

17.5: Solubility and pH

Learning Objectives

- To understand why the solubility of many compounds depends on pH.

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. In this section, we discuss the relationship between the solubility of these classes of compounds and pH.

The Effect of Acid–Base Equilibria on the Solubility of Salts

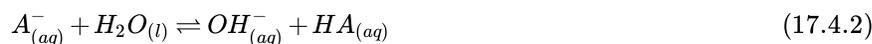
We begin our discussion by examining the effect of pH on the solubility of a representative salt, M^+A^- , where A^- is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:



with

$$K_{sp} = [M^+][A^-] \quad (17.4.1b)$$

The anion can also react with water in a hydrolysis reaction:



Because of the reaction described in [Equation 17.4.2](#), the predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-} , PO_4^{3-} , or CO_3^{2-} is increased, as described in [Section 17.1](#). If instead a strong acid is added to the solution, the added H^+ will react essentially completely with A^- to form HA. This reaction decreases $[A^-]$, which decreases the magnitude of the ion product ($Q = [M^+][A^-]$). According to Le Chatelier's principle, more MA will dissolve until $Q = K_{sp}$. Hence *an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid*. In contrast, pH has little to no effect on the solubility of salts whose anion is the conjugate base of a stronger weak acid or a strong acid, respectively (e.g., chlorides, bromides, iodides, and sulfates). For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:



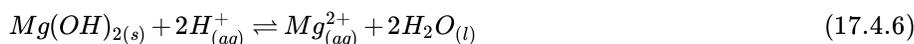
with

$$K_{sp} = 5.61 \times 10^{-12} \quad (17.4.3b)$$

When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH^- from solution:



The overall equation for the reaction of $Mg(OH)_2$ with acid is thus



As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in [Equation 17.4.6](#) is driven to the right, so more $Mg(OH)_2$ dissolves.

Such pH-dependent solubility is not restricted to salts that contain anions derived from water. For example, CaF_2 is a sparingly soluble salt:



with

$$K_{sp} = 3.45 \times 10^{-11} \quad (17.4.7b)$$

When strong acid is added to a saturated solution of CaF_2 , the following reaction occurs:



Because the forward reaction decreases the fluoride ion concentration, more CaF_2 dissolves to relieve the stress on the system. The net reaction of CaF_2 with strong acid is thus



Example 7 shows how to calculate the solubility effect of adding a strong acid to a solution of a sparingly soluble salt.

Note the Pattern

Sparingly soluble salts derived from weak acids tend to be more soluble in an acidic solution.

Example 17.4.1

Lead oxalate (PbC_2O_4), lead iodide (PbI_2), and lead sulfate (PbSO_4) are all rather insoluble, with K_{sp} values of 4.8×10^{-10} , 9.8×10^{-9} , and 2.53×10^{-8} , respectively. What effect does adding a strong acid, such as perchloric acid, have on their relative solubilities?

Given: K_{sp} values for three compounds

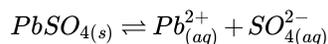
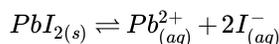
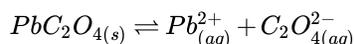
Asked for: relative solubilities in acid solution

Strategy:

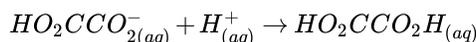
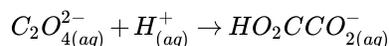
Write the balanced chemical equation for the dissolution of each salt. Because the strongest conjugate base will be most affected by the addition of strong acid, determine the relative solubilities from the relative basicity of the anions.

Solution:

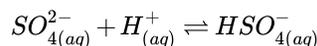
The solubility equilibria for the three salts are as follows:



The addition of a strong acid will have the greatest effect on the solubility of a salt that contains the conjugate base of a weak acid as the anion. Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form $\text{H}^+(\text{aq})$ and the corresponding anion. In contrast, oxalate is the fully deprotonated form of oxalic acid ($\text{HO}_2\text{CCO}_2\text{H}$), which is a weak diprotic acid ($\text{p}K_{\text{a}1} = 1.23$ and $\text{p}K_{\text{a}2} = 4.19$). Consequently, the oxalate ion has a significant affinity for one proton and a lower affinity for a second proton. Adding a strong acid to a saturated solution of lead oxalate will result in the following reactions:



These reactions will decrease $[\text{C}_2\text{O}_4^{2-}]$, causing more lead oxalate to dissolve to relieve the stress on the system. The $\text{p}K_{\text{a}}$ of HSO_4^- (1.99) is similar in magnitude to the $\text{p}K_{\text{a}1}$ of oxalic acid, so adding a strong acid to a saturated solution of PbSO_4 will result in the following reaction:



Because HSO_4^- has a $\text{p}K_{\text{a}}$ of 1.99, this reaction will lie largely to the left as written. Consequently, we predict that the effect of added strong acid on the solubility of PbSO_4 will be significantly less than for PbC_2O_4 .

Exercise

Which of the following insoluble salts— AgCl , Ag_2CO_3 , Ag_3PO_4 , and/or AgBr —will be substantially more soluble in 1.0 M HNO_3 than in pure water?

Answer: Ag_2CO_3 and Ag_3PO_4

Caves and their associated pinnacles and spires of stone provide one of the most impressive examples of pH-dependent solubility equilibria (part (a) in [Figure 17.6](#)). Perhaps the most familiar caves are formed from limestone, such as Carlsbad Caverns in New Mexico, Mammoth Cave in Kentucky, and Luray Caverns in Virginia. The primary reactions that are responsible for the formation of limestone caves are as follows:

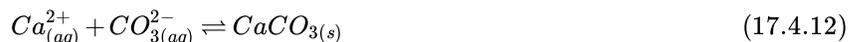
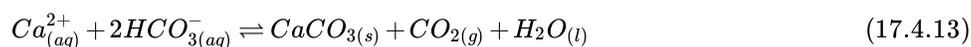


Figure 17.4.1 The Chemistry of Cave Formation (a) This cave in Campanet, Mallorca, Spain, and its associated formations are examples of pH-dependent solubility equilibria. (b) A cave forms when groundwater containing atmospheric CO_2 , forming an acidic solution, dissolves limestone (CaCO_3) in a process that may take tens of thousands of years. As groundwater seeps into a cave, water evaporates from the solution of CaCO_3 in CO_2 -rich water, producing a supersaturated solution and a shift in equilibrium that causes precipitation of the CaCO_3 . The deposited limestone eventually forms stalactites and stalagmites.

Limestone deposits that form caves consist primarily of CaCO_3 from the remains of living creatures such as clams and corals, which used it for making structures such as shells. When a saturated solution of CaCO_3 in CO_2 -rich water rises toward Earth's surface or is otherwise heated, CO_2 gas is released as the water warms. CaCO_3 then precipitates from the solution according to the following equation (part (b) in [Figure 17.4.1](#)):



The forward direction is the same reaction that produces the solid called *scale* in teapots, coffee makers, water heaters, boilers, and other places where hard water is repeatedly heated.

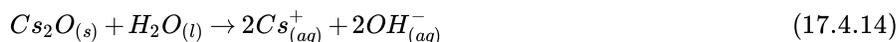
When groundwater-containing atmospheric CO_2 ([Equation 17.4.10](#) and [Equation 17.4.11](#)) finds its way into microscopic cracks in the limestone deposits, CaCO_3 dissolves in the acidic solution in the reverse direction of [Equation 17.4.13](#). The cracks gradually enlarge from 10–50 μm to 5–10 mm, a process that can take as long as 10,000 yr. Eventually, after about another 10,000 yr, a cave forms. Groundwater from the surface seeps into the cave and clings to the ceiling, where the water evaporates and causes the equilibrium in [Equation 17.4.13](#) to shift to the right. A circular layer of solid CaCO_3 is deposited, which eventually produces a long, hollow spire of limestone called a *stalactite* that grows down from the ceiling. Below, where the droplets land when they fall from the ceiling, a similar process causes another spire, called a *stalagmite*, to grow up. The same processes that carve out hollows below ground are also at work above ground, in some cases producing fantastically convoluted landscapes like that of Yunnan Province in China ([Figure 17.4.2](#)).



Figure 17.4.2 Solubility Equilibria in the Formation of Karst Landscapes Landscapes such as the steep limestone pinnacles of the Stone Forest in Yunnan Province, China, are formed from the same process that produces caves and their associated formations.

Acidic, Basic, and Amphoteric Oxides and Hydroxides

One of the earliest classifications of substances was based on their solubility in acidic versus basic solution, which led to the classification of oxides and hydroxides as being either basic or acidic. Basic oxides An oxide that reacts with water to produce a basic solution or dissolves readily in aqueous acid. and hydroxides either react with water to produce a basic solution or dissolve readily in aqueous acid. Acidic oxides An oxide that reacts with water to produce an acidic solution or dissolves in aqueous base. or hydroxides either react with water to produce an acidic solution or are soluble in aqueous base. As shown in Figure 17.4.3, there is a clear correlation between the acidic or the basic character of an oxide and the position of the element combined with oxygen in the periodic table. *Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements are acidic oxides.* Compare, for example, the reactions of a typical metal oxide, cesium oxide, and a typical nonmetal oxide, sulfur trioxide, with water:

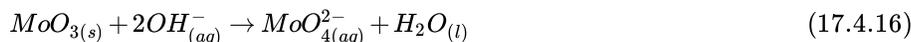


Cesium oxide reacts with water to produce a basic solution of cesium hydroxide, whereas sulfur trioxide reacts with water to produce a solution of sulfuric acid—very different behaviors indeed!

Note the Pattern

Metal oxides generally react with water to produce basic solutions, whereas nonmetal oxides produce acidic solutions.

The difference in reactivity is due to the difference in bonding in the two kinds of oxides. Because of the low electronegativity of the metals at the far left in the periodic table, their oxides are best viewed as containing discrete Mn^+ cations and O^{2-} anions. At the other end of the spectrum are nonmetal oxides; due to their higher electronegativities, nonmetals form oxides with covalent bonds to oxygen. Because of the high electronegativity of oxygen, however, the covalent bond between oxygen and the other atom, E, is usually polarized: $E^{\delta+}-O^{\delta-}$. The atom E in these oxides acts as a Lewis acid that reacts with the oxygen atom of water to produce an oxoacid. Oxides of metals in high oxidation states also tend to be acidic oxides for the same reason: they contain covalent bonds to oxygen. An example of an acidic metal oxide is MoO_3 , which is insoluble in both water and acid but dissolves in strong base to give solutions of the molybdate ion (MoO_4^{2-}):



	1	2	metal/nonmetal line		13	14	15	16	17
2	Li ₂ O	BeO			B ₂ O ₃	CO ₂	N ₂ O ₃ N ₂ O ₅	O	OF ₂
3	Na ₂ O	MgO			Al ₂ O ₃	SiO ₂	P ₂ O ₃ P ₂ O ₅	SO ₂ SO ₃	Cl ₂ O ₇
4	K ₂ O	CaO			Ga ₂ O ₃	GeO ₂	As ₂ O ₃ As ₂ O ₅	SeO ₂ SeO ₃	Br ₂ O
5	Rb ₂ O	SrO			In ₂ O ₃	SnO ₂	Sb ₂ O ₅	TeO ₃	I ₂ O ₅
6	Cs ₂ O	BaO			Tl ₂ O ₃	PbO ₂	Bi ₂ O ₅	Po	At

basic oxide
 amphoteric oxide
 acidic oxide

Figure 17.4.3 Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic Character. There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table. Oxides of metallic elements are generally basic oxides, which either react with water to form a basic solution or dissolve in aqueous acid. In contrast, oxides of nonmetallic elements are acidic oxides, which either react with water to form an acidic solution or are soluble in aqueous base. Oxides of intermediate character, called amphoteric oxides, are located along a diagonal line between the two extremes. Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex ion. (Radioactive elements are not classified.)

As shown in Figure 17.4.3, there is a gradual transition from basic metal oxides to acidic nonmetal oxides as we go from the lower left to the upper right in the periodic table, with a broad diagonal band of oxides of intermediate character separating the two extremes. Many of the oxides of the elements in this diagonal region of the periodic table are soluble in both acidic *and* basic solutions; consequently, they are called amphoteric oxides. An oxide that can dissolve in acid to produce water and dissolve in base to produce a soluble complex. (from the Greek *ampho*, meaning “both,” as in *amphiprotic*, which was defined in Section 16.1). Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex. As shown in Figure 17.4.4, for example, mixing the amphoteric oxide Cr(OH)₃ (also written as Cr₂O₃·3H₂O) with water gives a muddy, purple-brown suspension. Adding acid causes the Cr(OH)₃ to dissolve to give a bright violet solution of Cr³⁺(aq), which contains the [Cr(H₂O)₆]³⁺ ion, whereas adding strong base gives a green solution of the [Cr(OH)₄]⁻ ion. The chemical equations for the reactions are as follows:

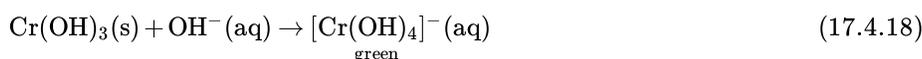
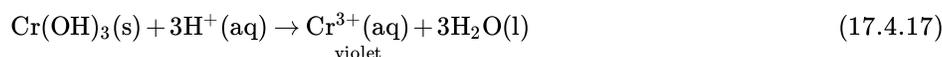


Figure 17.4.4 Chromium(III) Hydroxide [Cr(OH)₃ or Cr₂O₃·3H₂O] Is an Example of an Amphoteric Oxide All three beakers originally contained a suspension of brownish purple Cr(OH)₃(s) (center). When concentrated acid (6 M H₂SO₄) was added to the beaker on the left, Cr(OH)₃ dissolved to produce violet [Cr(H₂O)₆]³⁺ ions and water. The addition of concentrated base (6 M NaOH) to the beaker on the right caused Cr(OH)₃ to dissolve, producing green [Cr(OH)₄]⁻ ions.

Example 17.4.2

Aluminum hydroxide, written as either Al(OH)₃ or Al₂O₃·3H₂O, is amphoteric. Write chemical equations to describe the dissolution of aluminum hydroxide in (a) acid and (b) base.

Given: amphoteric compound

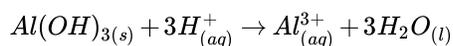
Asked for: dissolution reactions in acid and base

Strategy:

Using Equation 17.4.17 and Equation 17.4.18 as a guide, write the dissolution reactions in acid and base solutions.

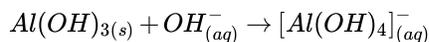
Solution:

1. An acid donates protons to hydroxide to give water and the hydrated metal ion, so aluminum hydroxide, which contains three OH^- ions per Al, needs three H^+ ions:



In aqueous solution, Al^{3+} forms the complex ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.

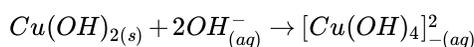
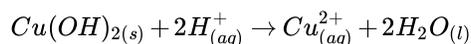
2. In basic solution, OH^- is added to the compound to produce a soluble and stable poly(hydroxo) complex:



Exercise

Copper(II) hydroxide, written as either $\text{Cu}(\text{OH})_2$ or $\text{CuO} \cdot \text{H}_2\text{O}$, is amphoteric. Write chemical equations that describe the dissolution of cupric hydroxide both in an acid and in a base.

Answer



Selective Precipitation Using pH

Many dissolved metal ions can be separated by the selective precipitation of the cations from solution under specific conditions. In this technique, pH is often used to control the concentration of the anion in solution, which controls which cations precipitate.

Note the Pattern

The concentration of anions in solution can often be controlled by adjusting the pH, thereby allowing the selective precipitation of cations.

Suppose, for example, we have a solution that contains 1.0 mM Zn^{2+} and 1.0 mM Cd^{2+} and want to separate the two metals by selective precipitation as the insoluble sulfide salts, ZnS and CdS . The relevant solubility equilibria can be written as follows:



with

$$K_{sp} = 1.6 \times 10^{-24} \quad (17.4.19b)$$

and



with

$$K_{sp} = 8.0 \times 10^{-27} \quad (17.4.20b)$$

Because the S^{2-} ion is quite basic and reacts extensively with water to give HS^- and OH^- , the solubility equilibria are more accurately written as $\text{MS}(s) = \text{M}^{2+}(aq) + \text{HS}^-(aq) + \text{OH}^-(aq)$ rather than $\text{MS}(s) = \text{M}^{2+}(aq) + \text{S}^{2-}(aq)$. Here we use the simpler form involving S^{2-} , which is justified because we take the reaction of S^{2-} with water into account later in the solution, arriving at the same answer using either equilibrium equation.

The sulfide concentrations needed to cause ZnS and CdS to precipitate are as follows:

$$K_{sp} = [\text{Zn}^{2+}][\text{S}^{2-}] \quad (17.4.21a)$$

$$1.6 \times 10^{-24} = (0.0010 \text{ M})[\text{S}^{2-}] \quad (17.4.21b)$$

$$1.6 \times 10^{-21} \text{ M} = [\text{S}^{2-}] \quad (17.4.21c)$$

and

$$K_{sp} = [\text{Cd}^{2+}][\text{S}^{2-}] \quad (17.4.22a)$$

$$8.0 \times 10^{-27} = (0.0010 \text{ M})[S^{2-}] \quad (17.4.22b)$$

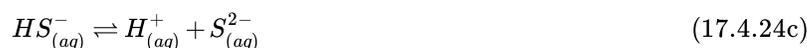
$$8.0 \times 10^{-24} \text{ M} = [S^{2-}] \quad (17.4.22c)$$

Thus sulfide concentrations between $1.6 \times 10^{-21} \text{ M}$ and $8.0 \times 10^{-24} \text{ M}$ will precipitate CdS from solution but not ZnS. How do we obtain such low concentrations of sulfide? A saturated aqueous solution of H_2S contains 0.10 M H_2S at 20°C . The pK_{a1} for H_2S is 6.97, and pK_{a2} corresponding to the formation of $[S^{2-}]$ is 12.90. The equations for these reactions are as follows:



with

$$pK_{a1} = 6.97 \text{ and hence } K_{a1} = 1.1 \times 10^{-7} \quad (17.4.24b)$$



with

$$pK_{a2} = 12.90 \text{ and hence } K_{a2} = 1.3 \times 10^{-13} \quad (17.4.24d)$$

We can show that the concentration of S^{2-} is 1.3×10^{-13} by comparing K_{a1} and K_{a2} and recognizing that the contribution to $[H^+]$ from the dissociation of HS^- is negligible compared with $[H^+]$ from the dissociation of H_2S . Thus substituting 0.10 M in the equation for K_{a1} for the concentration of H_2S , which is essentially constant regardless of the pH, gives the following:

$$K_{a1} = 1.1 \times 10^{-7} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x^2}{0.10 \text{ M}} \quad (17.4.5)$$

$$x = 1.1 \times 10^{-4} \text{ M} = [H^+] = [HS^-]$$

Substituting this value for $[H^+]$ and $[HS^-]$ into the equation for K_{a2} ,

$$K_{a2} = 1.3 \times 10^{-13} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(1.1 \times 10^{-4} \text{ M})x}{1.1 \times 10^{-4} \text{ M}} = x = [S^{2-}]$$

Although $[S^{2-}]$ in an H_2S solution is very low ($1.3 \times 10^{-13} \text{ M}$), bubbling H_2S through the solution until it is saturated would precipitate both metal ions because the concentration of S^{2-} would then be much greater than $1.6 \times 10^{-21} \text{ M}$. Thus we must adjust $[S^{2-}]$ to stay within the desired range. The most direct way to do this is to adjust $[H^+]$ by adding acid to the H_2S solution (recall Le Chatelier's principle), thereby driving the equilibrium in Equation 17.4.244 to the left. The overall equation for the dissociation of H_2S is as follows:



Now we can use the equilibrium constant K for the overall reaction, which is the product of K_{a1} and K_{a2} , and the concentration of H_2S in a saturated solution to calculate the H^+ concentration needed to produce $[S^{2-}]$ of $1.6 \times 10^{-21} \text{ M}$:

$$K = K_{a1}K_{a2} = (1.1 \times 10^{-7})(1.3 \times 10^{-13}) = 1.4 \times 10^{-20} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \quad (17.4.27)$$

$$[H^+]^2 = \frac{K[H_2S]}{[S^{2-}]} = \frac{(1.4 \times 10^{-20})(0.10 \text{ M})}{1.6 \times 10^{-21} \text{ M}} = 0.88 \quad (17.4.28)$$

$$[H^+] = 0.94$$

Thus adding a strong acid such as HCl to make the solution 0.94 M in H^+ will prevent the more soluble ZnS from precipitating while ensuring that the less soluble CdS will precipitate when the solution is saturated with H_2S .

Example 17.4.3

A solution contains 0.010 M Ca^{2+} and 0.010 M La^{3+} . What concentration of HCl is needed to precipitate $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ but not $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ if the concentration of oxalic acid is 1.0 M ? K_{sp} values are 2.32×10^{-9} for $\text{Ca}(\text{C}_2\text{O}_4)$ and 2.5×10^{-27} for $\text{La}_2(\text{C}_2\text{O}_4)_3$; $pK_{a1} = 1.25$ and $pK_{a2} = 3.81$ for oxalic acid.

Given: concentrations of cations, K_{sp} values, and concentration and pK_a values for oxalic acid

Asked for: concentration of HCl needed for selective precipitation of $\text{La}_2(\text{C}_2\text{O}_4)_3$

Strategy:

A Write each solubility product expression and calculate the oxalate concentration needed for precipitation to occur. Determine the concentration range needed for selective precipitation of $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$.

B Add the equations for the first and second dissociations of oxalic acid to get an overall equation for the dissociation of oxalic acid to oxalate. Substitute the $[\text{ox}^{2-}]$ needed to precipitate $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ into the overall equation for the dissociation of oxalic acid to calculate the required $[\text{H}^+]$.

Solution:

A Because the salts have different stoichiometries, we cannot directly compare the magnitudes of the solubility products. Instead, we must use the equilibrium constant expression for each solubility product to calculate the concentration of oxalate needed for precipitation to occur. Using ox^{2-} for oxalate, we write the solubility product expression for calcium oxalate as follows:

$$K_{sp} = [\text{Ca}^{2+}][\text{ox}^{2-}] = (0.010)[\text{ox}^{2-}] = 2.32 \times 10^{-9}$$

$$[\text{ox}^{2-}] = 2.32 \times 10^{-7} \text{ M}$$

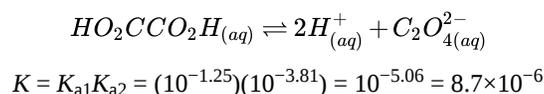
The expression for lanthanum oxalate is as follows:

$$K_{sp} = [\text{La}^{3+}]^2[\text{ox}^{2-}]^3 = (0.010)^2[\text{ox}^{2-}]^3 = 2.5 \times 10^{-27}$$

$$[\text{ox}^{2-}] = 2.9 \times 10^{-8} \text{ M}$$

Thus lanthanum oxalate is less soluble and will selectively precipitate when the oxalate concentration is between $2.9 \times 10^{-8} \text{ M}$ and $2.32 \times 10^{-7} \text{ M}$.

B To prevent Ca^{2+} from precipitating as calcium oxalate, we must add enough H^+ to give a maximum oxalate concentration of $2.32 \times 10^{-7} \text{ M}$. We can calculate the required $[\text{H}^+]$ by using the overall equation for the dissociation of oxalic acid to oxalate:



Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = \frac{[\text{H}^+]^2[\text{ox}^{2-}]}{[\text{HO}_2\text{CCO}_2\text{H}]} = \frac{[\text{H}^+]^2(2.32 \times 10^{-7})}{1.0}$$

$$[\text{H}^+] = 6.1 \text{ M}$$

Thus adding enough HCl to give $[\text{H}^+] = 6.1 \text{ M}$ will cause only $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ to precipitate from the solution.

Exercise

A solution contains 0.015 M Fe^{2+} and 0.015 M Pb^{2+} . What concentration of acid is needed to ensure that Pb^{2+} precipitates as PbS in a saturated solution of H_2S , but Fe^{2+} does not precipitate as FeS ? K_{sp} values are 6.3×10^{-18} for FeS and 8.0×10^{-28} for PbS .

Answer: 0.018 M H^+

Summary

The anion in many sparingly soluble salts is the conjugate base of a weak acid. At low pH, protonation of the anion can dramatically increase the solubility of the salt. Oxides can be classified as acidic oxides or basic oxides. **Acidic oxides** either react with water to give an acidic solution or dissolve in strong base; most acidic oxides are nonmetal oxides or oxides of metals in high oxidation states. **Basic oxides** either react with water to give a basic solution or dissolve in strong acid; most basic oxides are oxides of metallic elements. Oxides or hydroxides that are soluble in both acidic and basic solutions are called **amphoteric oxides**. Most elements whose oxides exhibit amphoteric behavior are located along the diagonal line separating metals and nonmetals in the periodic table. In solutions that contain mixtures of dissolved metal ions, the pH can be used to control the anion concentration needed to selectively precipitate the desired cation.

Key Takeaway

- The anion in sparingly soluble salts is often the conjugate base of a weak acid that may become protonated in solution, so the solubility of simple oxides and sulfides, both strong bases, often depends on pH.

Conceptual Problems

- Which of the following will show the greatest increase in solubility if 1 M HNO₃ is used instead of distilled water? Explain your reasoning.
 - CuCl₂
 - K[Pb(OH)₃]
 - Ba(CH₃CO₂)₂
 - CaCO₃
- Of the compounds Sn(CH₃CO₂)₂ and SnS, one is soluble in dilute HCl and the other is soluble only in hot, concentrated HCl. Which is which? Provide a reasonable explanation.
- Where in the periodic table do you expect to find elements that form basic oxides? Where do you expect to find elements that form acidic oxides?
- Because water can autoionize, it reacts with oxides either as a base (as OH⁻) or as an acid (as H₃O⁺). Do you expect oxides of elements in high oxidation states to be more acidic (reacting with OH⁻) or more basic (reacting with H₃O⁺) than the corresponding oxides in low oxidation states? Why?
- Given solid samples of CrO, Cr₂O₃, and CrO₃, which would you expect to be the most acidic (reacts most readily with OH⁻)? Which would be the most basic (reacts most readily with H₃O⁺)? Why?
- Which of these elements—Be, B, Al, N, Se, In, Tl, Pb—do you expect to form an amphoteric oxide? Why?

Numerical Problems

- A 1.0 L solution contains 1.98 M Al(NO₃)₃. What are [OH⁻] and [H⁺]? What pH is required to precipitate the cation as Al(OH)₃? $K_{sp} = 1.3 \times 10^{-33}$ and $K_a = 1.05 \times 10^{-5}$ for the hydrated Al³⁺ ion.
- A 1.0 L solution contains 2.03 M CoCl₂. What is [H⁺]? What pH is required to precipitate the cation as Co(OH)₂? $K_{sp} = 5.92 \times 10^{-15}$ and $K_a = 1.26 \times 10^{-9}$ for the hydrated Co²⁺ ion.
- Given 100 mL of a solution that contains 0.80 mM Ag⁺ and 0.80 mM Cu⁺, can the two metals be separated by selective precipitation as the insoluble bromide salts by adding 10 mL of an 8.0 mM solution of KBr? K_{sp} values are 6.27×10^{-9} for CuBr and 5.35×10^{-13} for AgBr. What maximum [Br⁻] will separate the ions?
- Given 100 mL of a solution that is 1.5 mM in Tl⁺, Zn²⁺, and Ni²⁺, which ions can be separated from solution by adding 5.0 mL of a 12.0 mM solution of Na₂C₂O₄?

Precipitate	K_{sp}
Tl ₂ C ₂ O ₄	2×10^{-4}
ZnC ₂ O ₄ ·2H ₂ O	1.38×10^{-9}
NiC ₂ O ₄	4×10^{-10}

How many milliliters of 12.0 mM Na₂C₂O₄ should be added to separate Tl⁺ and Zn²⁺ from Ni²⁺?

Answers

- [H⁺] = 4.56×10^{-3} ; [OH⁻] = 2.19×10^{-12} ; pH = 2.94
-
- No; both metal ions will precipitate; AgBr will precipitate as Br⁻ is added, and CuBr will begin to precipitate at [Br⁻] = 8.6×10^{-6} M.
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Contributors

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