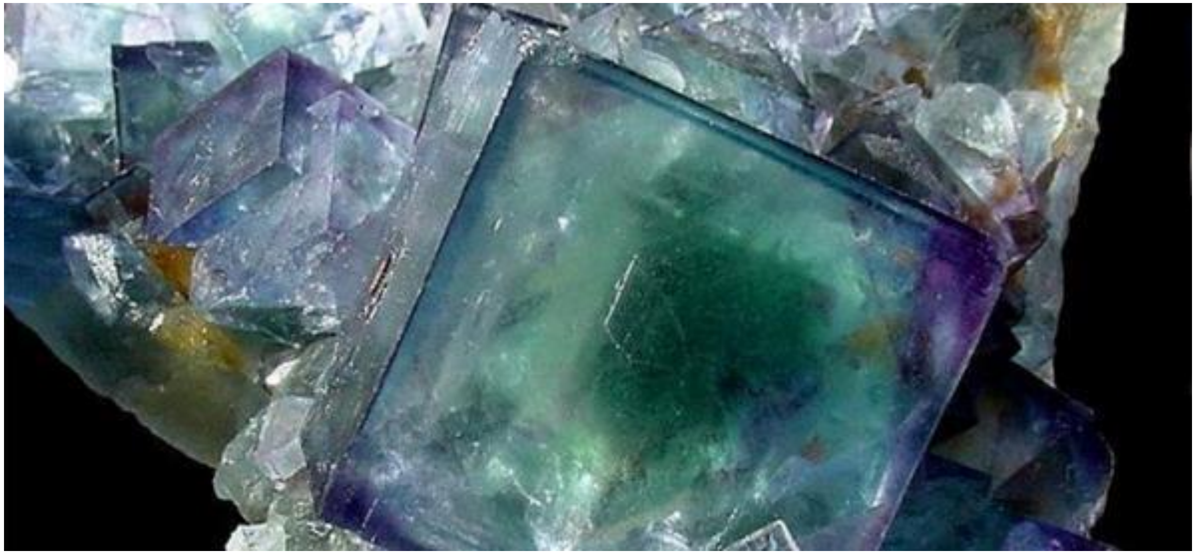
CHEMISTRY

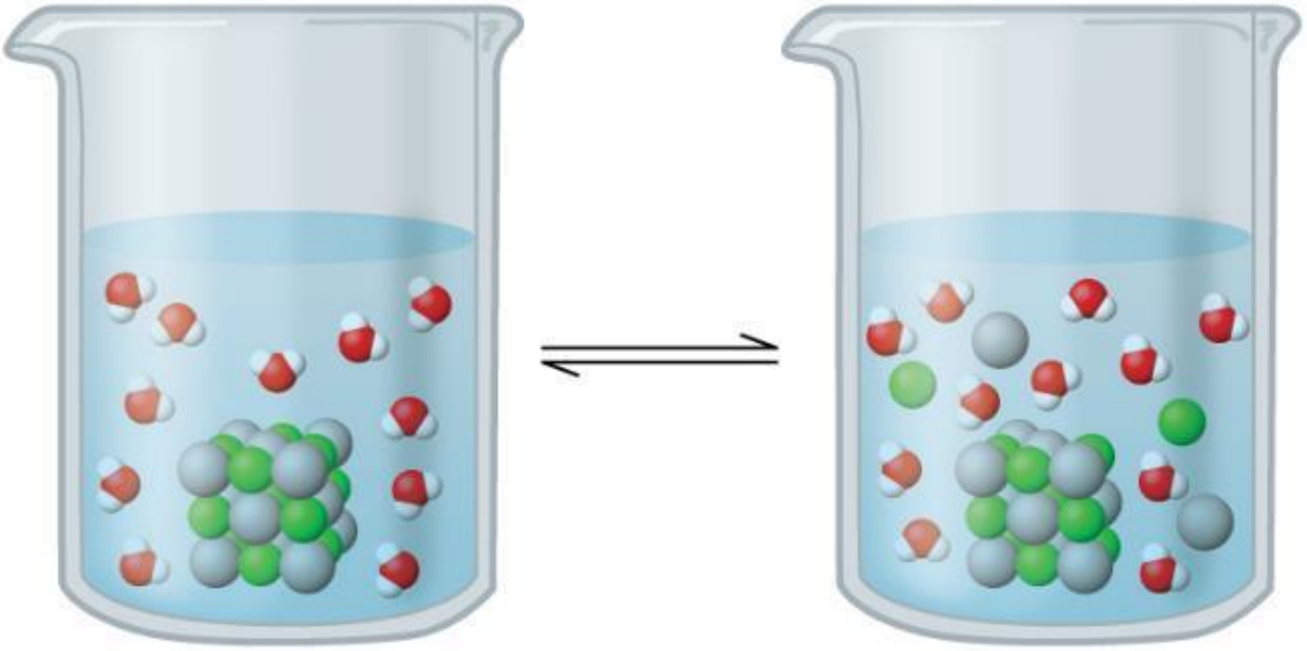
Chapter 15 EQUILIBRIA OF OTHER REACTION CLASSES (SOLUBILITY)

Kevin Kolack, Ph.D.
The Cooper Union
HW problems: 1, 9, 11, 27, 31, 39, 55



CH. 15 OUTLINE

- 15.1 Precipitation and Dissolution



SOLUBILITY EQUILIBRIA; FROM K TO K$_{SP}$

$$AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$$

$K_{sp} = [Ag^+][Cl^-]$ **K_{sp}** is the ***solubility product constant***

$MgF_2(s) \rightleftarrows Mg^{2+}(aq) + 2F^-(aq)$ $K_{sp} = [Mg^{2+}][F^-]^2$

$Ag_2CO_3(s) \rightleftarrows 2Ag^+(aq) + CO_3^{2-}(aq)$ $K_{sp} = [Ag^+]^2[CO_3^{2-}]$

$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$ $K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$

Remember: Q is “K right now”

Dissolution of an ionic solid in aqueous solution:

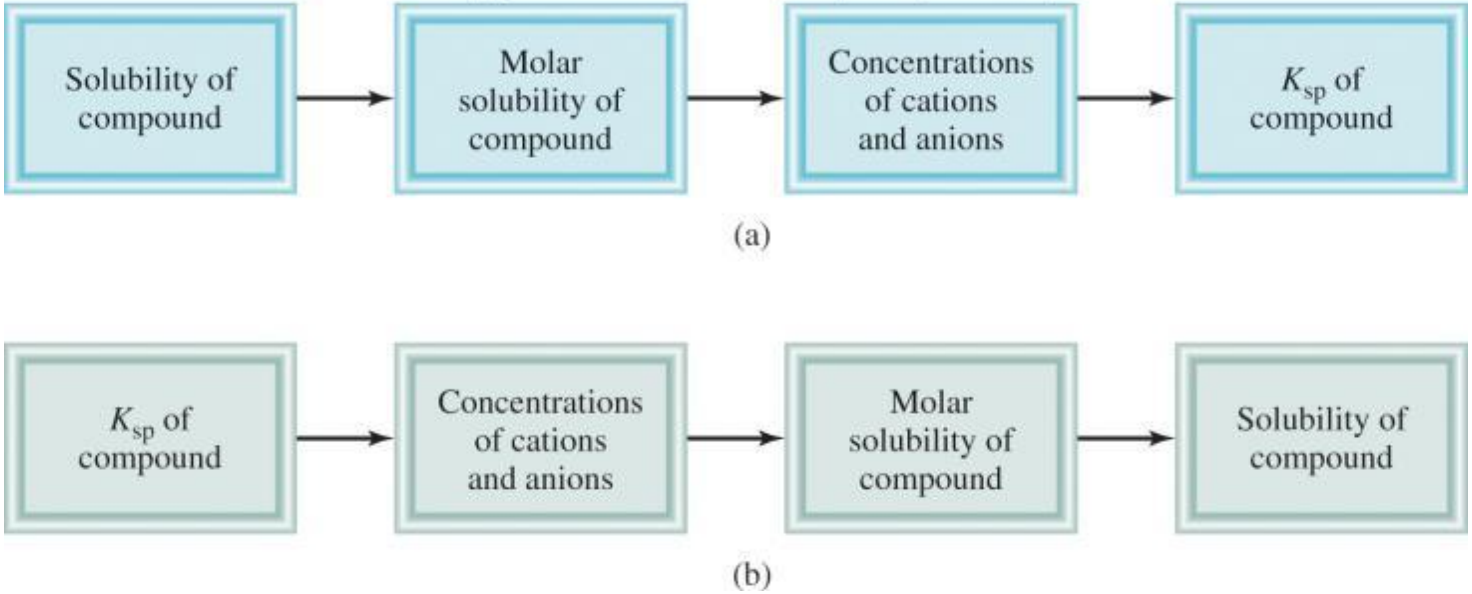
$Q < K_{sp}$	Unsaturated solution	No precipitate
$Q = K_{sp}$	Saturated solution	
$Q > K_{sp}$	Supersaturated solution	Precipitate will form

SOLUBILITY PRODUCTS

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [$Al(OH)_3$]	1.8×10^{-33}	Lead(II) chromate ($PbCrO_4$)	2.0×10^{-14}
Barium carbonate ($BaCO_3$)	8.1×10^{-9}	Lead(II) fluoride (PbF_2)	4.1×10^{-8}
Barium fluoride (BaF_2)	1.7×10^{-6}	Lead(II) iodide (PbI_2)	1.4×10^{-8}
Barium sulfate ($BaSO_4$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi_2S_3)	1.6×10^{-72}	Magnesium carbonate ($MgCO_3$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [$Mg(OH)_2$]	1.2×10^{-11}
Calcium carbonate ($CaCO_3$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF_2)	4.0×10^{-11}	Mercury(I) chloride (Hg_2Cl_2)	3.5×10^{-18}
Calcium hydroxide [$Ca(OH)_2$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [$Ca_3(PO_4)_2$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [$Cr(OH)_3$]	3.0×10^{-29}	Silver bromide ($AgBr$)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag_2CO_3)	8.1×10^{-12}
Copper(I) bromide ($CuBr$)	4.2×10^{-8}	Silver chloride ($AgCl$)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [$Cu(OH)_2$]	2.2×10^{-20}	Silver sulfate (Ag_2SO_4)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag_2S)	6.0×10^{-51}
Iron(II) hydroxide [$Fe(OH)_2$]	1.6×10^{-14}	Strontium carbonate ($SrCO_3$)	1.6×10^{-9}
Iron(III) hydroxide [$Fe(OH)_3$]	1.1×10^{-36}	Strontium sulfate ($SrSO_4$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate ($PbCO_3$)	3.3×10^{-14}	Zinc hydroxide [$Zn(OH)_2$]	1.8×10^{-14}
Lead(II) chloride ($PbCl_2$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

SOLUBILITY

- Molar solubility $(\mathrm{mol/L})$ is the number of moles of solute dissolved in $1\ \mathrm{L}$ of a saturated solution.
- Solubility $(\mathrm{g/L})$ is the number of grams of solute dissolved in $1\ \mathrm{L}$ of a saturated solution *at a specific temperature*.



EXAMPLE

- The solubility of calcium sulfate ($\mathrm{CaSO_4}$) is found to be $0.67\ \mathrm{g/L}$.
- Calculate the value of K_{sp} for calcium sulfate.

SOLUTION

Solution Consider the dissociation of $\mathrm{CaSO_4}$ in water. Let *s* be the molar solubility (in $\mathrm{mol/L}$) of $\mathrm{CaSO_4}$.

$$\mathrm{CaSO_4}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq)$$

Initial (*M*):		0	0
Change (*M*):	-*s*	+*s*	+*s*
Equilibrium (*M*):		*s*	*s*

- The solubility product for $\mathrm{CaSO_4}$ is
- $K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}][\mathrm{SO_4^{2-}}] = s^2$

SOLUTION (CONT'D)

First, we calculate the number of moles of $\mathrm{CaSO_4}$ dissolved in $1\ \mathrm{L}$ of solution:

$$\frac{0.67\mathrm{g}\ \cancel{\mathrm{CaSO_4}}}{1\ \mathrm{L\ soln}} \times \frac{1\ \mathrm{mol\ CaSO_4}}{136.2\ \mathrm{g}\ \cancel{\mathrm{CaSO_4}}} = 4.9 \times 10^{-3}\ \mathrm{mol/L} = s$$

From the solubility equilibrium we see that for every mole of $\mathrm{CaSO_4}$ that dissolves, 1 mole of $\mathrm{Ca^{2+}}$ and 1 mole of $\mathrm{SO_4^{2-}}$ are produced. Thus, at equilibrium,

$$[\mathrm{Ca^{2+}}] = 4.9 \times 10^{-3} M \text{ and } [\mathrm{SO_4^{2-}}] = 4.9 \times 10^{-3} M$$

SOLUTION (CONT'D)

Now we can calculate K_{sp}:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

$$= (4.9 \times 10^{-3})(4.9 \times 10^{-3})$$

$$= \mathbf{2.4 \times 10^{-5}}$$

EXAMPLE

Using the data below, calculate the solubility of copper(II) hydroxide, $\mathrm{Cu(OH)_2}$, in $\mathrm{g/L}$.

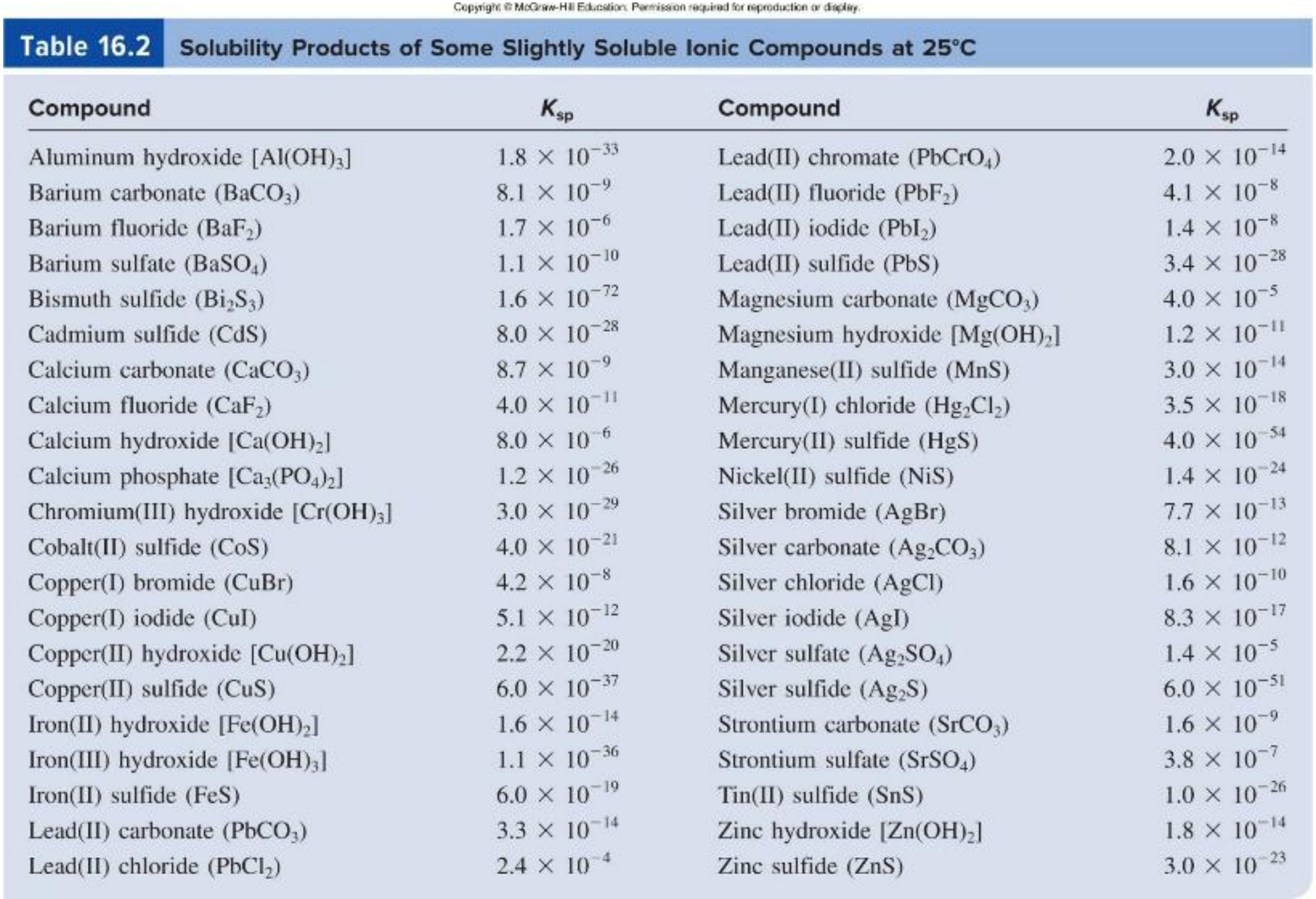


Table 16.2 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [$\mathrm{Al(OH)_3}$]	1.8×10^{-33}	Lead(II) chromate ($\mathrm{PbCrO_4}$)	2.0×10^{-14}
Barium carbonate ($\mathrm{BaCO_3}$)	8.1×10^{-9}	Lead(II) fluoride ($\mathrm{PbF_2}$)	4.1×10^{-8}
Barium fluoride ($\mathrm{BaF_2}$)	1.7×10^{-6}	Lead(II) iodide ($\mathrm{PbI_2}$)	1.4×10^{-8}
Barium sulfate ($\mathrm{BaSO_4}$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide ($\mathrm{Bi_2S_3}$)	1.6×10^{-72}	Magnesium carbonate ($\mathrm{MgCO_3}$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [$\mathrm{Mg(OH)_2}$]	1.2×10^{-11}
Calcium carbonate ($\mathrm{CaCO_3}$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride ($\mathrm{CaF_2}$)	4.0×10^{-11}	Mercury(I) chloride ($\mathrm{Hg_2Cl_2}$)	3.5×10^{-18}
Calcium hydroxide [$\mathrm{Ca(OH)_2}$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [$\mathrm{Ca_3(PO_4)_2}$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [$\mathrm{Cr(OH)_3}$]	3.0×10^{-29}	Silver bromide (AgBr)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate ($\mathrm{Ag_2CO_3}$)	8.1×10^{-12}
Copper(I) bromide (CuBr)	4.2×10^{-8}	Silver chloride (AgCl)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [$\mathrm{Cu(OH)_2}$]	2.2×10^{-20}	Silver sulfate ($\mathrm{Ag_2SO_4}$)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide ($\mathrm{Ag_2S}$)	6.0×10^{-51}
Iron(II) hydroxide [$\mathrm{Fe(OH)_2}$]	1.6×10^{-14}	Strontium carbonate ($\mathrm{SrCO_3}$)	1.6×10^{-9}
Iron(III) hydroxide [$\mathrm{Fe(OH)_3}$]	1.1×10^{-36}	Strontium sulfate ($\mathrm{SrSO_4}$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate ($\mathrm{PbCO_3}$)	3.3×10^{-14}	Zinc hydroxide [$\mathrm{Zn(OH)_2}$]	1.8×10^{-14}
Lead(II) chloride ($\mathrm{PbCl_2}$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

SOLUTION

Consider the dissociation of $\mathrm{Cu(OH)_2}$ in water:

$$\mathrm{Cu(OH)_2}(s) \rightleftharpoons \mathrm{Cu^{2+}}(aq) + \mathrm{2OH^-}(aq)$$

Initial (*M*):		0	0
Change (*M*):	-*s*	+*s*	+2*s*
Equilibrium (*M*):		*s*	2*s*

- Note that the molar concentration of $\mathrm{OH^-}$ is twice that of $\mathrm{Cu^{2+}}$. The solubility product of $\mathrm{Cu(OH)_2}$ is
- $$K_{\mathrm{sp}} = [\mathrm{Cu^{2+}}][\mathrm{OH^-}]^2 = (s)(2s)^2 = 4s^3$$

SOLUTION (CONT'D)

From the K_{sp}, we solve for the molar solubility of $\mathrm{Cu(OH)_2}$ as follows:

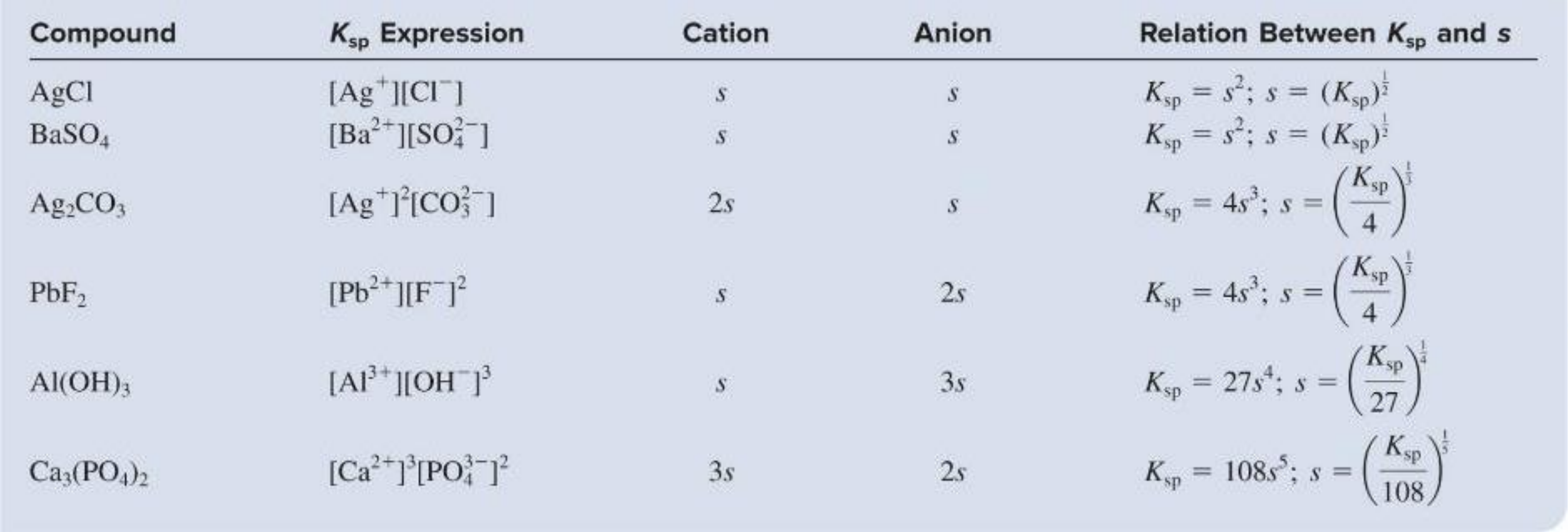
$$2.2 \times 10^{-20} = 4s^3$$

$$s^3 = \frac{2.2 \times 10^{-20}}{4} = 5.5 \times 10^{-21}$$

$s = 1.8 \times 10^{-7}\ M$ (so this is the answer if molar solubility was desired)

- Finally, from the molar mass of $\mathrm{Cu(OH)_2}$ and its molar solubility, we calculate the solubility in $\mathrm{g/L}$:
- $\text{solubility of } \mathrm{Cu(OH)_2} = \frac{1.8\times10^{-7}\ \cancel{\text{mol Cu(OH)}_2}}{1\ \text{L soln}} \times \frac{97.57\text{g Cu(OH)}_2}{1\ \cancel{\text{mol Cu(OH)}_2}}$
- $$= \mathbf{1.8 \times 10^{-5}\ g/L}$$

RELATIONSHIP OF K_{SP} AND MOLAR SOLUBILITY



Compound	K_{sp} Expression	Cation	Anion	Relation Between K_{sp} and s
$AgCl$	$[Ag^+][Cl^-]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	$2s$	s	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
PbF_2	$[Pb^{2+}][F^-]^2$	s	$2s$	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	s	$3s$	$K_{sp} = 27s^4;\ s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
$Ca_3(PO_4)_2$	$[Ca^{2+}]^3[PO_4^{3-}]^2$	$3s$	$2s$	$K_{sp} = 108s^5;\ s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

PREDICTING PRECIPITATION EXAMPLE

- Exactly $200\ \mathrm{mL}$ of $0.0040\ M\ \mathrm{BaCl_2}$ are mixed with exactly $600\ \mathrm{mL}$ of $0.0080\ M\ \mathrm{K_2SO_4}$.
- Will a precipitate form?

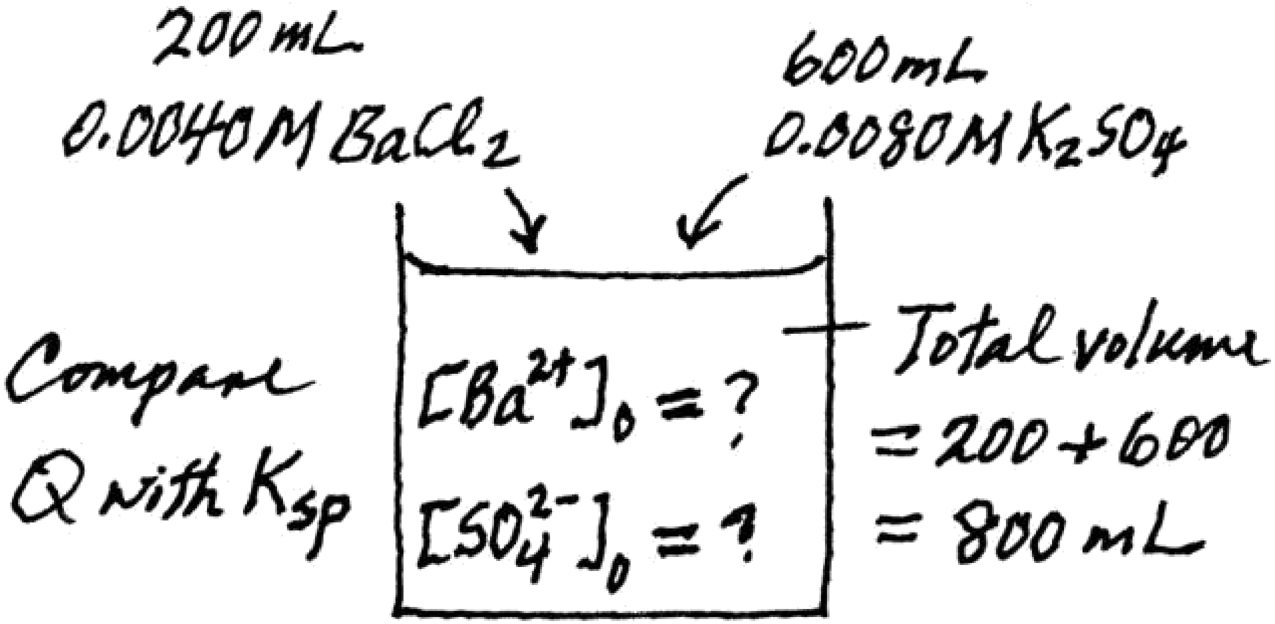
SOLUTION

Strategy

Under what condition will an ionic compound precipitate from solution? The ions in solution are Ba^{2+}, Cl^{-}, K^{+}, and SO_4^{2-}. According to the solubility rules listed in Table 4.2 (p. 125), the only precipitate that can form is BaSO_4. From the information given, we can calculate $[\mathrm{Ba}^{2+}]$ and $[\mathrm{SO}_4^{2-}]$ because we know the number of moles of the ions in the original solutions and the volume of the combined solution. Next, we calculate the ion product $\mathrm{Q}(\mathrm{Q} = [\mathrm{Ba}^{2+}]_0[\mathrm{SO}_4^{2-}]_0)$ and compare the value of *Q* with K_{sp} of BaSO_4 to see if a precipitate will form, that is, if the solution is supersaturated.

SOLUTION (CONT'D)

It is helpful to make a sketch of the situation.



SOLUTION (CONT'D)

Solution

The number of moles of Ba^{2+} present in the original $200\ \mathrm{mL}$ of solution is

$$200\ \mathrm{mL} \times \frac{0.0040\ \mathrm{mol\ Ba}^{2+}}{1\ \mathrm{L\ soln}} \times \frac{1\ \mathrm{L}}{1000\ \mathrm{mL}} = 8.0 \times 10^{-4}\ \mathrm{mol\ Ba}^{2+}$$

The total volume after combining the two solutions is

$800\ \mathrm{mL}$. The concentration of Ba^{2+} in the $800\ \mathrm{mL}$ volume is

$$[\mathrm{Ba}^{2+}] = \frac{8.0 \times 10^{-4}\ \mathrm{mol}}{800\ \mathrm{mL}} \times \frac{1000\ \mathrm{mL}}{1\ \mathrm{L\ soln}}$$

$$= 1.0 \times 10^{-3}\ M$$

SOLUTION (CONT'D)

The number of moles of SO_4^{2-} in the original $600\ mL$ solution is

$$600\ mL \times \frac{0.0080\ mol\ SO_4^{2-}}{1\ L\ soln} \times \frac{1\ L}{1000\ mL} = 4.8 \times 10^{-3}\ mol\ SO_4^{2-}$$

The concentration of SO_4^{2-} in the $800\ mL$ of the combined solution is

$$[SO_4^{2-}] = \frac{4.8 \times 10^{-3}\ mol}{800\ mL} \times \frac{1000\ mL}{1\ L\ soln}$$

$$= 6.0 \times 10^{-3}\ M$$

SOLUTION (CONT'D)

Now we must compare *Q* and K_{sp}. From Table 16.2,

- $\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$
- $K_{\text{sp}} = 1.1 \times 10^{-10}$

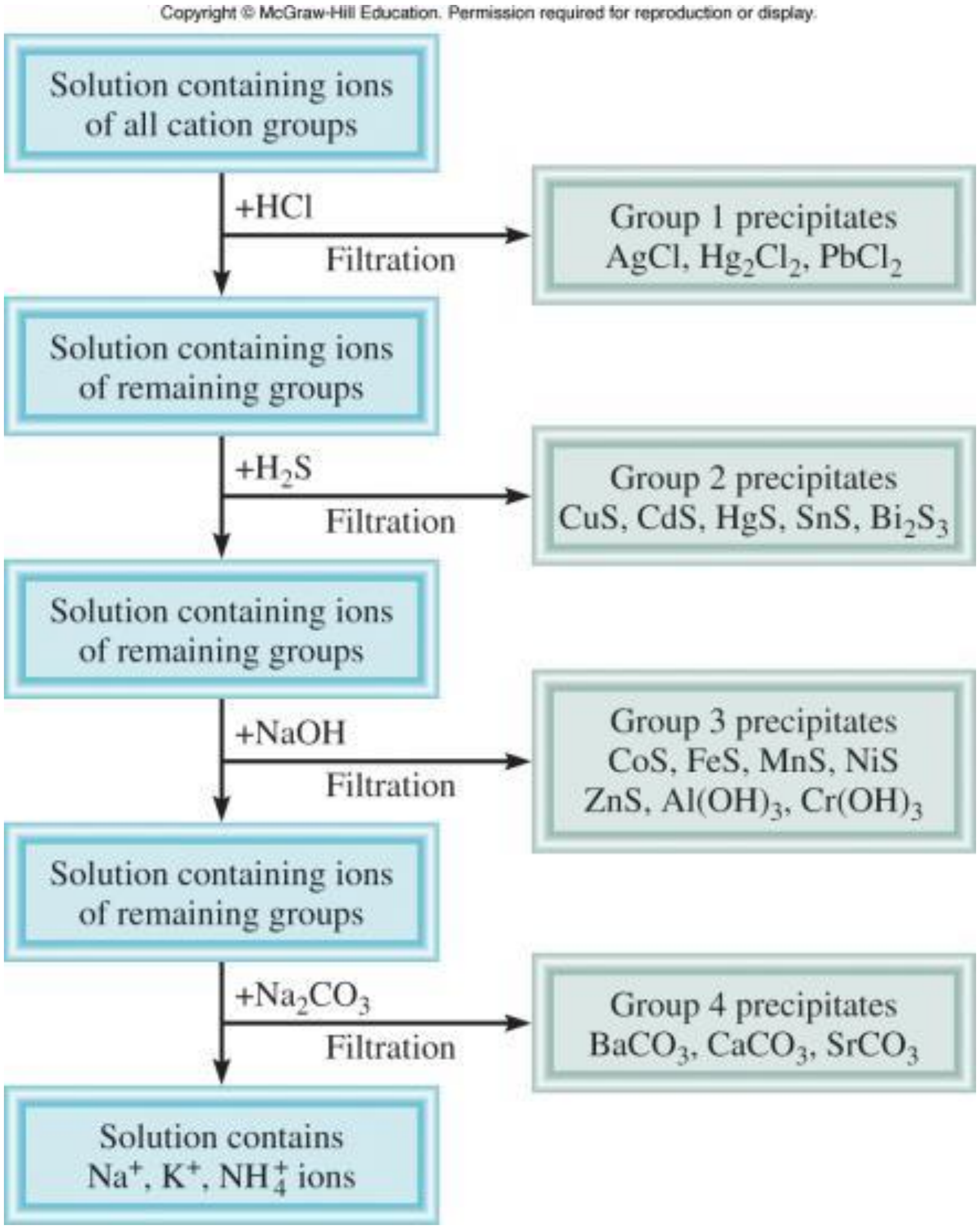
- As for *Q*,
- $\text{Q} = [\text{Ba}^{2+}]_0[\text{SO}_4^{2-}]_0 = (1.0 \times 10^{-3})(6.0 \times 10^{-3})$
- $= 6.0 \times 10^{-6}$
- Therefore, $Q > K_{\text{sp}}$
- The solution is supersaturated because the value of *Q* indicates that the concentrations of the ions are too large. Thus, some of the BaSO_4 will precipitate out of solution until $[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$

- You could determine the concentration of the remaining ions in solution following precipitation as well. See Example 15.10 on page 851.

FRACTIONAL (SELECTIVE) PRECIPITATION

- We can use varying solubility to selectively precipitate a product (away from an impurity)
- Sometimes called fractional crystallization or simply recrystallization

QUALITATIVE ANALYSIS OF CATIONS



Solution containing ions of all cation groups

+HCl

Filtration

Group 1 precipitates $AgCl$, Hg_2Cl_2, $PbCl_2$

Solution containing ions of remaining groups

$+H_2S$

Filtration

Group 2 precipitates CuS, CdS, HgS, SnS, Bi_2S_3

Solution containing ions of remaining groups

+NaOH

Filtration

Group 3 precipitates CoS, FeS, MnS, NiS, ZnS, $Al(OH)_3$, $Cr(OH)_3$

Solution containing ions of remaining groups

$+Na_2CO_3$

Filtration

Group 4 precipitates $BaCO_3$, $CaCO_3$, $SrCO_3$

Solution contains Na^+, K^+, NH_4^+ ions

PRECIPITATION REACTIONS WITH VARIOUS CATIONS

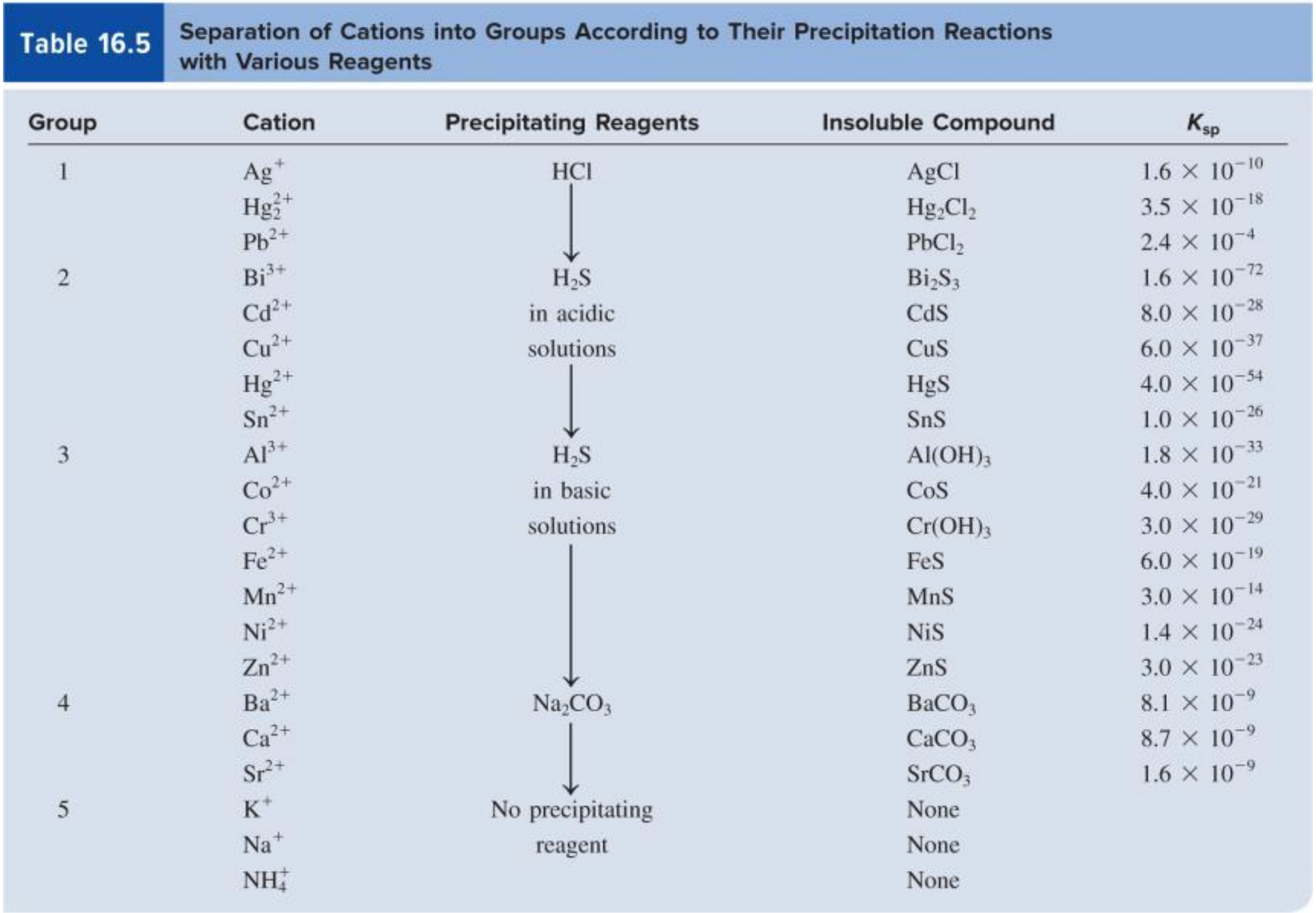


Table 16.5 Separation of Cations into Groups According to Their Precipitation Reactions with Various Reagents

Group	Cation	Precipitating Reagents	Insoluble Compound	K_{sp}
1	Ag^+	HCl	AgCl	1.6×10^{-10}
	Hg_2^{2+}		Hg_2Cl_2	3.5×10^{-18}
	Pb^{2+}	↓	$PbCl_2$	2.4×10^{-4}
2	Bi^{3+}	H_2S in acidic solutions	Bi_2S_3	1.6×10^{-72}
	Cd^{2+}		CdS	8.0×10^{-28}
	Cu^{2+}		CuS	6.0×10^{-37}
	Hg^{2+}		HgS	4.0×10^{-54}
	Sn^{2+}	↓	SnS	1.0×10^{-26}
3	Al^{3+}	H_2S in basic solutions	$Al(OH)_3$	1.8×10^{-33}
	Co^{2+}		CoS	4.0×10^{-21}
	Cr^{3+}		$Cr(OH)_3$	3.0×10^{-29}
	Fe^{2+}		FeS	6.0×10^{-19}
	Mn^{2+}		MnS	3.0×10^{-14}
	Ni^{2+}		NiS	1.4×10^{-24}
	Zn^{2+}	↓	ZnS	3.0×10^{-23}
4	Ba^{2+}	Na_2CO_3	$BaCO_3$	8.1×10^{-9}
	Ca^{2+}		$CaCO_3$	8.7×10^{-9}
	Sr^{2+}	↓	$SrCO_3$	1.6×10^{-9}
5	K^+	No precipitating reagent	None	
	Na^+		None	
	NH_4^+		None	

COMMON ION EFFECT AND SOLUBILITY

- The presence of a “common ion” decreases the solubility of the salt.
  - Application of LeChatelier’s principle

- Example: a source of either Ag^+ or Br^- will decrease the solubility of AgBr

$$\mathrm{AgBr}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Br}^-(aq)$$

EXAMPLE

Calculate the solubility of silver chloride (in $\mathrm{g/L}$) in a $6.5 \times 10^{-3}\ M$ silver nitrate solution.

SOLUTION

Strategy

This is a common-ion problem. The common ion here is $\mathrm{Ag^+}$, which is supplied by both AgCl and $\mathrm{AgNO_3}$. Remember that the presence of the common ion will affect only the solubility of AgCl (in $\mathrm{g/L}$), but not the K_{sp} value because it is an

equilibrium constant.

SOLUTION (CONT'D)

Solution

Step 1: The relevant species in solution are Ag^+ ions (from both AgCl and $\mathrm{AgNO_3}$) and Cl^- ions. The $\mathrm{NO_3^-}$ ions are spectator ions.

Step 2: Because $\mathrm{AgNO_3}$ is a soluble strong electrolyte, it dissociates completely:

$$\mathrm{AgNO_3}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Ag}^+(aq) + \mathrm{NO_3^-}(aq)$$

$$6.5 \times 10^{-3}\ M \qquad 6.5 \times 10^{-3}\ M$$

SOLUTION (CONT'D)

Let *s* be the molar solubility of AgCl in $\mathrm{AgNO_3}$ solution. We summarize the changes in concentrations as follows:

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

Initial (*M*):		6.5×10^{-3}	0.00
Change (*M*):	-*s*	+*s*	+*s*
Equilibrium (*M*):		$(6.5 \times 10^{-3} + s)$	*s*

- *Step 3:*
- $K_{\mathrm{sp}} = [\mathrm{Ag}^{+}][\mathrm{Cl}^{-}]$
- $1.6 \times 10^{-10} = (6.5 \times 10^{-3} + \mathrm{s})(\mathrm{s})$

SOLUTION (CONT'D)

Because AgCl is quite insoluble and the presence of Ag^+ ions from $\mathrm{AgNO_3}$ further lowers the solubility of AgCl, *s* must be very small compared with 6.5×10^{-3}. Therefore, applying the approximation $6.5 \times 10^{-3} + s \approx 6.5 \times 10^{-3}$, we obtain

- $1.6 \times 10^{-10} = (6.5 \times 10^{-3})s$
- $s = 2.5 \times 10^{-8}\ M$

- *Step 4:* At equilibrium

- $[\mathrm{Ag}^+] = (6.5 \times 10^{-3} + 2.5 \times 10^{-8})\ M \approx 6.5 \times 10^{-3}\ M$
- $[\mathrm{Cl}^+] = 2.5 \times 10^{-8}\ M$

SOLUTION (CONT'D)

and so our approximation was justified in step 3. Because all the Cl^- ions must come from AgCl, the amount of AgCl dissolved in $\mathrm{AgNO_3}$ solution also is $2.5 \times 10^{-8}\ M$.Then, knowing the molar mass of AgCl (143.4 g), we can calculate the solubility of AgCl as follows:

- $\text{solubility of AgCl in AgNO}_3\text{ solution} = \frac{2.5\times10^{-8}\text{ mol AgCl}}{1\text{ L soln}} \times \frac{143.4\text{ AgCl}}{1\text{ mol AgCl}}$
- $= \mathbf{3.6 \times 10^{-6}\ g/L}$

SOLUTION (CONT'D)

Check

The solubility of AgCl in pure water is $1.9 \times 10^{-3}\ \mathrm{g/L}$ (see the Practice Exercise in Example 16.9). Therefore, the lower solubility $(3.6 \times 10^{-6}\ \mathrm{g/L})$ in the presence of $\mathrm{AgNO_3}$ is reasonable. You should also be able to predict the lower

solubility using Le Châtelier's principle. Adding $\mathrm{Ag^+}$ ions shifts the equilibrium to the left, thus decreasing the solubility of AgCl.

pH AND SOLUBILITY

- The presence of a common ion **decreases** the solubility.
- Insoluble bases dissolve in acidic solutions
- Insoluble acids dissolve in basic solutions

$$\mathrm{Mg(OH)_2}(s) \rightleftarrows \mathrm{Mg^{2+}}(aq) + 2\mathrm{OH^-}(aq)$$

$$K_{\mathrm{sp}} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = 1.2 \text{ x } 10^{-11}$$

$$K_{\mathrm{sp}} = (s)(2s)^2 = 4s^3$$

$$4s^3 = 1.2 \text{ x } 10^{-11}$$

$$s = 1.4 \text{ x } 10^{-4}\ M$$

$$[\mathrm{OH^-}] = 2s = 2.8 \text{ x } 10^{-4}\ M$$

$$\mathrm{pOH} = 3.55$$

$$\mathrm{pH} = 10.45$$

At pH less than 10.45

there's less $[\mathrm{OH^-}]$

$$\mathrm{OH^-}(aq) + \mathrm{H^+}(aq) \rightarrow \mathrm{H_2O}\ (l)$$

Increase solubility of $\mathrm{Mg(OH)_2}$

At pH greater than 10.45

Raise $[\mathrm{OH^-}]$

Decrease solubility of $\mathrm{Mg(OH)_2}$

EXAMPLE

Which of the following compounds will be more soluble in acidic solution than in water:

(a) CuS

(b) $AgCl$

(c) $PbSO_4$

SOLUTION

Strategy

In each case, write the dissociation reaction of the salt into its cation and anion. The cation will not interact with the H^+ ion because they both bear positive charges. The anion will act as a proton acceptor only if it is the conjugate base of a

weak acid. How would the removal of the anion affect the solubility of the salt?

SOLUTION (CONT'D)

Solution

(a) The solubility equilibrium for CuS is

$$\mathrm{CuS}(s) \rightleftharpoons \mathrm{Cu}^{2+}(aq) + \mathrm{S}^{2-}(aq)$$

The sulfide ion is the conjugate base of the weak acid HS^-. Therefore, the S^{2-} ion reacts with the H^+ ion as follows:

$$\mathrm{S}^{2-}(aq) + \mathrm{H}^+(aq) \rightarrow \mathrm{HS}^-(aq)$$

This reaction removes the S^{2-} ions from solution. According to Le Châtelier's principle, the equilibrium will shift to the right to replace some of the S^{2-} ions that were removed, thereby increasing the solubility of CuS.

SOLUTION (CONT'D)

(b) The solubility equilibrium is

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

Because Cl^{-} is the conjugate base of a strong acid (HCl), the solubility of AgCl is not affected by an acid solution.

SOLUTION (CONT'D)

(c) The solubility equilibrium for $\mathrm{PbSO_4}$ is

$$\mathrm{PbSO_4}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) \ + \mathrm{SO_4^{2-}}(aq)$$

The sulfate ion is a weak base because it is the conjugate base of the weak acid $\mathrm{HSO_4^-}$. Therefore, the ion reacts with the $\mathrm{H^+}$ ion as follows:

$$\mathrm{SO_4^{2-}}(aq) + \mathrm{H^+}(aq) \rightarrow \mathrm{HSO_4^-}(aq)$$

This reaction removes the $\mathrm{SO_4^{2-}}$ions from solution. According to Le Châtelier's principle, the equilibrium will shift to the right to replace some of the $\mathrm{SO_4^{2-}}$ ions that were removed, thereby increasing the solubility of $\mathrm{PbSO_4}$.

EXAMPLE

Calculate the concentration of aqueous ammonia necessary to initiate the precipitation of iron(II) hydroxide from a $0.0030\ M$ solution of $\mathrm{FeCl_2}$.

SOLUTION

Strategy

For iron(II) hydroxide to precipitate from solution, the product $[\mathrm{Fe}^{2+}][\mathrm{OH}^-]^2$must be greater than its K_{sp}. First, we calculate $[\mathrm{OH}^-]$ from the known $[\mathrm{Fe}^{2+}]$ and the K_{sp} value listed in Table 16.2. This is the concentration of OH^- in a saturated solution of $\mathrm{Fe(OH)}_2$. Next, we calculate the concentration of NH_3 that will supply this concentration of OH^- ions. Finally, any NH_3 concentration greater than the calculated value will initiate the precipitation of $\mathrm{Fe(OH)}_2$ because the solution will become supersaturated.

SOLUTION (CONT'D)

Solution

Ammonia reacts with water to produce $\mathrm{OH^-}$ ions, which then react with $\mathrm{Fe^{2+}}$ to form $\mathrm{Fe(OH)_2}$. The equilibria of interest are

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

$$\mathrm{Fe^{2+}}(aq) + \mathrm{2OH^-}(aq) \rightleftharpoons \mathrm{Fe(OH)_2}(s)$$

First we find the $\mathrm{OH^-}$ concentration above which $\mathrm{Fe(OH)_2}$ begins to precipitate. We write

- $K_{\mathrm{sp}} = [\mathrm{Fe^{2+}}][\mathrm{OH^-}]^2 = 1.6 \text{ x } 10^{-14}$

SOLUTION (CONT'D)

Because $\mathrm{FeCl_2}$ is a strong electrolyte, $[\mathrm{Fe^{2-}}] = 0.0030\ M$ and

$$[\mathrm{OH^-}]^2 = \frac{1.6 \times 10^{-14}}{0.0030} = 5.3 \times 10^{-12}$$

$$[\mathrm{OH^-}] = 2.3 \times 10^{-6}\ M$$

Next, we calculate the concentration of $\mathrm{NH_3}$ that will supply $2.3 \times 10^{-6}\ M\ \mathrm{OH^-}$ ions. Let *x* be the initial concentration of $\mathrm{NH_3}$ in $\mathrm{mol/L}$.

SOLUTION (CONT'D)

We summarize the changes in concentrations resulting from the ionization of NH_3 as follows.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

	$NH_3(aq)$	$NH_4^+(aq)$	$OH^-(aq)$
Initial (M):	x	0.00	0.00
Change (M):	-2.3×10^{-6}	$+2.3 \times 10^{-6}$	$+2.3 \times 10^{-6}$
Equilibrium (M):	$(x - 2.3 \times 10^{-6})$	2.3×10^{-6}	2.3×10^{-6}

Next, substitute the equilibrium concentrations in the expression for the ionization constant.

SOLUTION (CONT'D)

$$K_\mathrm{b} = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]}$$

$$1.8 \times 10^{-5} = \frac{(2.3 \times 10^{-6})(2.3 \times 10^{-6})}{(x - 2.3 \times 10^{-6})}$$

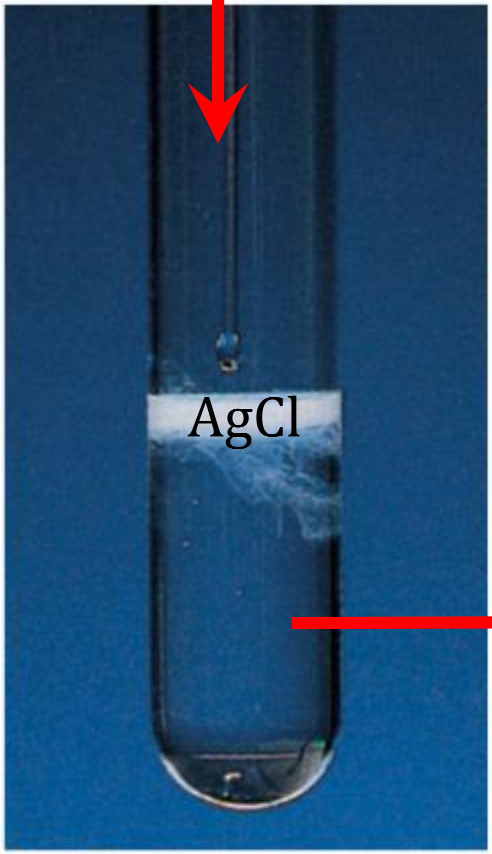
- Solving for *x*, we obtain

- $x = 2.6 \times 10^{-6}\ M$

- Therefore, the concentration of $\mathrm{NH_3}$ must be slightly greater than $2.6 \times 10^{-6}\ M$ to initiate the precipitation of $\mathrm{Fe(OH)_2}$.

EFFECT OF COMPLEXATION ON SOLUBILITY

$AgNO_3 + NaCl$



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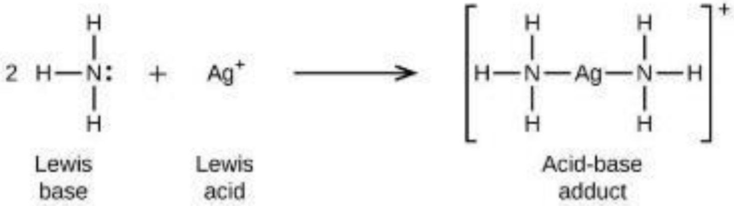

Addition of NH_3 solubilizes AgCl

$Ag(NH_3)_2Cl$ (aq)

Chapter 15 Equilibria of Other Reaction Classes (solubility)

HW problems: 1, 9, 11, 27, 31, 39, 55