

Solubility of Salts - K_{sp}

We now focus on another aqueous equilibrium system, slightly soluble salts.

These salts have a Solubility Product Constant, K_{sp} .

(We saw this in 1B with the sodium tetraborate solubility lab.)

For example, K_{sp} is defined for $\text{Cu}(\text{OH})_2(\text{s})$ as follows:



For a list of K_{sp} values at 25°C , refer to Appendix D-Table D.3.

These slightly soluble salts dissolve until K_{sp} is satisfied. At this point, we say the solution is saturated, and no more salt will dissolve. In terms of Q_{sp} we have the following possibilities:

1. $Q_{sp} < K_{sp}$
2. $Q_{sp} = K_{sp}$
3. $Q_{sp} > K_{sp}$

Other Aspects of Ionic Equilibria

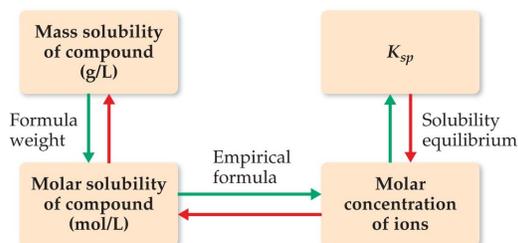
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K_{sp} Solubility

Write the chemical equilibrium and the K_{sp} equilibrium-constant expression for the solubility of $\text{Ca}_3(\text{PO}_4)_2$.

Solubility and K_{sp}

- The solubility of salts (saturated solution) are often expressed in one or more of the following units with the temperature also specified:
 - mol/L (molar solubility)
 - g/L, g/mL, g/100 mL or mg/L (Note that these are NOT densities.)
 - ppm or ppb (parts per million or parts per billion) for very insoluble salts.
- The above units for solubility are directly related to K_{sp} through equilibrium stoichiometry. Let's do some examples.



Other Aspects of Ionic Equilibria

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Solubility and K_{sp}

1. What is the molar solubility of $\text{Ca}_3(\text{PO}_4)_2$ at 25°C given a K_{sp} of 2.0×10^{-29} ?

1.1. What is the concentration of calcium ions?

1.2. What is this solubility in g/L solution?

1.3. What is this solubility in parts per million (ppm) and parts per billion (ppb)? (Assume a soln density of 1.0 g/mL)

$$ppm = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^6$$

$$ppb = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^9$$

K_{sp} from Experimental Data

A saturated solution of magnesium hydroxide in water has a pH of 10.38. Calculate the K_{sp} for magnesium hydroxide.

Relative Molar Solubility of Salts

The relative **MOLAR solubility** of salts (saturated solution) can be determined by comparing K_{sp} values. The greater the K_{sp} the more ions are in solution, hence the greater the molar solubility.

However, you can only directly compare salts that give equivalent numbers of ions in solution.

For example, you can compare the K_{sp} 's of all salts with a 1:1 ion ratio like: AgBr, $BaSO_4$ etc.

Or, you could compare K_{sp} 's of all salts with 1:2 and 2:1 ion ratios like: $BaCl_2$, Ag_2SO_4 , etc.

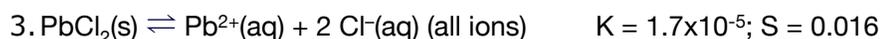
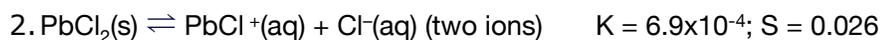
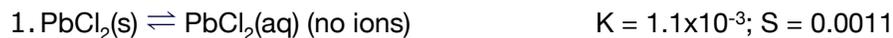
But you can't compare the K_{sp} AgBr directly to the K_{sp} Ag_2SO_4 to determine which is more soluble.

Which salt has a greater molar solubility soluble: AgBr or $BaSO_4$?

K_{sp} Values and Solubility Calcs. LIMITATIONS EXIST!

Unfortunately, solubilities calculated using K_{sp} values sometimes deviate appreciably from the experimentally measured solubilities! Why?

Reason 1 of 2: Some salts do not completely dissociate 100% into their respective ions. For example, $PbCl_2$ exists in three different forms in water, each with its own individual K value.



The experimental solubility of $PbCl_2$ is 0.036 M. Over twice the value predicted by K_{sp} alone.

K_{sp} Values and Solubility Calcs. LIMITATIONS

Reason 2: Some anions in salts are strongly basic. They react with water in a K_b equilibrium. This reduces the anion concentration available to satisfy K_{sp}. This in turn increases the solubility of the salt.

The three common ions that are basic enough to have considerable reaction with water are: S²⁻, CO₃²⁻, and PO₄³⁻.

For example consider Ca₃(PO₄)₂:

The K_{sp} equilibrium is: $\text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3 \text{Ca}^{2+}(\text{aq}) + 2 \text{PO}_4^{3-}(\text{aq})$ K_{sp} = 2.0x10⁻²⁹

Write the chemical reaction for the K_b equilibrium (hydrolysis) for PO₄³⁻ (aq):

K_b = ? (How do you determine the value?)

The experimental solubility of Ca₃(PO₄)₂ is somewhat higher than predicted by K_{sp} alone because some phosphate ion is removed from solution through the K_b reaction.

K_{sp} values are still useful for estimating solubilities, predicting trends and predicting relative solubilities. We just need to keep in mind that they have limitations!

We previously determined the molar solubility of Ca₃(PO₄)₂(s) using K_{sp} alone. Now let's determine its solubility including K_b with K_{sp} to find K_{net}.

The K_{sp} of Sulfide Salts INCLUDES K_b

Since the sulfide ion is very basic, K_b significantly increases the solubility of sulfide salts. For the metal sulfides, the K_{sp} values are actually K_{net} for the overall equilibrium that includes two processes:

- 1) the dissolution of the metal sulfide
- 2) the K_b hydrolysis reaction of the the sulfide ion.

(See the footnote at the bottom of Table D.3 in our text book)

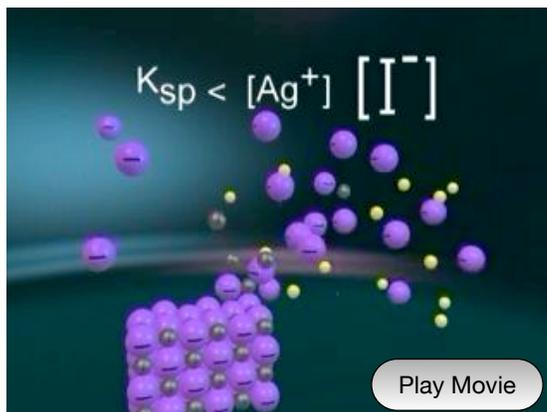
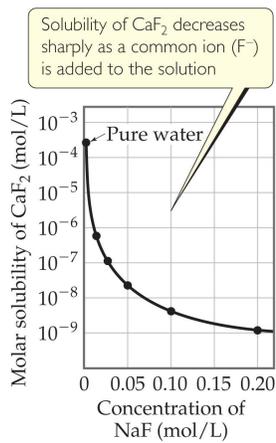
For CuS write the chemical reaction for each of the above equilibria, and for the net equilibrium:

1.	K ₁
2.	K _b >> 1
Net:	K _{sp} = K ₁ *K _b = 6x10 ⁻³⁷ (Table D.3)

Determine the pH of a saturated CuS solution.

Solubility of Salts and the *Common Ion Effect*

- Like the percent ionization of weak acids and bases, the solubility of salts is influenced by the presence of a common ion. **These salts are less soluble when a common ion is present** just like a weak acid's ionization is limited in the presence of significant conjugate base.



- The K_{sp} of silver iodide in water is 8.3×10^{-17} M. Calculate the molar solubility of silver iodide in:
 - Pure water
 - 0.010 M NaI (Common Ion Effect)

Other Aspects of Ionic Equilibria

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Solubility of Salts and the *Common Ion Effect*

- The barium ion, $\text{Ba}^{2+}(\text{aq})$, is poisonous when ingested. The lethal dose in mice is about 12 mg Ba^{2+} per kg of body mass. Despite this fact, BaSO_4 is widely used in medicine to obtain X-ray images of the gastrointestinal tract since Ba is a very good x-ray absorbing element.
 - Explain why $\text{BaSO}_4(\text{s})$ is safe to ingest, even though $\text{Ba}^{2+}(\text{aq})$ is poisonous.
 - Calculate the concentration of Ba^{2+} , in milligrams per liter, in saturated $\text{BaSO}_4(\text{aq})$ at 25°C .
 - Soluble MgSO_4 is often mixed with BaSO_4 when ingested. What function does the MgSO_4 serve?

Other Aspects of Ionic Equilibria

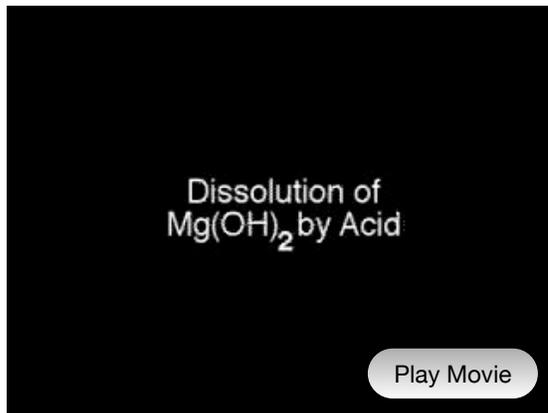
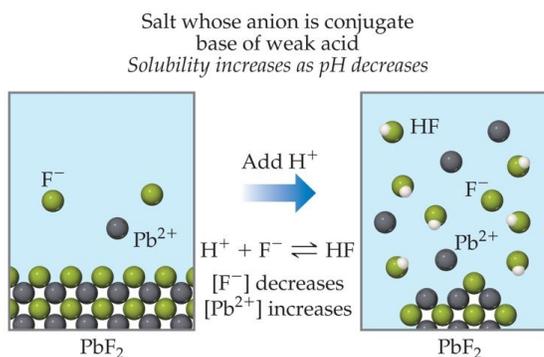
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Solubility of Salts with *pH* Adjustments

We have already seen that basic salts containing S^{2-} , CO_3^{2-} , and PO_4^{3-} ions are more soluble in water than expected because of the reaction of the basic anion with water through K_b .

- All salts that contain a basic anion will have their solubility increased in an acidic solution. In acidic solutions the basic anion reacts with the acid, forcing more of the salt to dissolve to reach equilibrium.

For example, PbF_2 and $Mg(OH)_2$ are practically insoluble in water. However, they are very soluble in dilute acids.



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Other Aspects of Ionic Equilibria

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Solubility of Salts with *pH* Adjustments

1. Which of the following slightly soluble salts will be more soluble in acidic solution than pure water? For those where the solubility increases, write the net ionic chemical reaction that occurs when a strong acid is present in solution:

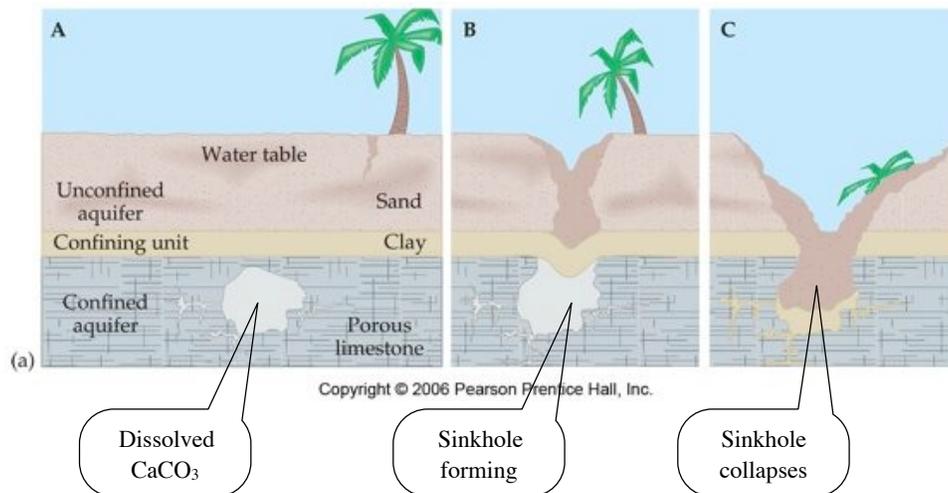
- a) $Al(OH)_3(s)$
- b) $BaSO_4(s)$
- c) $BaC_2O_4(s)$
- d) $PbCl_2$

Other Aspects of Ionic Equilibria

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Solubility of Salts and pH-Applications

A principle cause of sinkhole formation: dissolution of limestone (CaCO_3) by naturally acidic rain water as it percolates through the bedrock. Voids in the bedrock can cause sudden collapse of the overlying ground.



Other Aspects of Ionic Equilibria

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Sinkhole Formation



The large sinkhole shown here has destroyed several buildings and part of a highway.

Other Aspects of Ionic Equilibria

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Solubility of Salts and pH-Applications

- Two of the main crystalline components of kidney stones are calcium phosphate and calcium oxalate. What happens to the solubility of these compounds as pH is increased?
- Tooth enamel consists mainly of a mineral called hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})(\text{s})$, $K_{\text{sp}} = 6.8 \times 10^{-37}$, that is insoluble in pure water. When acids dissolve tooth enamel, the result is tooth decay. Write the net ionic equation that occurs between hydroxyapatite and $\text{H}_3\text{O}^+(\text{aq})$. Note, the phosphate ions are also protonated along with the hydroxide.
- Fluoridation of water and the use of fluoride toothpaste causes the OH^- ion in hydroxyapatite to be replaced with F^- forming $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ($K_{\text{sp}} = 6.8 \times 10^{-60}$). Suggest a reason why fluoride helps prevent tooth decay.

Complex Ion Formation, K_f

Complex ions are ions that usually contain a transition metal cation and one or more **ligands**. A ligand is either a neutral molecule or an anion that bonds to the metal cation through a Lewis acid-base reaction:

Metal Ion: Lewis acid - LIMITING REACTANT

Ligand: Lewis Base - EXCESS REACTANT



TABLE 17.1 Formation Constants for Some Metal Complex Ions in Water at 25°C

Complex Ion	K_f	Equilibrium Equation
$\text{Ag}(\text{NH}_3)_2^+$	1.7×10^7	$\text{Ag}^+(\text{aq}) + 2 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq})$
$\text{Ag}(\text{CN})_2^-$	1×10^{21}	$\text{Ag}^+(\text{aq}) + 2 \text{CN}^-(\text{aq}) \rightleftharpoons \text{Ag}(\text{CN})_2^-(\text{aq})$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	2.9×10^{13}	$\text{Ag}^+(\text{aq}) + 2 \text{S}_2\text{O}_3^{2-}(\text{aq}) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(\text{aq})$
CdBr_4^{2-}	5×10^3	$\text{Cd}^{2+}(\text{aq}) + 4 \text{Br}^-(\text{aq}) \rightleftharpoons \text{CdBr}_4^{2-}(\text{aq})$
$\text{Cr}(\text{OH})_4^-$	8×10^{29}	$\text{Cr}^{3+}(\text{aq}) + 4 \text{OH}^-(\text{aq}) \rightleftharpoons \text{Cr}(\text{OH})_4^-(\text{aq})$
$\text{Co}(\text{SCN})_4^{2-}$	1×10^3	$\text{Co}^{2+}(\text{aq}) + 4 \text{SCN}^-(\text{aq}) \rightleftharpoons \text{Co}(\text{SCN})_4^{2-}(\text{aq})$
$\text{Cu}(\text{NH}_3)_4^{2+}$	5×10^{12}	$\text{Cu}^{2+}(\text{aq}) + 4 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$
$\text{Cu}(\text{CN})_4^{2-}$	1×10^{25}	$\text{Cu}^{2+}(\text{aq}) + 4 \text{CN}^-(\text{aq}) \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}(\text{aq})$
$\text{Ni}(\text{NH}_3)_6^{2+}$	1.2×10^9	$\text{Ni}^{2+}(\text{aq}) + 6 \text{NH}_3(\text{aq}) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(\text{aq})$
$\text{Fe}(\text{CN})_6^{4-}$	1×10^{35}	$\text{Fe}^{2+}(\text{aq}) + 6 \text{CN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(\text{aq})$
$\text{Fe}(\text{CN})_6^{3-}$	1×10^{42}	$\text{Fe}^{3+}(\text{aq}) + 6 \text{CN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(\text{aq})$

- What can you conclude about the favorability of complex ion formation?
- What can you conclude about the free (uncomplexed) metal cation concentration in solutions where a complex ion can form and the ligand is in excess?

Complex Ion Formation, K_f

Determine the concentration of free (uncomplexed) silver ions in solution when 5.0 mL of a 6.0 M ammonia solution (ligand) is added to 45.0 mL of a 0.10 M silver nitrate solution (metal cation).

Complex Ion Formation and Solubility

Formation of complex ions is one way to dissolve “insoluble” salts. Consider the following sequence of additions to a solution containing Ag^+ ions.

Precipitation of AgCl

Complex ion formation

Precipitation of AgBr

Complex ion formation

$\text{AgCl}(s)$

$[\text{Ag}(\text{NH}_3)_2]^+(aq)$

$\text{AgBr}(s)$

$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}(aq)$

AgCl is precipitated by adding NaCl(aq) to AgNO₃(aq)

The AgCl is dissolved by adding excess aqueous NH₃

The silver-ammonia complex ion is changed to insoluble AgBr on addition of NaBr(aq).

The AgBr is dissolved by adding excess Na₂S₂O₃(aq).

Complex Ion Formation and Solubility

Using equilibrium constants (K_{sp} and K_f) we can show why each process in the previous illustration can be made favorable.

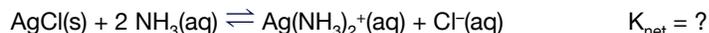
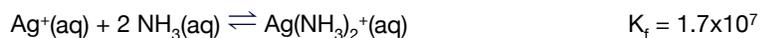
Step (a): Precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$)



What final concentration of $\text{Cl}^-(\text{aq})$ is required to precipitate 99.9% of the $\text{Ag}^+(\text{aq})$ ions from a 0.10 M $\text{AgNO}_3(\text{aq})$ solution? What mass of NaCl (molar mass = 58.44 g/mol) must be added to 100.0 mL of the solution to accomplish this? (Assume that the volume change of the solution is negligible upon addition of the NaCl.)

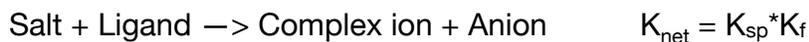
Complex Ion Formation and Solubility

Step (b): AgCl(s) dissolves when $\text{NH}_3(\text{aq})$ is added:



A high concentration of the ligand, $\text{NH}_3(\text{aq})$, in solution ensures that almost all the $\text{AgCl}(\text{s})$ will dissolve. This is an application of Le Chatelier's Principle.

This is a key point for dissolving insoluble salts by formation of a complex ion:



Calculations: Complex Ion Formation and Solubility

Step (b): What is the molar solubility of AgCl(s) in

a) pure H₂O(l):

b) a solution where the concentration of NH₃(aq) begins at 0.10 M:

Calculations: Complex Ion Formation and Solubility

Step (c): Ag(NH₃)₂⁺(aq) precipitates as AgBr(s) when NaBr(aq) is added.

Find K_{net} for this system.

Determine the concentration of complexed ion still in solution where the Ag(NH₃)₂⁺(aq) and NaBr(aq) concentrations both begin at 0.10 M.

Complex Ion Formation and Solubility

Step (d): AgBr(s) dissolves as Na₂S₂O₃(aq) is added. (Write the net ionic equation for the reaction below.)

Crystals of AgBr can be removed from black and white photographic film by reacting the AgBr(s) with aqueous sodium thiosulfate. In order to dissolve 2.5 g of AgBr in 1.00 L of solution, what concentration of thiosulfate ion is needed in solution at equilibrium?

Now calculate how many grams of solid Na₂S₂O₃ (molar mass = 158.11g/mol) must be added to dissolve the AgBr.

Amphoterism of Metal Oxides and Hydroxides

Definition of amphoteric: An amphoteric substance is slightly soluble in water, but soluble in either acidic or basic solutions.

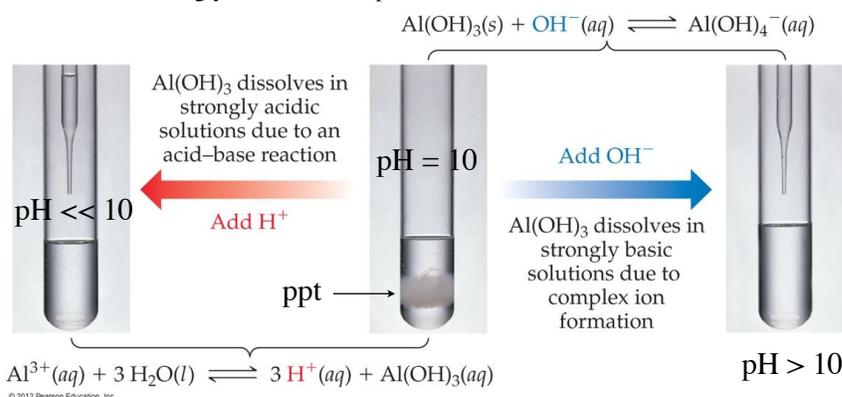
Example Al³⁺: (waters of hydration omitted for clarity)

1. $\text{Al(OH)}_3(\text{s}) + 3 \text{H}^+(\text{aq}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$ Acidic solution, pH < 7
2. $\text{Al}^{3+}(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{AlOH}^{2+}(\text{aq})$
3. $\text{AlOH}^{2+}(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{Al(OH)}_2^+(\text{aq})$
4. $\text{Al(OH)}_2^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{Al(OH)}_3(\text{s})$ Basic solution, pH ≈ 10
5. $\text{Al(OH)}_3(\text{s}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{Al(OH)}_4^-(\text{aq})$ Strongly basic solution, pH > 10

Other amphoteric oxides and hydroxides:

Cr³⁺, Zn²⁺, and Sn²⁺

Each will complex a different # of hydroxide ions - you will have to check a table of K_f values.



Amphoterism of Metal Oxides and Hydroxides

Zinc hydroxide is insoluble in water ($K_{sp} = 3.0 \times 10^{-16}$), but amphoteric. Write net ionic equations to show why $Zn(OH)_2$ is readily soluble in the following solutions:

(a) $CH_3COOH(aq)$

(b) $NH_3(aq)$: Zn^{2+} ions form the following complex ion: $[Zn(NH_3)_4]^{2+}$ with a $K_f = 4.1 \times 10^8$

(c) $OH^-(aq)$ Zn^{2+} ions form the following complex ion: $[Zn(OH)_4]^{2-}$ with a $K_f = 4.6 \times 10^{17}$

(c.1) What is the minimum pH required to dissolve 1.5 g of $Zn(OH)_2$ in a liter of solution?

Precipitation Reactions and Separation of Ions

Recall from previous slides about solubility:

$Q_{sp} < K_{sp}$: unsaturated soln. - no precipitation.

$Q_{sp} = K_{sp}$: saturated soln. - equilibrium.

$Q_{sp} > K_{sp}$: supersaturated soln. - a ppt. should form.

Using K_{sp} values:

1. We can determine if a ppt will form when two solutions are mixed that contain a cation and an anion that can combine to form a slightly soluble salt.
2. We can determine if different cations in solution can be quantitatively separated from each other by selective precipitation. In other words, we can determine if one cation can be removed from the solution as a precipitated salt before a second cation in solution is also precipitated.

Single Precipitation Reactions

Calcium ion triggers clotting of blood. Therefore, when blood is donated the receiving bag contains sodium oxalate to precipitate the Ca^{2+} , and thus prevent clotting. Typically, blood contains $9.7 \times 10^{-5} \text{ g Ca}^{2+}/\text{mL}$. To remove the calcium ions, a medical technologist treats a 104-mL blood sample with 100.0 mL of 0.155 M $\text{Na}_2\text{C}_2\text{O}_4$. Calculate the $[\text{Ca}^{2+}]$ left in solution after the treatment. (K_{sp} for calcium oxalate = 2.6×10^{-9})

Single Precipitation Reactions

1. Show that a precipitate of $\text{Mg}(\text{OH})_2$ will form in an aqueous solution that is 0.350 M MgCl_2 and 0.750 M NaOH .

2. Show that a precipitate of $\text{Mg}(\text{OH})_2$ will also form in an aqueous solution that is 0.350 M MgCl_2 and 0.750 M NH_3 . Hint: Find the $[\text{OH}^-]$ produced by the hydrolysis of NH_3 . Is it enough to ppt the Mg^{2+} ion?
 - 2.1. Explain why the $\text{Mg}(\text{OH})_2$ precipitate can be prevented from forming in (2) by adding NH_4Cl to the solution containing ammonia.

Single Precipitation Reactions

Calculate the minimum pH needed to precipitate $\text{Mn}(\text{OH})_2$ so completely that the concentration of Mn^{2+} is less than $1 \mu\text{g}$ per liter, that is 1 part per billion (ppb).

Selective Precipitation of Cations

Differences in molar solubilities between compounds **containing a common ion** can be used to selectively precipitate one ion from solution leaving the other ion in solution. We can **calculate the amount of the common ion needed to reach saturation for the most soluble ionic salt**. Addition of just a little less of the common ion will insure the most complete separation possible.

Quantitative, or complete, separation is considered possible if 99.9% of the least soluble salt precipitates before any of the most soluble salt starts to precipitate. Typically, the added reagent (containing the common ion) is quite concentrated so that its addition does not appreciably change the volume of the solution and dilute the solution containing the cations to be separated.

Solution of cations $\xrightarrow{\text{Add ppt agent}}$ Least soluble cation ppts first $\xrightarrow{\text{Centrifuge and decant}}$ Selective ppt complete

A 400.0 mL solution has $[\text{Ba}^{2+}] = 0.0040 \text{ M}$ and $[\text{Sr}^{2+}] = 0.0010 \text{ M}$.
A 0.800 M $\text{Na}_2\text{SO}_4(\text{aq})$ solution is added drop-wise.

Which ion, Ba^{2+} or Sr^{2+} , will precipitate first?
 K_{sp} for BaSO_4 is 1.1×10^{-10} , K_{sp} for SrSO_4 is 3.4×10^{-7}

Can the two cations be **quantitatively** (99.9%) separated by selective precipitation?

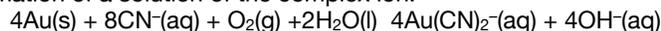
Applications

Precipitation Reactions:

- Precipitation of Mg^{2+} as $\text{Mg}(\text{OH})_2$ from sea water is the source of Mg metal.
- Titration of solutions containing $\text{Cl}^-(\text{aq})$ with AgNO_3 to quantitatively determine $[\text{Cl}^-]$. For this to work, we must be sure that almost all of the Cl^- precipitates as we add the AgNO_3 . How can we be sure of this?
- Determination of the amount of SO_4^{2-} in solution by precipitating as $\text{BaSO}_4(\text{s})$. The BaSO_4 formed is filtered off, dried and weighed. For this to work, the precipitation of SO_4^{2-} must be complete (99.9%). How can we be sure of this?

Complex Ion Formation:

- Complex ion formation can be used to extract gold from low-grade gold containing rock. The formation constant of $\text{Au}(\text{CN})_2^-$ is very large. A very small concentration of Au^+ ions are formed through oxidation of Au. This oxidation takes place in the presence of CN^- ions. Complex ion formation removes the Au^+ ions from solution, so more are formed. As a result, even though Au is not oxidized normally by air, bubbling air through a suspension of Au containing ore in the presence of CN^- leads to formation of a solution of the complex ion:



The resulting solution is filtered and the Au^+ reduced to $\text{Au}(\text{s})$.

- Aluminum ore contains Fe_2O_3 impurities along with the desired aluminum hydroxide, Al_2O_3 . A strong base is added to dissolve the Al_2O_3 as the $\text{Al}(\text{OH})_4^-$ complex ion ($K_f = 3 \times 10^{33}$). The iron (III) ion does not form a complex ion with hydroxide, therefore the Fe_2O_3 does not dissolve. The resulting solution is filtered and acid is added to the filtrate to precipitate $\text{Al}(\text{OH})_3$. The filtrate must not be made too acidic or the $\text{Al}(\text{OH})_3$ will redissolve!