

**Chapter 8 – Overview of
K_{sp}'s with Applications**

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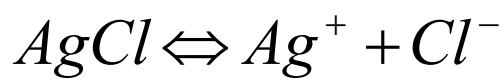
Sign-Off:

Chapter 8 – Overview of K_{sp} 's with Applications

In an earlier reading, you studied the concept of solubility. In this section, you'll go from the earlier "macro" version of solubility to the "micro" version of solubility that is explained mathematically and borders on the quantitative.

By definition, the solubility product is the product of the ion concentrations in a saturated solution; it's a fixed value; and is constant at a given temperature.

It is somewhat easily explained in an equilibrium expression as follows:



where

$$K = \frac{[Ag^+][Cl^-]}{[\underline{AgCl}]}$$

and by rearranging,

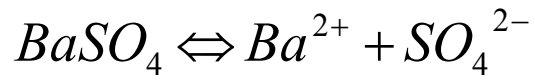
$$K[\underline{AgCl}] = [Ag^+][Cl^-] = K_{sp}$$

where the K_{sp} = the solubility product constant. (Note: underlined chemical formulas indicate that the chemical is insoluble or is a precipitated solid.) In spite of the constancy of actual value, you will find discrepancies in text-books. This is generally due to slight differences in methodology, barometric pressure and temperature, i.e., experimental conditions.

General Rules with K_{sp}

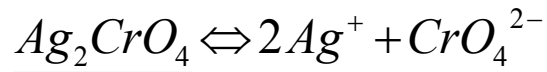
In general, if the ion product is **LESS THAN** the K_{sp} , the solution is less than saturated and there is no precipitate (ppt). If the ion product is **EQUAL TO** the K_{sp} , the solution is saturated and there is a very fine equilibrium that is constantly changing between no precipitate and a micro-precipitate. This equilibrium is so dynamic that one never observes the ppt. If the ion product is **GREATER THAN** the K_{sp} , the solution is super-saturated and there is a readily observable ppt.

Below are some examples of how to write the equilibrium expressions for various insoluble salts:



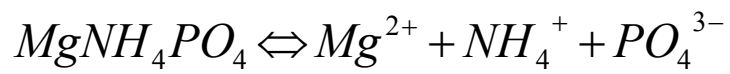
$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

Example 1



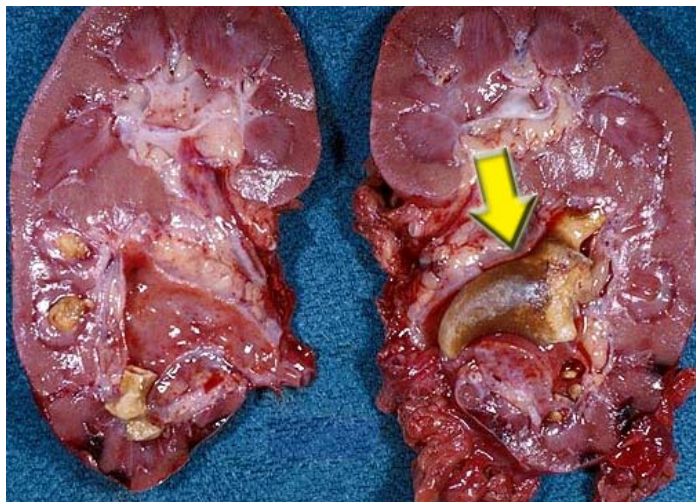
$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

Example 2 – Note the stoichiometric relationships in the expression.



$$K_{sp} = [Mg^{2+}][NH_4^+][PO_4^{3-}]$$

Example 3 – a more complex salt – “triple phosphate” – found in some urinary tract infections – precipitates so rapidly that it forms “staghorn calculi”:



These calculi are so-called because of their similarities to the head of a stag – male deer.

Now that we've used a few examples to write brief K_{sp} expressions, you try it with the following:

Salt	K_{sp} Expression
<u>PbCl₂</u>	
<u>CuS</u>	
<u>Ag₃PO₄</u>	
<u>CaC₂O₄</u>	
<u>MgNH₄AsO₄</u>	
<u>Bi₂S₃</u>	
<u>AgSCN</u>	

The Relationship between Solubility and Solubility Product

Using AgCl, again, as our example:



Let's let "S" (for solubility) be the number of moles of salt ions that dissolve per liter of solution. Let's write the K_{sp} expression for AgCl:

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

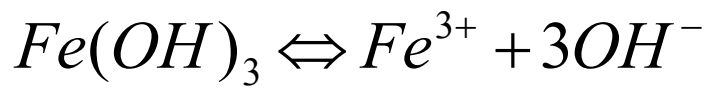
Now, let's substitute S for the ionic concentration of each ion:

$$K_{sp} = S \times S = S^2$$

and

$$S = \sqrt{K_{sp}} = \frac{\text{mol}}{L}$$

So, we can calculate the solubility of the salt based upon its solubility product. Let's try another example:



and the solubility product expression is:

$$K_{sp} = [Fe^{3+}][OH^-]^3$$

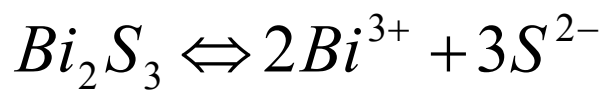
Note that the stoichiometry is conserved (one Fe(III) for every three hydroxide ions) by cubing (raising to the third power) the hydroxide ion concentration. Now, let's solve for the solubility based upon the molar concentration of ferric ion (I use King's method for determining solubility, basing solubility on the metallic ion concentration, BTW):

$$K_{sp} = S(3S)^3 = 27S^4$$

and

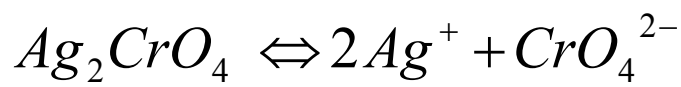
$$S = \sqrt[4]{\frac{K_{sp}}{27}}$$

Now, let's use a complex salt to demonstrate how NOT to calculate solubility by messing with the stoichiometry:



Wrong Method	Correct Method
$K_{sp} = [Bi^{3+}]^2 [S^{2-}]^3$ $= (2S)^2 (3S)^3$ $= 98S^5$ <p style="text-align: center;">so</p> $S = \sqrt[5]{\frac{K_{sp}}{98}}$	<p style="text-align: center;">Let $S \equiv [Bi^{3+}]$,</p> <p style="text-align: center;">then $[S^{2-}] = \frac{3}{2}S$</p> <p style="text-align: center;">\therefore</p> $K_{sp} = (S^2) \left(\frac{3}{2}S\right)^3 = 3.375 S^5$ <p style="text-align: center;">and $S = \sqrt[5]{\frac{K_{sp}}{3.375}}$</p>
$\sqrt[5]{\frac{K_{sp}}{98}} \neq \sqrt[5]{\frac{K_{sp}}{3.375}}$	

And let's reinforce this idea with the following example:



$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$$

Based on the stoichiometry, $S \equiv [Ag^+]$

$$\text{and } [CrO_4]^{2-} = \frac{1}{2}S$$

∴

$$K_{sp} = (S^2) \left(\frac{1}{2}S\right)$$

$$= \frac{1}{2}S^3$$

and

$$S = \sqrt[3]{2K_{sp}}$$

Conditions That Effect Both Solubility and Solubility Product

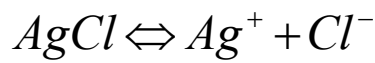
Increased temperature increases the solubility and the K_{sp} . The addition of an organic solvent to an aqueous solution reduces the solubility of a salt in the water. The smaller the particle size, the greater the solubility and the K_{sp} .

In General

The higher the K_{sp} , the more soluble the salt. The lower the K_{sp} , the less soluble the salt.

Common Ion Effect on Solubility

Let's go back to our silver chloride example where:



and

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

As the silver (I) ion concentration decreases, the chloride ion concentration must increase since the product of the two is a constant (K_{sp}) and we can see this as the chloride ion concentration is inversely proportional to the silver (I) ion concentration:

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

With silver (I) chromate:

$$[CrO_4^{2-}] = \frac{K_{sp}}{[Ag^+]^2}$$

the chromate ion concentration is inversely proportional to the square of the silver (I) ion concentration.

The really cool thing about this is that we can take advantage of it in precipitating one salt from another. How do we do that? When forming a precipitate, it is important to reduce its solubility so as to leave as little as possible in solution. This is typically done by adding a SLIGHT EXCESS of the precipitating agent, e.g., the HCl with Group I cations. With our AgCl example, we could visualize the reduction in silver (I) ion concentration in the following manner:

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

When forming a precipitate, it is common to add 1-2 drops in excess to facilitate precipitation. A large excess may form a complex with the ion to be removed as an insoluble salt and actually RESOLUBILIZE the ion.

Solubility in the Presence of a Common Ion

There are 4 steps to determining the solubility of a salt in the presence of a common ion (usually – and we know what happens with “usually” – an anion).

Step 1 is to write out the balanced dissociation equation and the K_{sp} expression.

Step 2 is to determine how you’ll define solubility (S).

Step 3 is making some decisions (they’re coming, shortly).

Step 4 is combining equations and solving for S.

Let's use the following as an example to walk our way through these steps:

Calculate the solubility of CaF_2 in 0.06 M NaF.

The K_{sp} for CaF_2 is 1.6×10^{-10} at 25°C .

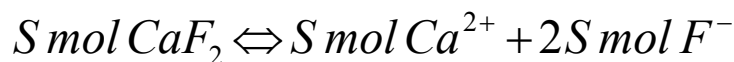
Step 1-- Dissociation equation and K_{sp} expression:



$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$$

Step 2 -- $S \equiv$ solubility of CaF_2 in mol/L.

Step 3 – Decisions, decisions:



$$\text{where } [\text{F}^-] = 0.06\text{M} + 2S$$

if we assume that $2S \ll \ll \ll \ll 0.06\text{M}$,

$$\therefore [\text{F}^-] = 0.06\text{M}$$

Step 4 – combine and solve:

$$K_{sp} = S(0.06)^2$$

$$1.6 \times 10^{-10} = S(0.06)^2$$

$$\frac{1.6 \times 10^{-10}}{(0.06)^2} = S = 4.4 \times 10^{-8} \text{ M}$$

And let's do another, albeit slightly different, example:

Some solid silver oxalate ($\text{Ag}_2\text{C}_2\text{O}_4$) is shaken with 0.05 M sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$). The silver ion concentration in solution is $1.4 \times 10^{-5} \text{ M}$. Calculate the K_{sp} for silver oxalate.

Combining all the steps, below:

$$\begin{aligned} \underline{\text{Ag}_2\text{C}_2\text{O}_4} &\Leftrightarrow 2\text{Ag}^+ + \text{C}_2\text{O}_4^{2-} \\ K_{sp} &= [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}] \\ [\text{Ag}^+] &= 1.4 \times 10^{-5} \text{ M} \\ [\text{C}_2\text{O}_4^{2-}] &= \frac{1}{2}(1.4 \times 10^{-5} \text{ M}) + 0.05 \text{ M} \approx 0.05 \text{ M} \\ K_{sp} &= (1.4 \times 10^{-5} \text{ M})^2 (0.05 \text{ M}) = 9.8 \times 10^{-12} \end{aligned}$$

Let's take advantage of the common ion effect to precipitate one salt preferentially over another (aka common ion effect with competition):

A solution contains 0.005 M KI and 0.05 M KCl. Silver nitrate (AgNO_3) is gradually added. Which precipitates first: AgI or AgCl?

Run the calculations side-by-side.	
AgI info	AgCl info
$\underline{\text{AgI}} \Leftrightarrow \text{Ag}^+ + \text{I}^-$ $K_{sp} = [\text{Ag}^+][\text{I}^-]$ $K_{sp} = 1.5 \times 10^{-16}$	$\underline{\text{AgCl}} \Leftrightarrow \text{Ag}^+ + \text{Cl}^-$ $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$ $K_{sp} = 1.8 \times 10^{-9}$
Determine the silver ion concentration $[\text{Ag}^+]$ for precipitation of the insoluble salt product.	
$\frac{K_{sp}}{\text{I}^-} = \frac{1.5 \times 10^{-16}}{0.005} = [\text{Ag}^+] =$ $[\text{Ag}^+] = 3 \times 10^{-14} \text{ M}$	$\frac{K_{sp}}{\text{Cl}^-} = \frac{1.8 \times 10^{-9}}{0.05} = [\text{Ag}^+] =$ $[\text{Ag}^+] = 3.6 \times 10^{-8} \text{ M}$
AgI precipitates FIRST because of the lower silver ion concentration necessary for precipitation of the insoluble salt product.	

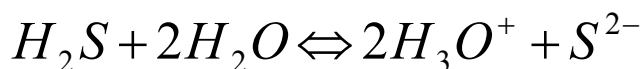
Applications and Manipulations of and with K_{sp} 's

With the above tools, we can begin to get a much better mathematical (arithmetic?) perspective on a great deal of inorganic chemistry as it applies to insoluble salts – remember from CHEM 121 that a salt is a metal and a non-metal or a metal and a polyatomic anion.

The first manipulation of these tools is to determine the pH necessary to maintain the separation of two cations when precipitated as sulfide salts.

When precipitating as sulfide salts, we use a hydrogen sulfide generator such as thioacetamide (TA). For the purposes of this discussion, we'll use hydrogen sulfide (H_2S) in the reactions. Hydrogen sulfide, BTW, is 200 times as poisonous as cyanide – this is because the sulfide ion anesthetizes the first cranial nerve (Cranial I), blocking your ability to continue smelling it and eventually causing death if no fresh air is sought.

The dissociation of hydrogen sulfide in water is as follows:



and

$$K_d = \frac{[H_3O^+][S^{2-}]}{[H_2S]}$$

As a general rule, the concentration of hydrogen sulfide in aqueous solution is about 0.1 M.

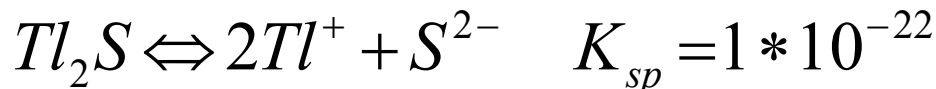
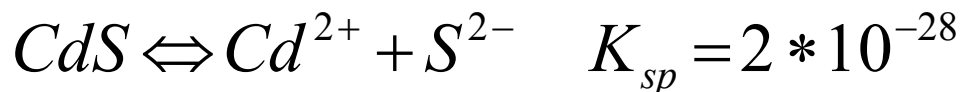
Another general rule requires discussion prior to jumping into an example. When separating 2 salts where one is as an insoluble precipitate, one must determine the concentration limit that is low enough that the presence of the ion left behind (in solution) may be neglected. As a general rule, that level is set at $1 \cdot 10^{-5}$ M. This value varies with faculty member and level of chemistry, e.g., in analytical chemistry at FHSU, I was taught that this level is $1 \cdot 10^{-6}$ M. For this course, we'll stick with the “ten to the minus fifth” rule.

Example

What is the pH necessary to maintain the separation of cadmium (II) (Cd^{2+}) and thallium (I) (Tl^+) when precipitated as their sulfide salts? Assume the “ten to the minus fifth” rule as a minimum remaining concentration. The solution is 0.1 M in each cation.

Solution

1. Determine the K_{sp} and dissociation expressions for each sulfide salt:



2. Let's start with CdS because it has the lowest K_{sp} and set the concentration of the cadmium (II) ion remaining as $1 * 10^{-5}$ M:

$$[1 * 10^{-5}][\text{S}^{2-}] = 2 * 10^{-28}$$

and

$$[\text{S}^{2-}] = \frac{2 * 10^{-28}}{1 * 10^{-5}} = 2 * 10^{-23} \text{ M to ppt Cd}^{2+} \text{ as a sulfide salt}$$

3. Let's do the same for the Tl_2S , remembering that this concentration is 0.1 M (from the example):

$$(0.1)^2 [\text{S}^{2-}] = 1 * 10^{-22}$$

$$[\text{S}^{2-}] = \frac{1 * 10^{-22}}{0.01} = 1 * 10^{-20} \text{ M to precipitate Tl}^+ \text{ as a sulfide salt}$$

4. Now, let's calculate the pH's necessary to separate these two ions, using the sulfide ion concentrations we've CALCULATED above. We'll start with the [cadmium sulfide](#), first, rearranging the K_d expression for H_2S from above:

$$[H_3O^+]^2 [S^{2-}] = (6.8 * 10^{-23})(0.1)$$

and

$$[H_3O^+] = \sqrt{\frac{6.8 * 10^{-24}}{2 * 10^{-23}}} = 0.583$$

so

$$pH = -\log 0.583 = 0.234$$

5. Let's do the thallium sulfide, now, summarizing:

$$[H_3O^+] = \sqrt{\frac{6.8 * 10^{-24}}{1 * 10^{-20}}} = 0.0261$$

and

$$pH = -\log 0.0261 = 1.58$$

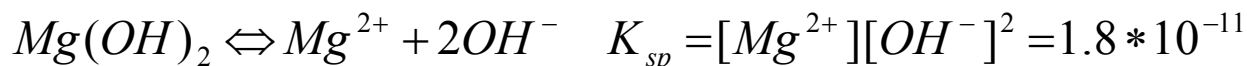
What this calculation tells us is that when the pH is less than 1.58, CdS precipitates. When the pH is equal to or greater than 1.58, Tl₂S precipitates.

A variation of the sulfide precipitation is the hydroxide precipitation of cations.

Example

Is the difference between the solubilities of the hydroxide salts of iron (III) and magnesium (II) ions sufficient to permit the separation of these two cations in a solution that is 0.1 M in each cation? If possible, what hydroxide ion concentration is required to precipitate each cation?

1. Write the K_{sp} expressions and the dissociation expressions:



2. Based on the 2 K_{sp}'s, the ferric hydroxide precipitates first. Using the **"ten to the minus fifth" rule**, solve for the hydroxide ion concentration necessary to ppt the ferric hydroxide:

$$[1 * 10^{-5}][OH^{-}]^3 = 4 * 10^{-38}$$

$$[OH^{-}] = \sqrt[3]{\frac{4 * 10^{-38}}{1 * 10^{-5}}} = 1.59 * 10^{-11} M$$

3. ASIDE: the pOH, then equals 10.80; therefore, the pH is 3.2; translation: this precipitates in acidic solution.
4. We still need to determine the hydroxide ion concentration to precipitate the magnesium (II) ion as an insoluble salt. Precipitation won't occur until the K_{sp} is overcome. We know that the Mg^{2+} concentration is 0.1 M, so:

$$[0.1][OH^{-}]^2 = 1.8 * 10^{-11}$$

$$[OH^{-}] = \sqrt{\frac{1.8 * 10^{-11}}{0.1}} = 1.3 * 10^{-5} M$$

Thus, when the hydroxide ion concentration is greater than $1.3 * 10^{-5} M$, precipitation of the Mg salt will occur.

To summarize: to ppt the ferric salt, the hydroxide ion concentration must be greater than $1.59 * 10^{-11} M$; to ppt the magnesium salt, the hydroxide ion concentration must be greater than $1.3 * 10^{-5} M$.

Miscellaneous K_{sp} Applications

This section is best approached by jumping right into examples.

Example 1: Will lead sulfate precipitate if 100 mL of 0.001 M lead nitrate is added to 100 mL of 0.002 M magnesium sulfate?

1. Determine the final lead (II) ion concentration:

$$[Pb^{2+}] = \frac{100 mL * 0.001 M}{200 mL} = 5 * 10^{-4} M$$

2. Determine the final sulfate ion concentration:

$$[SO_4^{2-}] = \frac{100 \text{ mL} * 0.002 \text{ M}}{200 \text{ mL}} = 1 * 10^{-3} \text{ M}$$

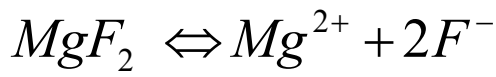
3. Determine the ion product:

$$[Pb^{2+}][SO_4^{2-}] = (5 * 10^{-4})(1 * 10^{-3}) = 5 * 10^{-7}$$

The ion product is less than the K_{sp} , so there will be no precipitation in this example.

Example 2: In a saturated solution of magnesium fluoride in water, the magnesium (II) ion concentration is $2.7 * 10^{-3} \text{ M}$. What is the K_{sp} for magnesium fluoride?

1. Write the dissociation expression and K_{sp} expression for MgF_2 :



and

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

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

2. Using what we wrote above, let's solve for the K_{sp} :

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

Substituting for $[F^{-}] = 2[Mg^{2+}]$

$$K_{sp} = [Mg^{2+}](2[Mg^{2+}])^2$$

$$K_{sp} = 4[Mg^{2+}]^3 = 4(2.7 * 10^{-3} \text{ M})^3 = 7.87 * 10^{-8}$$

Example 3: If a solution is 0.01 M in strontium (II) ions and barium (II) ions, what percent of barium (II) ions remains unprecipitated before strontium sulfate precipitates following the addition of sodium sulfate to the solution?

1. Write the dissociation and K_{sp} expressions (abbreviated, now):



2. Determine what the concentration of sulfate ion is necessary to JUST ppt strontium sulfate:

$$(0.01 M)[SO_4^{2-}] = 2.8 * 10^{-7}$$

then

$$[SO_4^{2-}] = 2.8 * 10^{-5} M$$

3. Substitute this value into the ionic expression for barium sulfate:

$$[Ba^{2+}](2.8 * 10^{-5}) = 1.08 * 10^{-10}$$

then

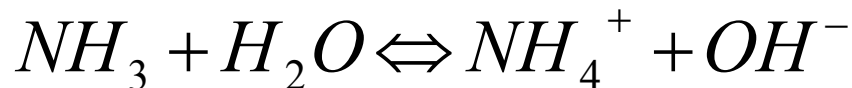
$$[Ba^{2+}] = 3.857 * 10^{-6} M$$

This value represents how much barium (II) ion remains unprecipitated from what was originally present. Now we can calculate the percent of the barium (II) ion that remains unprecipitated:

% Ba^{2+} remaining in solution unprecipitated

$$= \frac{3.857 * 10^{-6} M}{0.01 M} * 100 = 0.0386\%$$

Example 4: If ammonia follows the reaction below:

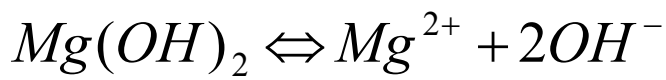


and the K_b or K_i (take your pick) is 1.8×10^{-5} , calculate the hydroxide ion concentration if the solution with which you are working is 0.4 M in NH_3 and 0.3 M in NH_4^+ .

$$K_i = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[0.3]x}{[0.4]}$$
$$[OH^-] = \frac{(0.4)(1.8 \times 10^{-5})}{(0.3)} = 2.4 \times 10^{-5} M$$

Is this enough hydroxide ion to precipitate Mg^{2+} as magnesium hydroxide if the magnesium (II) ion concentration is 0.01 M?

1. Write the dissociation and K_{sp} expressions:



$$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.1 \times 10^{-11}$$

2. Solve for the minimal concentration of hydroxide ion necessary to just make the K_{sp} :

$$[OH^-] = \sqrt{\frac{K_{sp}}{Mg^{2+}}} = \sqrt{\frac{1.1 \times 10^{-11}}{0.01}} = 3.32 \times 10^{-5} M$$

3. Determine the difference between the two calculations:

$$\frac{[\textit{What you have}] - [\textit{What you need}]}{[\textit{What you need}]} * 100 = \% \textit{ Long or Short}$$

$$\frac{2.4 * 10^{-5} M - 3.32 * 10^{-5} M}{3.32 * 10^{-5} M} * 100 = -27.7\%$$

So, there is not enough hydroxide ion in your solution of ammonia to ppt the magnesium (II) ion as an insoluble salt – almost 28% short of the necessary concentration.

Problems

Table of K _{sp} 's	
Chemical	K _{sp}
Aluminum hydroxide	1.4*10 ⁻³⁴
Copper (II) hydroxide	2.2*10 ⁻²⁰
Silver thiocyanate	1.0*10 ⁻¹²
Tin (II) sulfide	1.0*10 ⁻²⁸
Zinc sulfide	8*10 ⁻²⁵
Calcium sulfate	2.0*10 ⁻⁴
Silver iodide	1.5*10 ⁻¹⁶
Silver chloride	1.8*10 ⁻¹⁰

- Given the dissociation of aluminum hydroxide: $\text{Al(OH)}_3 \leftrightarrow \text{Al}^{3+} + 3 \text{OH}^-$, determine the solubility in g/L of the aluminum hydroxide if the solution is 0.05M in hydroxide. **Answer: 8.74*10⁻²⁹ g/L**
- What is the pH necessary to precipitate zinc (II) ion but not tin (II) ion as sulfides if the solution is 0.1 M in each cation? Use the ten to the minus fifth rule. **Answer: 0.0353**
- Will silver thiocyanate form if 26 mL of 0.03 M silver nitrate are mixed with 74 mL of 0.045 M potassium thiocyanate? **Answer: Yes**
- If a solution is 0.005 M in aluminum (III) ions and copper (II) ions, what percent of aluminum (III) ions remains unprecipitated before copper (II) hydroxide precipitates following the addition of KOH to the solution? **Answer: 0.000303%**
- Plaster is still occasionally used to make casts to immobilize fractures as they heal. Plaster is, essentially, calcium sulfate (CaSO₄). One weakness of plaster casts is that one must wrap them in plastic when showering – otherwise the cast will “dissolve” (which is why fiberglass gained popularity with everyone except x-

ray techs for casts). If the density of the plaster is 0.97 g/cm^3 and one showers with water flowing at a rate of 600 L/hr and the cast is 2 cm thick (and uniform), how long will it take the water to make a hole 5 cm in diameter through the cast?

Answer: Approximately 2 minutes

6. A solution contains 0.04 M NaI and 0.008 M NaCl . Silver nitrate is gradually poured into this solution. Which precipitates first? **Answer: AgI**

**Chapter 9 -- Titr-
Precipitometric
Determination of a K_{sp} :
Modified Mohr Method**

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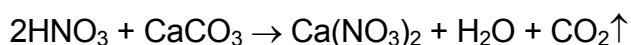
Sign-Off:

Chapter 9 -- Titri-Precipitometric Determination of a K_{sp} :

Modified Mohr Method

Introduction

Solubility product constants (K_{sp} 's) are a form of equilibrium constant for a solid which dissociates in aqueous solution. Indeed, the equilibrium constant (K_{eq}) is an integral part of the K_{sp} . Chemical reactions can be examined in an arithmetic manner as follows:

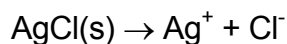


Calcium nitrate and calcium carbonate are both solids and have an activity of 1. Water is so concentrated in aqueous systems, anyway, that the concentration change of the water in the reaction is negligible. The K_{eq} may, therefore, be written as:

$$K_{eq} = \frac{[\text{Ca}(\text{NO}_3)_2] [\text{H}_2\text{O}] [\text{CO}_2]}{[\text{HNO}_3]^2 [\text{CaCO}_3]}$$

$$K_{eq} = \frac{[\text{CO}_2]}{[\text{HNO}_3]^2} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

K_{eq} 's may be written for solids that dissociate in water as follow:



$$K_{eq} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}(s)]}$$

Since solids have an activity of 1,

$$K_{eq} [AgCl] = [Ag^+] [Cl^-] = K_{sp}$$

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

K_{sp} data gives us much information about chemical compounds. The "Big 5" are as follow:

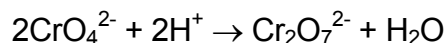
1. If the ion product (the product of the concentrations of the respective ions) is $< K_{sp}$, there will be no precipitate;
2. If the ion product = K_{sp} , precipitation of the solid just begins and the solution is saturated;
3. If the ion product is $> K_{sp}$, the solution is supersaturated and precipitation is obvious;
4. The smaller the K_{sp} of a compound, the less water soluble it is;
5. The "bigger" the K_{sp} of a compound, the more water soluble it is.

This experiment allows the student to become acquainted with K_{sp} 's and some of the factors associated with the determination thereof prior to applying these principles in the qualitative analysis of 5 groups of cations.

Mohr Method

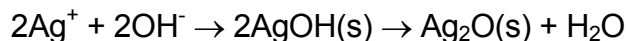
Classically, the Mohr method is used to determine chloride and bromide ion concentrations with a known amount of silver ion. The endpoint of the titration is detected by observing the brick red color change from yellow chromate to silver chromate. The optimal concentration of the chromate ion is about $2.5 \times 10^{-3} M$.

pH is important to regulate with this method because with too much acid, the yellow chromate is displaced to form dichromate ion:



Silver dichromate is more soluble than silver chromate. The reason this is so important is that MORE silver ions are necessary for the reaction to be visible -- if the reaction goes to completion at all.

The second reason pH is important is that if the reaction mixture is too basic, there is a possibility that brown silver oxide will form:



Therefore, the pH is regulated between 7 and 10. Excess NaHCO_3 seems to be an appropriate choice to maintain the pH in this range.

Application

How may one use this method in K_{sp} determination? Let's assume a student has completed a titration and made the following observations:

5 mL 0.1M Ag^+ were required to titrate 35 mL 1.6×10^{-8} M Cl^- . Determine the K_{sp} for AgCl .

First of all, determine the final concentration of silver ions:

$$\frac{(0.1M \text{Ag}^+)(5 \text{mL})}{(35 + 5)\text{mL}} = 0.0125M \text{Ag}^+$$

Then determine the final concentration of chloride ions:

$$\frac{(1.6 \times 10^{-8} M \text{Cl}^-)(35 \text{mL})}{(35 + 5)\text{mL}} = 1.4 \times 10^{-8} M \text{Cl}^-$$

Lastly, calculate the K_{sp} from your concentration information:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (0.0125)(1.4 \times 10^{-8}) = 1.75 \times 10^{-10} = 1.8 \times 10^{-10}$$

Experimental

Obtain 20 mL of $4.5 \times 10^{-8} \text{ M NaCl}$. Add solid NaHCO_3 a bit at a time until fizzing stops. Add 1.5 mL $2.5 \times 10^{-3} \text{ M CrO}_4^{2-}$ and mix. Titrate the sample with 0.1 M AgNO_3 to the first visualization of the end point (color changes from bright yellow to off yellow – this part's tricky – go SLOWLY). Report the volume necessary to reach this point, below. Perform the titration in triplicate and calculate the average K_{sp} for AgCl .

K_{sp} of AgCl Data Table			
	TRIAL 1	TRIAL 2	TRIAL 3
Final Volume Ag^+ (mL)			
Initial Volume Ag^+ (mL)			
Volume Ag^+ (mL) used			
Final Molar Concentration Cl^-			
Final Molar Concentration Ag^+			
K_{sp}			
Average K_{sp}			
% Error (compared to text [CRC] value)			

Dispose of your solutions as directed by your instructor.

Questions

1. The K_{sp} for QX_3 is 3.6×10^{-5} . If the concentration of Q^{3+} ($[\text{Q}^{3+}]$) = $5 \times 10^{-4} \text{ M}$ and the concentration of X^- = $3 \times 10^{-9} \text{ M}$, will QX_3 precipitate? Why or why not?
2. How would increasing the temperature in the previous question effect the solubility of QX_3 ?
3. Decreasing the temperature?
4. If $[\text{Q}^{3+}] = 1 \times 10^{-2} \text{ M}$ and $[\text{X}^-] = 3 \times 10^{-1} \text{ M}$, will QX_3 precipitate? Why or why not?
5. If $[\text{Q}^{3+}] = 3.6 \times 10^{-2} \text{ M}$ and $[\text{X}^-] = 1 \times 10^{-3} \text{ M}$, will QX_3 precipitate? Why or why not?
6. Write the K_{sp} expression for the following reaction:

