

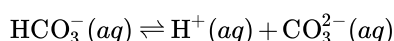
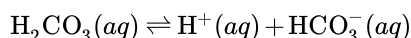
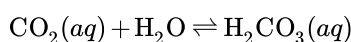
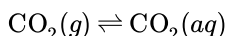
15.3: Coupled Equilibria

Learning Objectives

- Describe examples of systems involving two (or more) simultaneous chemical equilibria
- Calculate reactant and product concentrations for multiple equilibrium systems
- Compare dissolution and weak electrolyte formation

There are times when one equilibrium reaction does not adequately describe the system being studied. Sometimes we have more than one type of equilibrium occurring at once (for example, an acid-base reaction and a precipitation reaction).

The ocean is a unique example of a system with multiple equilibria, or multiple states of solubility equilibria working simultaneously. Carbon dioxide in the air dissolves in sea water, forming carbonic acid (H_2CO_3). The carbonic acid then ionizes to form hydrogen ions and bicarbonate ions (HCO_3^-), which can further ionize into more hydrogen ions and carbonate ions (CO_3^{2-}):



The excess H^+ ions make seawater more acidic. Increased ocean acidification can then have negative impacts on reef-building coral, as they cannot absorb the calcium carbonate they need to grow and maintain their skeletons (Figure 15.3.1). This in turn disrupts the local biosystem that depends upon the health of the reefs for its survival. If enough local reefs are similarly affected, the disruptions to sea life can be felt globally. The world's oceans are presently in the midst of a period of intense acidification, believed to have begun in the mid-nineteenth century, and which is now accelerating at a rate faster than any change to oceanic pH in the last 20 million years.

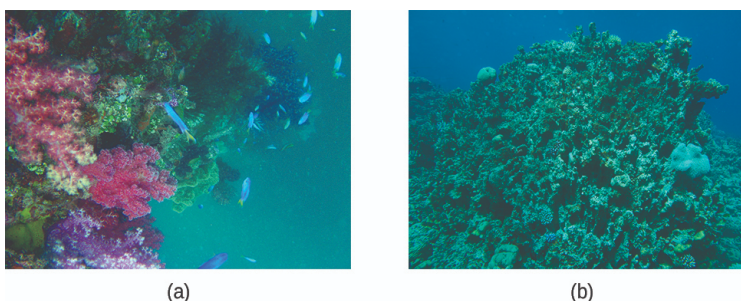


Figure 15.3.1: Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonate skeletons because of excess ocean acidification, the unhealthy reef (b) is only capable of hosting a small fraction of the species as before, and the local food chain starts to collapse. (credit a: modification of work by NOAA Photo Library; credit b: modification of work by "prilfish"/Flickr).

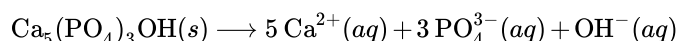
Learn more about ocean [acidification](#) and how it affects other marine creatures.

Slightly soluble solids derived from weak acids generally dissolve in strong acids, unless their solubility products are extremely small. For example, we can dissolve CuCO_3 , FeS , and $\text{Ca}_3(\text{PO}_4)_2$ in HCl because their basic anions react to form weak acids (H_2CO_3 , H_2S , and H_2PO_4^-). The resulting decrease in the concentration of the anion results in a shift of the equilibrium concentrations to the right in accordance with Le Chatelier's principle.

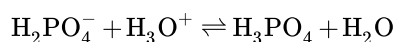
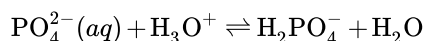
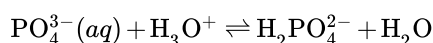


Figure 15.3.2: Crystal of the mineral hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, is shown here. Pure apatite is white, but like many other minerals, this sample is colored because of the presence of impurities.

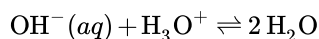
Of particular relevance to us is the dissolution of hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, in acid. Apatites are a class of calcium phosphate minerals (Figure 15.3.2); a biological form of hydroxylapatite is found as the principal mineral in the enamel of our teeth. A mixture of hydroxylapatite and water (or saliva) contains an equilibrium mixture of solid $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and dissolved Ca^{2+} , PO_4^{3-} , and OH^- ions:



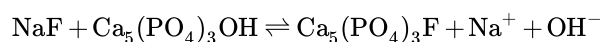
When exposed to acid, phosphate ions react with hydronium ions to form hydrogen phosphate ions and ultimately, phosphoric acid:



Hydroxide ion reacts to form water:



These reactions decrease the phosphate and hydroxide ion concentrations, and additional hydroxylapatite dissolves in an acidic solution in accord with Le Chatelier's principle. Our teeth develop cavities when acid waste produced by bacteria growing on them causes the hydroxylapatite of the enamel to dissolve. Fluoride toothpastes contain sodium fluoride, NaF, or stannous fluoride [more properly named tin(II) fluoride], SnF_2 . They function by replacing the OH^- ion in hydroxylapatite with F^- ion, producing fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$:



The resulting $\text{Ca}_5(\text{PO}_4)_3\text{F}$ is slightly less soluble than $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, and F^- is a weaker base than OH^- . Both of these factors make the fluorapatite more resistant to attack by acids than hydroxylapatite. See the Chemistry in Everyday Life feature on the role of fluoride in preventing tooth decay for more information.

Role of Fluoride in Preventing Tooth Decay

As we saw previously, fluoride ions help protect our teeth by reacting with hydroxylapatite to form fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Since it lacks a hydroxide ion, fluorapatite is more resistant to attacks by acids in our mouths and is thus less soluble, protecting our teeth. Scientists discovered that naturally fluorinated water could be beneficial to your teeth, and so it became common practice to add fluoride to drinking water. Toothpastes and mouthwashes also contain amounts of fluoride (Figure 15.3.3).

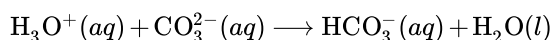


Figure 15.3.3: Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk).

Unfortunately, excess fluoride can negate its advantages. Natural sources of drinking water in various parts of the world have varying concentrations of fluoride, and places where that concentration is high are prone to certain health risks when there is

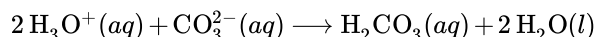
no other source of drinking water. The most serious side effect of excess fluoride is the bone disease, skeletal fluorosis. When excess fluoride is in the body, it can cause the joints to stiffen and the bones to thicken. It can severely impact mobility and can negatively affect the thyroid gland. Skeletal fluorosis is a condition that over 2.7 million people suffer from across the world. So while fluoride can protect our teeth from decay, the US Environmental Protection Agency sets a maximum level of 4 ppm (4 mg/L) of fluoride in drinking water in the US. Fluoride levels in water are not regulated in all countries, so fluorosis is a problem in areas with high levels of fluoride in the groundwater.

When acid rain attacks limestone or marble, which are calcium carbonates, a reaction occurs that is similar to the acid attack on hydroxylapatite. The hydronium ion from the acid rain combines with the carbonate ion from calcium carbonates and forms the hydrogen carbonate ion, a weak acid:

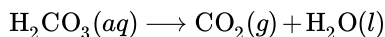


Calcium hydrogen carbonate, $\text{Ca}(\text{HCO}_3)_2$, is soluble, so limestone and marble objects slowly dissolve in acid rain.

If calcium carbonate is added to a concentrated acid, hydronium ion reacts with the carbonate ion according to the equation:



(Acid rain is usually not sufficiently acidic to cause this reaction; however, laboratory acids are.) The solution may become saturated with the weak electrolyte carbonic acid, which is unstable, and carbon dioxide gas can be evolved:



These reactions decrease the carbonate ion concentration, and additional calcium carbonate dissolves. If enough acid is present, the concentration of carbonate ion is reduced to such a low level that the reaction quotient for the dissolution of calcium carbonate remains less than the solubility product of calcium carbonate, even after all of the calcium carbonate has dissolved.

✓ Example 15.3.1: Prevention of Precipitation of $\text{Mg}(\text{OH})_2$

Calculate the concentration of ammonium ion that is required to prevent the precipitation of $\text{Mg}(\text{OH})_2$ in a solution with $[\text{Mg}^{2+}] = 0.10 \text{ M}$ and $[\text{NH}_3] = 0.10 \text{ M}$.

Solution

Two equilibria are involved in this system:

- Reaction (1): $\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2 \text{OH}^-(aq)$; $K_{\text{sp}} = 8.9 \times 10^{-12}$
- Reaction (2): $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$ $K_{\text{sp}} = 1.8 \times 10^{-5}$

To prevent the formation of solid $\text{Mg}(\text{OH})_2$, we must adjust the concentration of OH^- so that the reaction quotient for Equation (1), $Q = [\text{Mg}^{2+}][\text{OH}^-]^2$, is less than K_{sp} for $\text{Mg}(\text{OH})_2$. (To simplify the calculation, we determine the concentration of OH^- when $Q = K_{\text{sp}}$.) $[\text{OH}^-]$ can be reduced by the addition of NH_4^+ , which shifts Reaction (2) to the left and reduces $[\text{OH}^-]$.

1. We determine the $[\text{OH}^-]$ at which $Q = K_{\text{sp}}$ when $[\text{Mg}^{2+}] = 0.10 \text{ M}$:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.10)[\text{OH}^-]^2 = 8.9 \times 10^{-12}$$

$$[\text{OH}^-] = 9.4 \times 10^{-6} \text{ M}$$

Solid $\text{Mg}(\text{OH})_2$ will not form in this solution when $[\text{OH}^-]$ is less than $9.4 \times 10^{-6} \text{ M}$.

- We calculate the $[\text{NH}_4^+]$ needed to decrease $[\text{OH}^-]$ to $9.4 \times 10^{-6} \text{ M}$ when $[\text{NH}_3] = 0.10$.

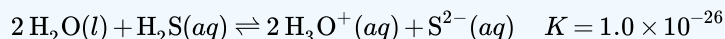
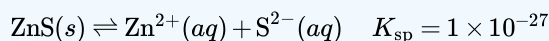
$$K_{\text{b}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{[\text{NH}_4^+](9.4 \times 10^{-6})}{0.10} = 1.8 \times 10^{-5}$$

$$[\text{NH}_4^+] = 0.19 \text{ M}$$

When $[\text{NH}_4^+]$ equals 0.19 M , $[\text{OH}^-]$ will be $9.4 \times 10^{-6} \text{ M}$. Any $[\text{NH}_4^+]$ greater than 0.19 M will reduce $[\text{OH}^-]$ below $9.4 \times 10^{-6} \text{ M}$ and prevent the formation of $\text{Mg}(\text{OH})_2$.

? Exercise 15.3.1

Consider the two equilibria:



and calculate the concentration of hydronium ion required to prevent the precipitation of ZnS in a solution that is 0.050 M in Zn^{2+} and saturated with H_2S (0.10 M H_2S).

Answer

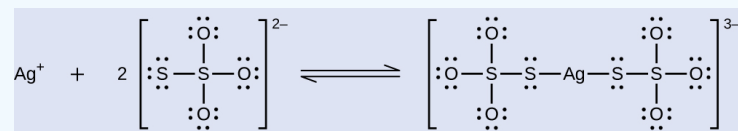
$$[\text{H}_3\text{O}^+] > 0.2 \text{ M}$$

($[\text{S}^{2-}]$ is less than $2 \times 10^{-26} \text{ M}$ and precipitation of ZnS does not occur.)

Therefore, precise calculations of the solubility of solids from the solubility product are limited to cases in which the only significant reaction occurring when the solid dissolves is the formation of its ions.

✓ Example 15.3.2: Multiple Equilibria

Unexposed silver halides are removed from photographic film when they react with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, called hypo) to form the complex ion $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ ($K_f = 4.7 \times 10^{13}$). The reaction with silver bromide is:



What mass of $\text{Na}_2\text{S}_2\text{O}_3$ is required to prepare 1.00 L of a solution that will dissolve 1.00 g of AgBr by the formation of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$?

Solution

Two equilibria are involved when AgBr dissolves in a solution containing the $\text{S}_2\text{O}_3^{2-}$ ion:

- Reaction (1): $\text{AgBr}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq) \quad K_{\text{sp}} = 5.0 \times 10^{-13}$
- Reaction (2): $\text{Ag}^+(aq) + \text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq) \quad K_f = 4.7 \times 10^{13}$

In order for 1.00 g of AgBr to dissolve, the $[\text{Ag}^+]$ in the solution that results must be low enough for Q for Reaction (1) to be smaller than K_{sp} for this reaction. We reduce $[\text{Ag}^+]$ by adding $\text{S}_2\text{O}_3^{2-}$ and thus cause Reaction (2) to shift to the right. We need the following steps to determine what mass of $\text{Na}_2\text{S}_2\text{O}_3$ is needed to provide the necessary $\text{S}_2\text{O}_3^{2-}$.

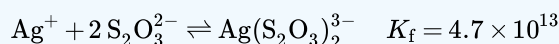
1. We calculate the $[\text{Br}^-]$ produced by the complete dissolution of 1.00 g of AgBr ($5.33 \times 10^{-3} \text{ mol AgBr}$) in 1.00 L of solution:

$$[\text{Br}^-] = 5.33 \times 10^{-3} \text{ M}$$

- We use $[\text{Br}^-]$ and K_{sp} to determine the maximum possible concentration of Ag^+ that can be present without causing reprecipitation of AgBr:

$$[\text{Ag}^+] = 9.4 \times 10^{-11} \text{ M}$$

- We determine the $[\text{S}_2\text{O}_3^{2-}]$ required to make $[\text{Ag}^+] = 9.4 \times 10^{-11} \text{ M}$ after the remaining Ag^+ ion has reacted with $\text{S}_2\text{O}_3^{2-}$ according to the equation:



Because $5.33 \times 10^{-3} \text{ mol}$ of AgBr dissolves:

$$[(5.33 \times 10^{-3}) - (9.4 \times 10^{-11})] = 5.33 \times 10^{-3} \text{ mol Ag}(\text{S}_2\text{O}_3)_2^{3-}$$

Thus, at equilibrium: $[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] = 5.33 \times 10^{-3} \text{ M}$, $[\text{Ag}^+] = 9.4 \times 10^{-11} \text{ M}$, and $Q = K_f = 4.7 \times 10^{13}$.

$$K_f = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2} = 4.7 \times 10^{13}$$

$$[\text{S}_2\text{O}_3^{2-}] = 1.1 \times 10^{-3} \text{ M}$$

When $[\text{S}_2\text{O}_3^{2-}]$ is $1.1 \times 10^{-3} \text{ M}$, $[\text{Ag}^+]$ is $9.4 \times 10^{-11} \text{ M}$ and all AgBr remains dissolved.

- We determine the total number of moles of $\text{S}_2\text{O}_3^{2-}$ that must be added to the solution. This equals the amount that reacts with Ag^+ to form $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ plus the amount of free $\text{S}_2\text{O}_3^{2-}$ in solution at equilibrium. To form $5.33 \times 10^{-3} \text{ mol}$ of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ requires $2 \times (5.33 \times 10^{-3}) \text{ mol}$ of $\text{S}_2\text{O}_3^{2-}$. In addition, $1.1 \times 10^{-3} \text{ mol}$ of unreacted $\text{S}_2\text{O}_3^{2-}$ is present (Step 3). Thus, the total amount of $\text{S}_2\text{O}_3^{2-}$ that must be added is:

$$2 \times (5.33 \times 10^{-3} \text{ mol } \text{S}_2\text{O}_3^{2-}) + 1.1 \times 10^{-3} \text{ mol } \text{S}_2\text{O}_3^{2-} = 1.18 \times 10^{-2} \text{ mol } \text{S}_2\text{O}_3^{2-}$$

- We determine the mass of $\text{Na}_2\text{S}_2\text{O}_3$ required to give $1.18 \times 10^{-2} \text{ mol } \text{S}_2\text{O}_3^{2-}$ using the molar mass of $\text{Na}_2\text{S}_2\text{O}_3$:

$$1.18 \times 10^{-2} \text{ mol } \text{S}_2\text{O}_3^{2-} \times \frac{158.1 \text{ g } \text{Na}_2\text{S}_2\text{O}_3}{1 \text{ mol } \text{Na}_2\text{S}_2\text{O}_3} = 1.9 \text{ g } \text{Na}_2\text{S}_2\text{O}_3$$

Thus, 1.00 L of a solution prepared from 1.9 g $\text{Na}_2\text{S}_2\text{O}_3$ dissolves 1.0 g of AgBr.

? Exercise 15.3.2

$\text{AgCl}(s)$, silver chloride, is well known to have a very low solubility: $\text{Ag}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$, $K_{sp} = 1.6 \times 10^{-10}$. Adding ammonia significantly increases the solubility of AgCl because a complex ion is formed: $\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$, $K_f = 1.7 \times 10^7$. What mass of NH_3 is required to prepare 1.00 L of solution that will dissolve 2.00 g of AgCl by formation of $\text{Ag}(\text{NH}_3)_2^+$?

Answer

1.00 L of a solution prepared with 4.81 g NH_3 dissolves 2.0 g of AgCl.

15.3.1: Dissolution versus Weak Electrolyte Formation

We can determine how to shift the concentration of ions in the equilibrium between a slightly soluble solid and a solution of its ions by applying Le Chatelier's principle. For example, one way to control the concentration of manganese(II) ion, Mn^{2+} , in a solution is to adjust the pH of the solution and, consequently, to manipulate the equilibrium between the slightly soluble solid manganese(II) hydroxide, manganese(II) ion, and hydroxide ion:



This could be important to a laundry because clothing washed in water that has a manganese concentration exceeding 0.1 mg per liter may be stained by the manganese. We can reduce the concentration of manganese by increasing the concentration of hydroxide ion. We could add, for example, a small amount of NaOH or some other base such as the silicates found in many laundry detergents. As the concentration of OH^- ion increases, the equilibrium responds by shifting to the left and reducing the concentration of Mn^{2+} ion while increasing the amount of solid $\text{Mn}(\text{OH})_2$ in the equilibrium mixture, as predicted by Le Chatelier's principle.

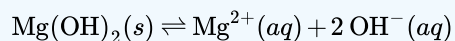
✓ Example 15.3.3: Solubility Equilibrium of a Slightly Soluble Solid

What is the effect on the amount of solid $\text{Mg}(\text{OH})_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $\text{Mg}(\text{OH})_2$ in water at equilibrium?

- MgCl_2
- KOH
- an acid
- NaNO_3
- $\text{Mg}(\text{OH})_2$

Solution

The equilibrium among solid Mg(OH)_2 and a solution of Mg^{2+} and OH^- is:



- (a) The reaction shifts to the left to relieve the stress produced by the additional Mg^{2+} ion, in accordance with Le Chatelier's principle. In quantitative terms, the added Mg^{2+} causes the reaction quotient to be larger than the solubility product ($Q > K_{sp}$), and Mg(OH)_2 forms until the reaction quotient again equals K_{sp} . At the new equilibrium, $[\text{OH}^-]$ is less and $[\text{Mg}^{2+}]$ is greater than in the solution of Mg(OH)_2 in pure water. More solid Mg(OH)_2 is present.
- (b) The reaction shifts to the left to relieve the stress of the additional OH^- ion. Mg(OH)_2 forms until the reaction quotient again equals K_{sp} . At the new equilibrium, $[\text{OH}^-]$ is greater and $[\text{Mg}^{2+}]$ is less than in the solution of Mg(OH)_2 in pure water. More solid Mg(OH)_2 is present.
- (c) The concentration of OH^- is reduced as the OH^- reacts with the acid. The reaction shifts to the right to relieve the stress of less OH^- ion. In quantitative terms, the decrease in the OH^- concentration causes the reaction quotient to be smaller than the solubility product ($Q < K_{sp}$), and additional Mg(OH)_2 dissolves until the reaction quotient again equals K_{sp} . At the new equilibrium, $[\text{OH}^-]$ is less and $[\text{Mg}^{2+}]$ is greater than in the solution of Mg(OH)_2 in pure water. More Mg(OH)_2 is dissolved.
- (d) NaNO_3 contains none of the species involved in the equilibrium, so we should expect that it has no appreciable effect on the concentrations of Mg^{2+} and OH^- . (As we have seen previously, dissolved salts change the activities of the ions of an electrolyte. However, the salt effect is generally small, and we shall neglect the slight errors that may result from it.)
- (e) The addition of solid Mg(OH)_2 has no effect on the solubility of Mg(OH)_2 or on the concentration of Mg^{2+} and OH^- . The concentration of Mg(OH)_2 does not appear in the equation for the reaction quotient:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of Q , and no shift is required to restore Q to the value of the equilibrium constant.

? Exercise 15.3.3

What is the effect on the amount of solid NiCO_3 that dissolves and the concentrations of Ni^{2+} and CO_3^{2-} when each of the following are added to a mixture of the slightly soluble solid NiCO_3 and water at equilibrium?

- $\text{Ni(NO}_3)_2$
- KClO_4
- NiCO_3
- K_2CO_3
- HNO_3 (reacts with carbonate giving HCO_3^- or H_2O and CO_2)

Answer

(a) mass of $\text{NiCO}_3(s)$ increases, $[\text{Ni}^{2+}]$ increases, $[\text{CO}_3^{2-}]$ decreases; (b) no appreciable effect; (c) no effect except to increase the amount of solid NiCO_3 ; (d) mass of $\text{NiCO}_3(s)$ increases, $[\text{Ni}^{2+}]$ decreases, $[\text{CO}_3^{2-}]$ increases; (e) mass of $\text{NiCO}_3(s)$ decreases, $[\text{Ni}^{2+}]$ increases, $[\text{CO}_3^{2-}]$ decreases

Summary

Several systems we encounter consist of multiple equilibria, systems where two or more equilibria processes are occurring simultaneously. Some common examples include acid rain, fluoridation, and dissolution of carbon dioxide in sea water. When looking at these systems, we need to consider each equilibrium separately and then combine the individual equilibrium constants into one solubility product or reaction quotient expression using the tools from the first equilibrium chapter. Le Chatelier's principle also must be considered, as each reaction in a multiple equilibria system will shift toward reactants or products based on what is added to the initial reaction and how it affects each subsequent equilibrium reaction.

Glossary

multiple equilibrium

system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

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