}(s) \rightleftharpoons \operatorname{Ag}^+(aq) + \operatorname{I}^-(aq)$	$K_{\rm sp}$	=	$[Ag^+][I^-$
(b) $\operatorname{CaCO}_3(s) \rightleftharpoons \operatorname{Ca}^{2^+}(aq) + \operatorname{CO}_3^{2^-}(aq)$	$K_{\rm sp}$	=	[Ca ²⁺][CO ₂
(c) $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^{-}(aq)$	$K_{\rm sp}$	=	[Mg ²⁺][OH
(d) Mg(NH ₄)PO ₄ (s) \rightleftharpoons Mg ²⁺ (aq) + NH ₄ ⁺ (aq) + PO ₄ ³⁻ (aq)	$K_{\rm sp}$	=	$[Mg^{2+}][NH_4^{+}]$
(e) $\operatorname{Ca}_5(\operatorname{PO}_4)\operatorname{3OH}(s) \rightleftharpoons \operatorname{5Ca}^{2+}(aq) + \operatorname{3PO}_4^{3-}(aq) + \operatorname{OH}^-(aq)$	$K_{\rm sp}$	=	$[Ca^{2+}]^{5}[PO_{4}^{3-}]$

Check Your Learning

Write the dissolution equation and the solubility product for each of the following slightly soluble compounds: (a) BaSO₄

(b) Ag₂SO₄

(

(c) Al(OH) $_3$

(d) Pb(OH)Cl

✓ Answer

(a)
$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

(b) $Ag_2 SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$
(c) $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$
(d) $Pb(OH)Cl(s) \rightleftharpoons Pb^{2+}(aq) + OH^-(aq) + Cl^-(aq)$
 $K_{sp} = [Ag^+]^2 [SO_4^{2-}];$
 $K_{sp} = [Al^{3+}][OH^-]^3;$
 $K_{sp} = [Pb^{2+}][OH^-][Cl^-]$

K_{sp} and Solubility

The K_{sp} of a slightly soluble ionic compound may be simply related to its measured solubility provided the dissolution process involves only dissociation and solvation, for example:

$$M_p X_q(s) \rightleftharpoons p M^{m^+}(aq) + q X^{n^-}(aq)$$

For cases such as these, one may derive K_{sp} values from provided solubilities, or vice-versa. Calculations of this sort are most conveniently performed using a compound's molar solubility, measured as moles of dissolved solute per liter of saturated solution.

Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, CaF_{2} , is a slightly soluble solid that dissolves according to the equation:

$$\operatorname{CaF}_{2}(s) \rightleftharpoons \operatorname{Ca}^{2+}(aq) + 2\operatorname{F}^{-}(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.15×10^{-4} *M*. What is the solubility product of fluorite?

Solution

According to the stoichiometry of the dissolution equation, the fluoride ion molarity of a CaF_2 solution is equal to twice its calcium ion molarity:

$$[F^{-}] = (2 \text{ mol } F^{-} / 1 \text{ mol } Ca^{2+}) = (2)(2.15 \times 10^{-4} \text{ } M) = 4.30 \times 10^{-4} \text{ } M$$

Substituting the ion concentrations into the K_{sp} expression gives

$$K_{\rm sp} = [{\rm Ca}^{2^+}][{\rm F}^-]^2 = (2.15 \times 10^{-4})(4.30 \times 10^{-4})^2 = 3.98 \times 10^{-11}$$

Check Your Learning

In a saturated solution of Mg(OH)₂, the concentration of Mg²⁺ is 1.31×10^{-4} *M*. What is the solubility product for Mg(OH)₂?

$$Mg(OH)_{\gamma}(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^{-}(aq)$$

✓ Answer

8.99 × 10⁻¹²

Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3

 \times

10⁻⁹. Calculate the molar solubility of copper bromide.

Solution

The dissolution equation and solubility product expression are

$$\operatorname{CuBr}(s) \rightleftharpoons \operatorname{Cu}^+(aq) + \operatorname{Br}^-(aq)$$

$$K_{\rm sp} = [{\rm Cu}^+][{\rm Br}^-]$$

Following the ICE approach to this calculation yields the table

	CuBr (s) 🧮	── Cu ⁺ (aq) -	+ Br⁻ (<i>aq</i>)
Initial concentration (M)		0	0
Change (<i>M</i>)		+ <i>x</i>	+ <i>x</i>
Equilibrium concentration (M)		X	X

Substituting the equilibrium concentration terms into the solubility product expression and solving for x yields

$$K_{\rm sp} = [{\rm Cu}^+][{\rm Br}^-]$$

$$6.3 \times 10^{-9} = (x)(x) = x^2$$

$$x = \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5} M$$

Since the dissolution stoichiometry shows one mole of copper(I) ion and one mole of bromide ion are produced for each moles of Br dissolved, the molar solubility of CuBr is 7.9×10^{-5} M.

Check Your Learning

The K_{sp} of Agl is 1.5×10^{-16} . Calculate the molar solubility of silver iodide.

 Answer
1.2
×
10 ⁻⁸ <i>M</i>

Determination of Molar Solubility from K_{sp}

The K_{sp} of calcium hydroxide, Ca(OH)₂, is 1.3×10^{-6} . Calculate the molar solubility of calcium hydroxide.

Solution

The dissolution equation and solubility product expression are

$$\operatorname{Ca(OH)}_{2}(s) \rightleftharpoons \operatorname{Ca}^{2+}(aq) + 2\operatorname{OH}^{-}(aq)$$

$$K_{\rm sp} = [{\rm Ca}^{2+}][{\rm OH}^{-}]^2$$

The ICE table for this system is

	$Ca(OH)_2(s) \Longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$		
Initial concentration (M)		0	0
Change (<i>M</i>)		+x	+2x
Equilibrium concentration (M)		x	2 <i>x</i>

Substituting terms for the equilibrium concentrations into the solubility product expression and solving for *x* gives

$$K_{\rm sp} = [{\rm Ca}^{2+}][{\rm OH}^{-}]^2$$

$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$

$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 6.9 \times 10^{-3} M$$

As defined in the ICE table, *x* is the molarity of calcium ion in the saturated solution. The dissolution stoichiometry shows a 1:1 relation between moles of calcium ion in solution and moles of compound dissolved, and so, the molar solubility of $Ca(OH)_2$ is 6.9×10^{-3} *M*.

Check Your Learning

The K_{sp} of Pbl₂ is 1.4×10⁻⁸. Calculate the molar solubility of lead(II) iodide.

 Answer 	
1.5	
×	
10 ⁻³ M	

Determination of K_{sp} from Gram Solubility

Many of the pigments used by artists in oil-based paints (Figure 30.2) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, PbCrO₄, is 4.6×10^{-6} g/L. Determine the solubility product for PbCrO₄.

Figure 30.2

Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow (PbCrO₄), examples include Prussian blue (Fe_7(CN)_{18}), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)



Solution

Before calculating the solubility product, the provided solubility must be converted to molarity:

$$[PbCrO_4] = \frac{4.6 \times 10^{-6} \text{ g PbCrO}_4}{1 \text{ L}} \times \frac{1 \text{ mol PbCrO}_4}{323.2 \text{ g PbCrO}_4}$$
$$= \frac{1.4 \times 10^{-8} \text{ mol PbCrO}_4}{1 \text{ L}}$$
$$= 1.4 \times 10^{-8} M$$

The dissolution equation for this compound is

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

The dissolution stoichiometry shows a 1:1 relation between the molar amounts of compound and its two ions, and so both $[Pb^{2+}]$ and

are equal to the molar solubility of PbCrO₄:

$$[Pb^{2+}] = [CrO_4^{2-}] = 1.4 \times 10^{-8} M$$

 $K_{\rm sp} = [{\rm Pb}^{2+}]$

 $= (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$

Check Your Learning

The solubility of TICI [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.12 grams per liter at 20 °C. What is its solubility product?

Answer	
1.69	
×	
10 ⁻⁴	

Calculating the Solubility of Hg₂Cl₂

Calomel, Hg₂Cl₂, is a compound composed of the diatomic ion of mercury(I),

Hg₂²⁺,

and chloride ions, Cl⁻. Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel has a very low solubility, as suggested by its very small K_{sp} :

$$\mathrm{Hg}_{2} \mathrm{Cl}_{2}(s) \rightleftharpoons \mathrm{Hg}_{2}^{2+}(aq) + 2\mathrm{Cl}^{-}(aq) \qquad K_{\mathrm{sp}} = 1.1 \times 10^{-18}$$

Calculate the molar solubility of Hg₂Cl₂.

Solution

The dissolution stoichiometry shows a 1:1 relation between the amount of compound dissolved and the amount of mercury(I) ions, and so the molar solubility of Hg_2Cl_2 is equal to the concentration of

 Hg_{2}^{2+}

ions

Following the ICE approach results in

	$Hg_2Cl_2(s) \Longrightarrow Hg_2^{2+}(aq) + 2Cl^{-}(aq)$		
Initial concentration (M)		0	0
Change (<i>M</i>)		+x	+2x
Equilibrium concentration (M)		X	2 <i>x</i>

Substituting the equilibrium concentration terms into the solubility product expression and solving for x gives

$$K_{\rm sp} = [{\rm Hg}_2^{2+}][{\rm Cl}^-]^2$$

$$1.1 \times 10^{-18} = (x)(2x)^2$$

 $4x^3 = 1.1 \times 10^{-18}$

$$x = \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} = 6.5 \times 10^{-7} M$$
$$[Hg_2^{2+}] = 6.5 \times 10^{-7} M = 6.5 \times 10^{-7} M$$
$$[Cl^{-}] = 2x = 2(6.5 \times 10^{-7}) = 1.3 \times 10^{-6} M$$

The dissolution stoichiometry shows the molar solubility of $\mathrm{Hg}_{2}\mathrm{CI}_{2}$ is equal to

[Hg₂²⁺],

or 6.5×10⁻⁷ *M*.

Check Your Learning

Determine the molar solubility of MgF₂ from its solubility product: K_{sp} = 6.4×10⁻⁹.

Answer	
1.2	
×	
10 ⁻³ <i>M</i>	

30.1.8 HOW SCIENCES INTERCONNECT

Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 2.3×10^{-8} , very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 30.3).

Figure 30.3

A suspension of barium sulfate coats the intestinal tract, permitting greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons)



Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Visit this <u>website</u> for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

30.1.9 Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Ca^{2+}][CO_3^{2-}] = 8.7 \times 10^{-9}$$

It is important to realize that this equilibrium is established in any aqueous solution containing Ca^{2+} and CO_3^{2-} ions, not just in a solution formed by saturating water with calcium carbonate. Consider, for example, mixing aqueous solutions of the soluble compounds sodium carbonate and calcium nitrate. If the concentrations of calcium and carbonate ions in the mixture do not yield a reaction quotient, Q_{sp} , that exceeds the solubility product, K_{sp} , then no precipitation will occur. If the ion concentrations yield a reaction quotient greater than the solubility product, then precipitation will occur, lowering those concentrations until equilibrium is established ($Q_{sp} = K_{sp}$). The comparison of Q_{sp} to K_{sp} to predict precipitation is an example of the general approach to predicting the direction of a reaction first introduced in the chapter on equilibrium. For the specific case of solubility equilibria:

 $Q_{sp} < K_{sp}$: the reaction proceeds in the forward direction (solution is not saturated; no precipitation observed)

 $Q_{sp} > K_{sp}$: the reaction proceeds in the reverse direction (solution is supersaturated; precipitation will occur)

This predictive strategy and related calculations are demonstrated in the next few example exercises.

Precipitation of Mg(OH)₂

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$
 $K_{sp} = 8.9 \times 10^{-12}$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough Ca(OH)₂ is added to give a [OH⁻] of 0.0010 *M*?

Solution

Calculation of the reaction quotient under these conditions is shown here:

$$Q = [Mg^{2+}][OH^{-}]^{2} = (0.0537)(0.0010)^{2} = 5.4 \times 10^{-8}$$

Because *Q* is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 8.9 \times 10^{-12}$), the reverse reaction will proceed, precipitating magnesium hydroxide until the dissolved ion concentrations have been sufficiently lowered, so that $Q_{sp} = K_{sp}$.

Check Your Learning

Predict whether CaHPO₄ will precipitate from a solution with $[Ca^{2+}] = 0.0001 M$ and

[HPO₄²⁻]

= 0.001 *M*.

✓ Answer

No precipitation of CaHPO₄; Q = 1

 \times

```
10^{-7}, which is less than K_{\rm sp} (7 × 10^{-7})
```

Precipitation of AgCl

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4} -*M* solution of AgNO₃ and a 2.0×10^{-4} -*M* solution of NaCl are mixed?

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$\operatorname{AgCl}(s) \rightleftharpoons \operatorname{Ag}^+(aq) + \operatorname{Cl}^-(aq)$$

The solubility product is 1.6×10^{-10} (see <u>Appendix J</u>).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of AgNO₃ and NaCl is greater than K_{sp} . Because the volume doubles when equal volumes of AgNO₃ and NaCl solutions are mixed, each concentration is reduced to half its initial value

$$\frac{1}{2}(2.0 \times 10^{-4}) M = 1.0 \times 10^{-4} M$$

The reaction quotient, Q, is greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [Ag^+][Cl^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sl}$$

AgCl will precipitate from the mixture until the dissolution equilibrium is established, with Q equal to K_{sp} .

Check Your Learning

Will KClO₄ precipitate when 20 mL of a 0.050-M solution of K⁺ is added to 80 mL of a 0.50-M solution of

$$ClO_4^-?$$

(Hint: Use the dilution equation to calculate the concentrations of potassium and perchlorate ions in the mixture.)

✓ Answer

No, *Q* = 4.0

 \times

 10^{-3} , which is less than $K_{sp} = 1.05$

Х

10⁻²

Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion,

for this purpose (Figure 30.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, CaC_2O_4 ·H₂O (calcium oxalate monohydrate). The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} *M*. What concentration of

ion must be established before CaC_2O_4 $\cdot H_2O$ begins to precipitate? Figure 30.4

Anticoagulants can be added to blood that will combine with the Ca²⁺ ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)



Solution

The equilibrium expression is:

$$\operatorname{CaC}_2\operatorname{O}_4(s) \rightleftharpoons \operatorname{Ca}^{2^+}(aq) + \operatorname{C}_2\operatorname{O}_4^{2^-}(aq)$$

For this reaction:

$$K_{\rm sp} = [{\rm Ca}^{2+}][{\rm C}_2 {\rm O}_4^{2-}] = 1.96 \times 10^{-8}$$

(see Appendix J)

Substitute the provided calcium ion concentration into the solubility product expression and solve for oxalate concentration:

$$Q = K_{\rm sp} = [{\rm Ca}^{2+}][{\rm C}_2 {\rm O}_4^{2-}] = 1.96 \times 10^{-8}$$

$$(2.2 \times 10^{-3})[C_2 O_4^{2-}] = 1.96 \times 10^{-8}$$

$$[C_2 O_4^{2^-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6} M$$

A concentration of

 $[{\rm C_2\,O_4}^{2^-}]$

= 8.9×10^{-6} *M* is necessary to initiate the precipitation of CaC₂O₄ under these conditions.

Check Your Learning

If a solution contains 0.0020 mol of

$$\operatorname{CrO_4}^{2-}$$

per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Concentrations Following Precipitation

Clothing washed in water that has a manganese $[Mn^{2+}(aq)]$ concentration exceeding 0.1 mg/L (1.8×10⁻⁶ *M*) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be decreased by adding a base to precipitate $Mn(OH)_2$. What pH is required to keep $[Mn^{2+}]$ equal to 1.8×10^{-6} *M*?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$\operatorname{Mn(OH)}_{2}(s) \rightleftharpoons \operatorname{Mn}^{2+}(aq) + 2\operatorname{OH}^{-}(aq) \qquad K_{\operatorname{sp}} = 2 \times 10^{-13}$$

At equilibrium:

$$K_{\rm sp} = [{\rm Mn}^{2+}][{\rm OH}^{-}]^2$$

or

$$(1.8 \times 10^{-6})[OH^{-}]^{2} = 2 \times 10^{-13}$$

so

$$[OH^{-}] = 3.3 \times 10^{-4} M$$

Calculate the pH from the pOH:

 $pOH = -log[OH^-] = -log(3.3 \times 10 - 4) = 3.48$ pH = 14.00 - pOH = 14.00 - 3.48 = 10.52

(final result rounded to one significant digit, limited by the certainty of the K_{sp})

Check Your Learning

The first step in the preparation of magnesium metal is the precipitation of Mg(OH)₂ from sea water by the addition of Ca(OH)₂. The concentration of Mg²⁺(*aq*) in sea water is 5.37×10^{-2} *M*. Calculate the pH at which [Mg²⁺] is decreased to 1.0×10^{-5} *M*



30.1.14 Predicting Precipitation Q vs. Ksp



30.1.15 Ksp: Concentration of lons in Solution



In solutions containing two or more ions that may form insoluble compounds with the same counter ion, an experimental strategy called selective precipitation may be used to remove individual ions from solution. By increasing the counter ion concentration in a controlled manner, ions in solution may be precipitated individually, assuming their compound solubilities are adequately different. In solutions with equal concentrations of target ions, the ion forming the least soluble compound will precipitate first (at the lowest concentration of counter ion), with the other ions subsequently precipitating as their compound's solubilities are reached. As an illustration of this technique, the next example exercise describes separation of a two halide ions via precipitation of one as a silver salt.

30.1.16 CHEMISTRY IN EVERYDAY LIFE

The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure 30.5). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions

 (PO_4^{3-})

are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.

Figure 30.5

Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: "eutrophication&hypoxia"/Wikimedia Commons)



One common way to remove phosphates from water is by the addition of calcium hydroxide, or lime, $Ca(OH)_2$. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3OH$, which then precipitates out of the solution:

$$5Ca^{2+} + 3PO_4^{3-} + OH^- \rightleftharpoons Ca_5(PO_4)_2 \cdot OH(s)$$

Because the amount of calcium ion added does not result in exceeding the solubility products for other calcium salts, the anions of those salts remain behind in the wastewater. The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View this <u>site</u> for more information on how phosphorus is removed from wastewater.

Precipitation of Silver Halides

A solution contains 0.00010 mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

Solution

The two equilibria involved are:

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq) \qquad K_{sp} = 1.6 \times 10^{-10}$$
$$AgBr(s) \rightleftharpoons Ag^{+}(aq) + Br^{-}(aq) \qquad K_{sp} = 5.0 \times 10^{-13}$$

If the solution contained about *equal* concentrations of Cl^- and Br^- , then the silver salt with the smaller K_{sp} (AgBr) would precipitate first. The concentrations are not equal, however, so the [Ag⁺] at which AgCl begins to precipitate and the [Ag⁺] at which AgBr begins to precipitate must be calculated. The salt that forms at the lower [Ag⁺] precipitates first.

AgBr precipitates when Q equals K_{sp} for AgBr

$$Q_{\rm sp} = K_{\rm sp} = [{\rm Ag}^+][{\rm Br}^-] = [{\rm Ag}^+](0.00010) = 5.0 \times 10^{-12}$$

$$[\mathrm{Ag}^+] = \frac{5.0 \times 10^{-13}}{0.00010} = 5.0 \times 10^{-9} M$$

AgBr begins to precipitate when $[Ag^+]$ is 5.0×10^{-9} M.

For AgCl: AgCl precipitates when Q equals K_{sp} for AgCl (1.6×10⁻¹⁰). When [Cl⁻] = 0.10 M:

$$Q_{\rm sp} = K_{\rm sp} = [{\rm Ag}^+][{\rm Cl}^-] = [{\rm Ag}^+](0.10) = 1.6 \times 10^{-10}$$

$$[\mathrm{Ag}^+] = \frac{1.6 \times 10^{-10}}{0.10} = 1.6 \times 10^{-9} M$$

AgCl begins to precipitate when $[Ag^+]$ is 1.6×10^{-9} M.

AgCl begins to precipitate at a lower [Ag⁺] than AgBr, so AgCl begins to precipitate first. Note the chloride ion concentration of the initial mixture was significantly greater than the bromide ion concentration, and so silver chloride precipitated first despite having a K_{sp} greater than that of silver bromide.

Check Your Learning

If silver nitrate solution is added to a solution which is 0.050 M in both Cl⁻ and Br⁻ ions, at what [Ag⁺] would precipitation begin, and what would be the formula of the precipitate?

 Answer 	
[Ag ⁺] = 1.0	
×	
10 ⁻¹¹ <i>M</i> ; AgBr precipitates first	

Files

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Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (15.1)



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