CHEMISTRY 1220
CHAPTER 17 PRACTICE EXAM

All questions listed below are problems taken from old Chemistry 123 exams given here at The Ohio State University. Read Chapter 17.4 – 17.7 and complete the following problems. These problems will not be graded or collected, but will be very similar to what you will see on an exam.

K_sp and Molar Solubility (Section 17.4)

The solubility product expression equals the product of the concentrations of the ions involved in the equilibrium, each raised to the power of its coefficient in the equilibrium expression.

For example: \( \text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \)
\[ K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 \]

Why isn’t the concentration of \( \text{PbCl}_2 \) in the denominator of the \( K_{sp} \)? Recall from Section 15.4 that whenever a pure solid or pure liquid is in a heterogeneous (multiple phases present) equilibrium, its concentration is not included in the equilibrium expression.

1. The solubility product expression for \( \text{La}_2(\text{CO}_3)_3 \) is \( K_{sp} = ? \)

First, write the equilibrium expression. The subscript following each atom in the solid is the number of ions of that atom in solution. The total charges must add to zero:
\( \text{La}_2(\text{CO}_3)_3(s) \rightleftharpoons 2\text{La}^{3+}(aq) + 3\text{CO}_3^{2-}(aq) \)

Given the information above and the equilibrium expression:
\[ K_{sp} = [\text{La}^{3+}]^2[\text{CO}_3^{2-}]^3 \]

2. The solubility product expression for \( \text{Zn}_3(\text{PO}_4)_2 \) is \( K_{sp} = ? \)

\( \text{Zn}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Zn}^{2+}(aq) + 2\text{PO}_4^{3-}(aq) \)
\[ K_{sp} = [\text{Zn}^{2+}]^3[\text{PO}_4^{3-}]^2 \]

3. The solubility product expression for \( \text{Al}_2(\text{CO}_3)_3 \) is \( K_{sp} = ? \)

\( \text{Al}_2(\text{CO}_3)_3(s) \rightleftharpoons 2\text{Al}^{3+}(aq) + 3\text{CO}_3^{2-}(aq) \)
\[ K_{sp} = [\text{Al}^{3+}]^2[\text{CO}_3^{2-}]^3 \]

4. The solubility product expression for \( \text{Fe(OH)}_3 \) is \( K_{sp} = ? \)

\( \text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3\text{OH}^-(aq) \)
\[ K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3 \]

Solubility differs from the solubility product constant in that solubility is the amount of a substance that dissolves to form a saturated solution. It is often expressed as grams of solute per liter of solution or as number of moles of solute per liter solution (molar solubility). It can change if the concentrations of other ions or pH change. \( K_{sp} \) is a unit-less number that is the equilibrium constant for the solid-ion equilibrium. It is a measure of how much the solid dissolves to give a saturated
solution. It is constant for a given solute at a specific temperature. However, because both deal with saturated solutions, $K_{sp}$ can be calculated from solubility and vice versa.

5. Calculate the molar solubility of $\text{CrF}_3$ in water. $K_{sp}$ for $\text{CrF}_3$ is $6.6 \times 10^{-11}$.

To calculate solubility from $K_{sp}$, set up an ICE table for the equilibrium expression. The column for the solid can be ignored because its concentration does not appear in the equilibrium expression. Assume initially that none of the salt has dissolved (initial concentrations= 0 M). The change in concentration will be $-nx$ M, where $n$=the coefficient of the ion in the equilibrium expression. Equilibrium concentrations are the resultant concentrations from the “initial” and “change” rows (i.e. the sum):

$$\begin{align*}
\text{CrF}_3(s) & \rightleftharpoons \text{Cr}^{3+}(aq) + 3\text{F}^{-}(aq) \\
\text{Initial} & \quad 0 \quad 0 \\
\text{Change} & \quad +1x \quad +3x \\
\text{Equilibrium} & \quad +x \quad +3x
\end{align*}$$

These equilibrium concentrations can be substituted into the solubility product expression. Since $K_{sp}$ is given, we can solve for $x$, which is the molar solubility:

$$K_{sp}=[\text{Cr}^{3+}][\text{F}^{-}]^3 = (x)(3x)^3 = 27x^4 = 6.6 \times 10^{-11}$$

$$x = 1.3 \times 10^{-3} \text{ M}$$

6. What is the molar solubility for $\text{PbCrO}_4$? $K_{sp}$ $\text{PbCrO}_4 = 2.8 \times 10^{-13}$

$$\begin{align*}
\text{PbCrO}_4(s) & \rightleftharpoons \text{Pb}^{2+}(aq) + \text{CrO}_4^{2-}(aq) \\
\text{Initial} & \quad 0 \quad 0 \\
\text{Change} & \quad +1x \quad +1x \\
\text{Equilibrium} & \quad +x \quad +x
\end{align*}$$

$$K_{sp}=[\text{Pb}^{2+}][\text{CrO}_4^{2-}] = (x)(x) = x^2 = 2.8 \times 10^{-13}$$

$$x = 5.3 \times 10^{-7} \text{ M}$$

7. The solubility of $\text{BaF}_2$ is 1.3 g/L. What is the solubility product constant?

Conversely, $K_{sp}$ can be calculated from either solubility or molar solubility. First, convert solubility in g/L to mol/L (M) since the concentrations used in $K_{sp}$ are in mol/L (M). If the given solubility is already in mol/L, this step is unnecessary:

$$\frac{1.3 \text{ g BaF}_2}{1 \text{ L}} \times \frac{1 \text{ mol BaF}_2}{175.33 \text{ g BaF}_2} = 0.0074 \text{ mol/L} = 0.0074 \text{ M BaF}_2$$

From this molar concentration and the equilibrium expression, we can calculate the equilibrium concentrations of each ion using their respective coefficients in the equilibrium:

$$\begin{align*}
\text{BaF}_2(s) & \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{F}^{-}(aq) \\
0.0074 \text{ M BaF}_2 & \times \frac{1 \text{ mol Ba}^{2+}}{1 \text{ mol BaF}_2} = 0.0074 \text{ M Ba}^{2+}
\end{align*}$$
With these concentrations and the solubility-product expression, we can calculate \( K_{sp} \). Don’t forget the exponents!

\[
K_{sp} = [\text{Ba}^{2+}] [\text{F}^-]^2 = (0.0074)(0.0148)^2 = 1.6 \times 10^{-6}
\]

8. One liter of a saturated solution of silver sulfate contains 4.5 g of \( \text{Ag}_2\text{SO}_4 \). Calculate the solubility product constant for \( \text{Ag}_2\text{SO}_4 \).

\[
\frac{4.5 \text{ g } \text{Ag}_2\text{SO}_4}{1 \text{ L}} \times \frac{1 \text{ mol } \text{Ag}_2\text{SO}_4}{311.81 \text{ g } \text{Ag}_2\text{SO}_4} = 0.0144 \text{ mol/L} = 0.0144 \text{ M } \text{Ag}_2\text{SO}_4
\]

\[
\text{Ag}_2\text{SO}_4 (s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq)
\]

\[
0.0144 \text{ M } \text{Ag}_2\text{SO}_4 \times \frac{2 \text{ mol } \text{Ag}^+}{1 \text{ mol } \text{Ag}_2\text{SO}_4} = 0.0288 \text{ M } \text{Ag}^+
\]

\[
0.0144 \text{ M } \text{Ag}_2\text{SO}_4 \times \frac{1 \text{ mol } \text{SO}_4^{2-}}{1 \text{ mol } \text{Ag}_2\text{SO}_4} = 0.0144 \text{ M } \text{SO}_4^{2-}
\]

\[
K_{sp} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}] = (0.0288)^2(0.0144) = 1.2 \times 10^{-5}
\]

9. The solubility of copper(II) iodate, \( \text{Cu(IO}_3)_2 \), is 1.3 g/L at 25 °C. Calculate the solubility product constant for copper(II) iodate.

\[
K_{sp} = 1.2 \times 10^{-7}
\]

10. Calculate the \( K_{sp} \) value for \( \text{Bi}_2\text{S}_3 \), which has a solubility of \( 1.0 \times 10^{-15} \) mol/L at 25 °C.

\[
K_{sp} = 1.1 \times 10^{-73}
\]

11. The solubility of lead (II) chloride is \( 1.6 \times 10^{-2} \) M. What is the \( K_{sp} \) of \( \text{PbCl}_2 \)?

\[
K_{sp} = 1.6 \times 10^{-5}
\]

12. The solubility of \( \text{CaCO}_3 \) (limestone) is 9.5 mg in 1800 mL. What is the \( K_{sp} \) of \( \text{CaCO}_3 \) (Formula Weight = 100.1 g/mol)?

If mg or mL is given instead of g or L, an extra step is required to ensure correct units are used:

\[
\frac{9.5 \text{ mg}}{1800 \text{ mL}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ L}}{1 \text{ mL}} = 0.000528 \text{ g/L}...
\]

\[
K_{sp} = 2.8 \times 10^{-9}
\]

13. The \( K_{sp} \) for \( \text{CaF}_2 \) is \( 3.9 \times 10^{-11} \). What is the solubility of \( \text{CaF}_2 \) in water in grams/liter?

This problem is solved just like problems 5 and 6. However, molar solubility (M=mol/L) must be converted into g/L using the molecular weight of the solid:

\[
...2.14 \times 10^{-4} \text{ mol } \text{CaF}_2 \times \frac{78.08 \text{ g } \text{CaF}_2}{1 \text{ mol }} = 1.6 \times 10^{-2} \text{ g/L}
\]

14. The \( K_{sp} \) for \( \text{Sn(OH)}_2 \) is \( 2.0 \times 10^{-26} \). What is the solubility of \( \text{Sn(OH)}_2 \) in water in grams/liter?

\[
2.6 \times 10^{-7} \text{ g/L}
\]

15. What is the solubility of iodide ions in a saturated solution of lead (II) iodide (\( K_{sp} = 1.4 \times 10^{-8} \))?
Be careful! This question asks for the solubility of **iodide ions**, not necessarily that of the ionic compound.

\[
\begin{array}{|c|c|c|c|}
\hline
& \text{PbI}_2(\text{s}) & \text{Pb}^{2+}(\text{aq}) & 2\text{I}^-(\text{aq}) \\
\hline
\text{Initial} & \text{-----} & 0 \text{ M} & 0 \text{ M} \\
\text{Change} & \text{-----} & +1x \text{ M} & +2x \text{ M} \\
\text{Equilibrium} & \text{-----} & +x \text{ M} & +2x \text{ M} \\
\hline
\end{array}
\]

\[K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = (x)(2x)^2 = 4x^3 = 1.4 \times 10^{-8}\]

\[x = 1.5 \times 10^{-3} \text{ M}\]

HOWEVER, this is NOT the final answer because, according to the ICE table, the equilibrium concentration (solubility) of **iodide ions** in the saturated solution is 2x:

\[2x = 2(1.5 \times 10^{-3} \text{ M}) = 3.0 \times 10^{-3} \text{ M}\]

16. Which compound is the least soluble (mol/L) in water?
   (a) CaCO\textsubscript{3}  \(K_{sp} = 2.8 \times 10^{-9}\)
   (b) PbI\textsubscript{2}  \(K_{sp} = 8.7 \times 10^{-9}\)
   (c) AgBr  \(K_{sp} = 5.0 \times 10^{-13}\)
   (d) Fe(OH)\textsubscript{2}  \(K_{sp} = 8.0 \times 10^{-16}\)
   (e) Co(OH)\textsubscript{2}  \(K_{sp} = 1.6 \times 10^{-15}\)

You can directly compare solids with the same ratio of cation to anion (i.e. higher \(K_{sp}\), more soluble) to eliminate some possible answer choices. However, if the ratios differ, the molar solubility (x) for EACH compound must be calculated using an ICE table because the lowest \(K_{sp}\) does not necessarily correspond to the lowest molar solubility.

   (a) 5.29 \times 10^{-5} \text{ mol/L}
   (b) 1.30 \times 10^{-3} \text{ mol/L}
   (c) 7.07 \times 10^{-7} \text{ mol/L}
   (d) 5.85 \times 10^{-6} \text{ mol/L}
   (e) 7.37 \times 10^{-6} \text{ mol/L}

Of these values, (c) is the lowest. So AgBr is the least soluble (even though its \(K_{sp}\) is not the lowest).

17. Which of the following salts has the highest concentration of silver ion when dissolved in water?

\begin{align*}
\text{AgCl} & \quad K_{sp} = 1.6 \times 10^{-10} \\
\text{Ag}_2\text{CO}_3 & \quad K_{sp} = 8.1 \times 10^{-12} \\
\text{AgBr} & \quad K_{sp} = 5.0 \times 10^{-13} \\
\end{align*}

Calculate the molar concentration of silver ion for each of the salts.

   (a) 1.26 \times 10^{-5} \text{ M}
   (b) 2.53 \times 10^{-4} \text{ M} (make sure to multiply x by 2!)
   (c) 7.07 \times 10^{-7} \text{ M}

Of these concentrations, (b) is the highest. So Ag\textsubscript{2}CO\textsubscript{3} has the highest concentration of silver ion.

(Note: this is not just because silver has a subscript of 2 after it in Ag\textsubscript{2}CO\textsubscript{3}; you must calculate the actual concentration for each compound).

18. Which compound is least soluble in water?
Dr. Fus

a) Co(OH)\textsubscript{2} \quad K\text{sp} = 1.6 \times 10^{-15}

b) Fe(OH)\textsubscript{2} \quad K\text{sp} = 8.0 \times 10^{-16}

c) AgBr \quad K\text{sp} = 5.0 \times 10^{-13}

d) CaCO\textsubscript{3} \quad K\text{sp} = 2.8 \times 10^{-9}

e) PbI\textsubscript{2} \quad K\text{sp} = 8.7 \times 10^{-9}

Make sure to calculate molar solubility and not merely compare K\text{sp} values if the ion ratios differ.

(a) 7.37 \times 10^{-6} mol/L

(b) 5.85 \times 10^{-6} mol/L

(c) 7.07 \times 10^{-7} mol/L

(d) 5.29 \times 10^{-5} mol/L

(e) 1.30 \times 10^{-3} mol/L

Of these values, (c) is the lowest. So AgBr is the least soluble.

Qualitative Analysis Group I (Section 17.7 & “Isolation and Characterization of Metal Ions: Exploitation of Differences in Solubility” Lab)

19. An aqueous solution contains the following twelve ions: Zn\textsuperscript{2+}, Co\textsuperscript{2+}, Pb\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Sn\textsuperscript{2+}, Fe\textsuperscript{2+}, Sb\textsuperscript{3+}, Al\textsuperscript{3+}, Cr\textsuperscript{3+}, Bi\textsuperscript{3+}, and Ag\textsuperscript{+} and cold dilute HCl is added. What precipitate(s) will form?

Look at the solubility rules. All chloride salts are soluble EXCEPT those with Ag\textsuperscript{+}, Hg\textsuperscript{2+}, and Pb\textsuperscript{2+}. Therefore, of the cations listed, PbCl\textsubscript{2}(s) and AgCl(s) will form.

20. Why must the dilute HCl added in to the solution in question 19 be cold?

PbCl\textsubscript{2} is slightly soluble in water. Solubility decreases as temperature decreases. So by using cold water, we ensure that PbCl\textsubscript{2}(s) precipitates from the solution.

21. Why is it better to use dilute HCl in question 19 dilute rather than use concentrated HCl?

We use dilute HCl to prevent the precipitation of basic chlorides and hydroxides.

22. In the group I analysis, what is the basis of separation for AgCl(s) and PbCl\textsubscript{2}(s). Why is this separation possible?

By heating the solution, we separate PbCl\textsubscript{2} and AgCl because the solubility of PbCl\textsubscript{2} increases dramatically with increasing temperature, so its precipitate dissolves upon heating. However, the solubility of AgCl remains fairly constant, so it remains solid.

23. What color is PbCrO\textsubscript{4}(s)?

Yellow

Factors Influencing Solubility (Section 17.5)

24. How many moles of MgF\textsubscript{2} (K\text{sp} = 6.4 \times 10^{-9}) will dissolve in 0.50 L of 0.20 M NaF?

This is an example of the common ion effect. Because some F\textsuperscript{-} is already in the solution due to the presence NaF, the solubility of MgF\textsubscript{2} will decrease because its solubility equilibrium will shift left away from the “added ion”, in accordance with LeChatelier’s Principle:

\[ \text{MgF}_2 (s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{F}^{-}(aq) \]

To find the number of moles of MgF\textsubscript{2} that will dissolve in 0.50 L of solution, we must calculate the molar solubility of MgF\textsubscript{2} in this solution, using an ICE table. **Remember, because NaF is completely
soluble in water, the initial concentration of F\(^{-}\) is NOT 0 M, it is the concentration of F\(^{-}\) from NaF (in this case, 0.20 M):

\[
\begin{array}{|c|c|c|}
\hline
\text{MgF}_2(s) & \xrightleftharpoons{} & \text{Mg}^{2+}(aq) + 2\text{F}^{-}(aq) \\
\hline
\text{Initial} & \text{-----} & 0 \text{ M} \text{ 0.20 M} \\
\text{Change} & \text{-----} & +1x \text{ M} +2x \text{ M} \\
\text{Equilibrium} & \text{-----} & x \text{ M} 2x+0.20 \text{ M} \\
\hline
\end{array}
\]

\[K_{sp}=[\text{Mg}^{2+}] [\text{F}^{-}]^2 = (x)(2x+0.20)^2\]

This presents a problem because the added 0.20 M makes this a quadratic equation. However, as long as \(K_{sp}\) is low (which it almost always is), the \(2x\) can be ignored:

\[K_{sp} = (x)(0.20)^2 = 6.4 \times 10^{-9}\]

\[x = 1.6 \times 10^{-7} \text{ M}\]

However, this problem asks for moles of MgF\(_2\) in 0.5 L of solution, so to get the final answer:

\[1.6 \times 10^{-7} \text{ mol} \times 0.50 \text{ L} = 8.0 \times 10^{-8} \text{ mol}\]

25. Calculate the molar solubility of CrF\(_3\) in 0.20 M NaF.

\[
\begin{array}{|c|c|c|}
\hline
\text{CrF}_3(s) & \xrightleftharpoons{} & \text{Cr}^{3+}(aq) + 3\text{F}^{-}(aq) \\
\hline
\text{Initial} & \text{-----} & 0 \text{ M} \text{ 0.20 M} \\
\text{Change} & \text{-----} & +1x \text{ M} +3x \text{ M} \\
\text{Equilibrium} & \text{-----} & x \text{ M} 3x+0.20 \text{ M} \\
\hline
\end{array}
\]

\[K_{sp}=[\text{Cr}^{3+}] [\text{F}^{-}]^3 = (x)(2x+0.20)^3 = (x)(0.20)^3 = 6.6 \times 10^{-11}\]

\[x = 8.25 \times 10^{-9} \text{ M}\]

26. What is the molar solubility of MgF\(_2\) in 0.40 M F\(^{-}\)? \(K_{sp} \text{ MgF}_2 = 6.4 \times 10^{-9}\)

\[
\begin{array}{|c|c|c|}
\hline
\text{MgF}_2(s) & \xrightleftharpoons{} & \text{Mg}^{2+}(aq) + 2\text{F}^{-}(aq) \\
\hline
\text{Initial} & \text{-----} & 0 \text{ M} \text{ 0.40 M} \\
\text{Change} & \text{-----} & +1x \text{ M} +2x \text{ M} \\
\text{Equilibrium} & \text{-----} & x \text{ M} 2x+0.40 \text{ M} \\
\hline
\end{array}
\]

\[K_{sp}=[\text{Mg}^{2+}] [\text{F}^{-}]^2 = (x)(2x+0.40)^2 = (x)(0.40)^2 = 6.4 \times 10^{-9}\]

\[x = 4.0 \times 10^{-8} \text{ M}\]

27. The solubility product constant for BiI\(_3\) is 8.1 \times 10^{-19}. Calculate the molar solubility of BiI\(_3\) in 0.20 M Bi(NO\(_3\))\(_3\). Be careful! Here, the common ion is the cation, unlike in the previous problems:

\[
\begin{array}{|c|c|c|}
\hline
\text{BiI}_3(s) & \xrightleftharpoons{} & \text{Bi}^{3+}(aq) + 3\text{I}^{-}(aq) \\
\hline
\text{Initial} & \text{-----} & 0.20 \text{ M} 0 \text{ M} \\
\text{Change} & \text{-----} & +1x \text{ M} +3x \text{ M} \\
\text{Equilibrium} & \text{-----} & x + 0.20 \text{ M} 3x \text{ M} \\
\hline
\end{array}
\]

\[K_{sp}=[\text{Bi}^{3+}] [\text{I}^{-}]^3 = (x+0.20)(3x)^3 = (0.20)(27x^3) = 8.1 \times 10^{-19}\]

\[x = 5.3 \times 10^{-9} \text{ M}\]
28. As the pH decreases, how will the solubility of Cu(OH)$_2$ be affected?
To determine the effect of an acid/base or change in pH, write out the solubility equilibrium expression:

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

If the pH is decreased, the concentration of H$^+$ ions increases. These H$^+$ ions can neutralize the OH$^-$ ions from the above equilibrium, forming H$_2$O, and this decreases the concentration of OH$^-$ in solution. According to LeChatelier's Principle, the equilibrium will then shift to the right, thereby increasing the solubility of Cu(OH)$_2(s)$.

29. The $K_{sp}$ for Zn(OH)$_2$ is $5.0 \times 10^{-17}$. Determine the molar solubility of Zn(OH)$_2$ in buffered solution with a pH of 11.50?
First, determine the concentration of OH$^-$ when the pH is 11.50:

$$
pH=-\log[H^+]=11.50
$$

$$
[H^+]=3.16 \times 10^{-12} \text{ M}
$$

$$
[H^+][OH^-]=1.0 \times 10^{-14} \text{ (always true)}
$$

$$
(3.16 \times 10^{-12} \text{ M}) \times [OH^-]=1.0 \times 10^{-14}
$$

$$
[OH^-]=3.16 \times 10^{-3} \text{ M}
$$

Now, the problem is similar to a common-ion problem. However, because the solution is buffered, it resists changes in pH. Therefore, the concentration of OH$^-$ does NOT change:

$$
\text{Initial} \quad \text{Zn(OH)}_2(s) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})
$$

<table>
<thead>
<tr>
<th>Initial</th>
<th>---</th>
<th>0 M</th>
<th>$3.16 \times 10^{-3}$ M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>---</td>
<td>+1x M</td>
<td>NO CHANGE</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>---</td>
<td>x M</td>
<td>$3.16 \times 10^{-3}$ M</td>
</tr>
</tbody>
</table>

$$
K_{sp}=[\text{Zn}^{2+}][\text{OH}^-]^2=(x)(3.16 \times 10^{-3})^2=5.0 \times 10^{-17}
$$

$$
x=5.0 \times 10^{-12} \text{ M}
$$

30. Calculate the solubility of Cu(OH)$_2$ in a solution buffered at pH = 8.50. $K_{sp}$ for Cu(OH)$_2 = 1.6 \times 10^{-19}$

$$
pH=-\log[H^+]=8.50
$$

$$
[H^+]=3.16 \times 10^{-9} \text{ M}
$$

$$
[H^+][OH^-]=1.0 \times 10^{-14} \text{ (always true)}
$$

$$
(3.16 \times 10^{-9} \text{ M}) \times [OH^-]=1.0 \times 10^{-14}
$$

$$
[OH^-]=3.16 \times 10^{-6} \text{ M}
$$

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

<table>
<thead>
<tr>
<th>Initial</th>
<th>---</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>---</td>
<td>+1x M</td>
<td>NO CHANGE</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>---</td>
<td>x M</td>
<td>$3.16 \times 10^{-6}$ M</td>
</tr>
</tbody>
</table>

$$
K_{sp}=[\text{Cu}^{2+}][\text{OH}^-]^2=(x)(3.16 \times 10^{-6})^2=1.6 \times 10^{-19}
$$

$$
x=1.6 \times 10^{-8} \text{ M}
$$
31. Calculate the molar solubility of Mn(OH)_2 when buffered at pH = 11.40. The K_sp for Mn(OH)_2 is 1.6 \times 10^{-13}.

\[
\begin{align*}
pH &= -\log[\text{H}^+] = 11.40 \\
[\text{H}^+] &= 3.98 \times 10^{-12} \text{ M} \\
[\text{OH}^-] &= 1.0 \times 10^{-14} \text{ (always true)} \\
(3.98 \times 10^{-12} \text{ M})^2[\text{OH}^-] &= 1.0 \times 10^{-14} \\
[\text{OH}^-] &= 2.51 \times 10^{-3} \text{ M}
\end{align*}
\]

\[
\begin{array}{|c|c|c|}
\hline
\text{Initial} & \text{Mn(OH)}_2(\text{s}) & \text{Mn}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq}) \\
\hline
\text{Change} & \text{----} & +1x \text{ M} \\
\hline
\text{Equilibrium} & \text{----} & x \text{ M} \\
\hline
\end{array}
\]

\[
K_{sp} = [\text{Mn}^{2+}][\text{OH}^-]^2 = (2.51 \times 10^{-3})^2 = 1.6 \times 10^{-13}
\]

\[
x = 2.5 \times 10^{-8} \text{ M}
\]

32. What is the pH of a saturated solution of Cu(OH)_2 (K_sp = 2.6 \times 10^{-19})?

To determine the pH, we need to determine the concentration of H^+ using an ICE table:

\[
\begin{align*}
\text{Cu(OH)}_2(\text{s}) & \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq}) \\
\text{Initial} & \text{----} & 0 \text{ M} & 0 \text{ M} \\
\text{Change} & \text{----} & +1x \text{ M} & +2x \text{ M} \\
\text{Equilibrium} & \text{----} & x \text{ M} & 2x \text{ M}
\end{align*}
\]

\[
K_{sp} = [\text{Cu}^{2+}][\text{OH}^-]^2 = (2x)^2 = 4x^2 = 2.6 \times 10^{-19}
\]

\[
x = 4.0 \times 10^{-7} \text{ M}
\]

*Remember to multiply x by 2 in this problem because the equilibrium concentration of OH^- is 2x:

\[
\begin{align*}
[\text{OH}^-] &= 2x = 2(4.0 \times 10^{-7} \text{ M}) = 8.0 \times 10^{-7} \text{ M} \\
[\text{H}^+] &= [\text{OH}^-] = 1.0 \times 10^{-14} \\
[\text{H}^+][\text{OH}^-] &= 1.0 \times 10^{-14} \\
[\text{H}^+] &= 1.2 \times 10^{-8} \text{ M}
\end{align*}
\]

\[
pH = -\log[\text{H}^+] = -\log(1.2 \times 10^{-8}) = 7.9
\]

33. What is the molar solubility (mol/L) of Cr(OH)_3 at pH = 10.00? K_sp for Cr(OH)_3 is 6.3 \times 10^{-31} and K_f for Cr(OH)_3 is 8 \times 10^{29}.

In this problem, a complex ion is formed. This effect increases solubility and trumps both the common-ion and pH effects. To determine the molar solubility of a solid whose ion forms a complex ion, we need to find the overall equilibrium expression and "overall K" for both the dissolution of the solid and the formation of the complex-ion. Identical species on opposite sides of the equilibrium arrow cancel. When "adding" two equilibria, the overall K is the product of the individual K values:

\[
\begin{align*}
\text{Cr(OH)}_3(\text{s}) & \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3\text{OH}^- (\text{aq}) & K_{sp} = 6.3 \times 10^{-31} \\
\text{Cr}^{3+}(\text{aq}) + 4\text{OH}^- (\text{aq}) & \rightleftharpoons \text{Cr(OH)}_4^-(\text{aq}) & K_f = 8.0 \times 10^{29} \\
\text{Cr(OH)}_3(\text{s}) + \text{OH}^- (\text{aq}) & \rightleftharpoons \text{Cr(OH)}_4^-(\text{aq}) & K = K_{sp} \times K_f = (6.3 \times 10^{-31})(8.0 \times 10^{29}) = 5.04 \times 10^{-1}
\end{align*}
\]

Calculate the initial concentration of OH^- from the given pH:

\[
pH = -\log[\text{H}^+] = 10.00
\]
\[
[H^+]=1.0 \times 10^{-10} \text{ M} \\
[H^+][OH^-]=1.0 \times 10^{-14} \text{ (always true)} \\
(1.0 \times 10^{-10} \text{ M})[OH^-]=1.0 \times 10^{-14} \\
[OH^-]=1.0 \times 10^{-4} \text{ M}
\]

Now, set up an ICE table for the overall expression using the overall K. Assuming the solution is buffered at a pH of 10.00, the concentration of OH\(^-\) will not change:

<table>
<thead>
<tr>
<th></th>
<th>Cr(OH)(_3) (s)</th>
<th>OH(^-) (aq)</th>
<th>Cr(OH)(_4) (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>----</td>
<td>1.0 x 10(^{-4})</td>
<td>0 M</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>----</td>
<td>NO CHANGE</td>
<td>+x M</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>----</td>
<td>1.0 x 10(^{-4})</td>
<td>x M</td>
</tr>
</tbody>
</table>

\[K = \frac{[\text{Cr(OH}_4]^-}{[\text{OH}^-]} = 5.04 \times 10^{-1} \]
\[x = 5.0 \times 10^{-5} \text{ M}\]

34. Calculate the concentration of free cadmium ion, [Cd\(^{2+}\)], in a solution that contains 0.20 M Cd(NO\(_3\))\(_2\) in 2.0 M NaCN. Cadmium ion forms the complex ion, Cd(CN)\(_4\)^{2-}, for which K\(_f\) is 6.0 \times 10\(^{18}\).

To solve problems like this, you need to take a 2-step approach. First, assume all of the Cd\(^{2+}\) is converted to the complex ion:

<table>
<thead>
<tr>
<th></th>
<th>Cd(^{2+}) (aq)</th>
<th>4CN (aq)</th>
<th>Cd(CN)(_4)^{2-} (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>0.20 M</td>
<td>2.0 M</td>
<td>0 M</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-0.20 M</td>
<td>-4(0.20) M</td>
<td>+0.20 M</td>
</tr>
<tr>
<td><strong>Final (NOT equilibrium)</strong></td>
<td>0 M</td>
<td>1.2 M</td>
<td>0.20 M</td>
</tr>
</tbody>
</table>

Next, use the FINAL concentrations from the first table as the INITIAL concentrations for a new table of the REVERSE reaction (dissociation of the complex ion) to determine the equilibrium concentration of free Cd\(^{2+}\):

<table>
<thead>
<tr>
<th></th>
<th>Cd(CN)(_4)^{2-} (aq)</th>
<th>Cd(^{2+}) (aq)</th>
<th>4CN (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>0.20 M</td>
<td>0 M</td>
<td>1.2 M</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>-x M</td>
<td>+x M</td>
<td>+4x M</td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>0.20-x M</td>
<td>x M</td>
<td>1.2+4x M</td>
</tr>
</tbody>
</table>

These equilibrium concentrations refer to the reverse reaction, so they do not correspond to K\(_f\), instead they correspond to K\(_d\), the dissociation constant, which is 1/K\(_f\) (K for a reverse reaction always equals the inverse of K for the forward reaction):

\[K_d = \frac{[\text{Cd}^{2+}][\text{CN}^-]^4}{[\text{Cd(CN)}_4^{2-}]} = (x)(1.2+4x)^4 = \frac{2.07x}{0.20} = \frac{1}{6.0 \times 10^{18}}\]
\[x = 1.6 \times 10^{-20} \text{ M}\]
35. Calculate the molar solubility of CdCO₃ in 1.5 M NH₃. Note that Cd²⁺ forms the Cd(NH₃)₄²⁺ complex ion for which $K_f$ is $1.3 \times 10^7$. $K_{sp}$ for CdCO₃ is $5.2 \times 10^{-12}$.

\[
\text{CdCO}_3(s) \rightleftharpoons \text{Cd}^{2+}(aq) + \text{CO}_3^{2-}(aq) \\
K_{sp} = 5.2 \times 10^{-12}
\]

\[
\text{Cd}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cd(NH}_3)_4^{2+}(aq) \\
K_f = 1.3 \times 10^7
\]

\[
\text{CdCO}_3(s) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cd(NH}_3)_4^{2+}(aq) + \text{CO}_3^{2-}(aq)
\]

\[
K = K_{sp} \times K_f = (5.2 \times 10^{-12}) (1.3 \times 10^7) = 6.76 \times 10^{-5}
\]

\[
\begin{array}{c|c|c|c|c}
\text{CdCO}_3(s) & + & 4\text{NH}_3(aq) & \rightleftharpoons & \text{Cd(NH}_3)_4^{2+}(aq) & + & \text{CO}_3^{2-}(aq) \\
\hline
\text{Initial} & --- & 1.5 \ M & 0 \ M & 0 \ M \\
\text{Change} & --- & -4x \ M & +x \ M & +x \ M \\
\text{Equilibrium} & --- & 1.5-4x \ M & x \ M & x \ M
\end{array}
\]

\[
K = [\text{Cd(NH}_3)_4^{2+}][\text{CO}_3^{2-}] = \frac{x^2}{(1.5-4x)^4} = 6.76 \times 10^{-5}
\]

\[
x = 1.8 \times 10^{-2} \ M
\]

36. What is the concentration of free cobalt ion in a solution that is $4.75 \times 10^{-2} \ M$ Co²⁺ and $5.0 \ M$ NH₃? $K_f$ for Co(NH₃)₄²⁺ = $8.3 \times 10^4$

\[
\text{Co}^{2+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons \text{Co(NH}_3)_4^{2+}(aq)
\]

\[
\begin{array}{c|c|c|c|c}
\text{Co}^{2+}(aq) & + & 6\text{NH}_3(aq) & \rightleftharpoons & \text{Co(NH}_3)_4^{2+}(aq) \\
\hline
\text{Initial} & 4.75 \times 10^{-2} \ M & 5.0 \ M & 0 \ M \\
\text{Change} & -4.75 \times 10^{-2} \ M & -6(4.75 \times 10^{-2} \ M) & +4.75 \times 10^{-2} \ M \\
\text{Final (NOT equilibrium)} & 0 \ M & 4.715 \ M & 4.715 \times 10^{-2} \ M
\end{array}
\]

\[
K = [\text{Co}^{2+}][\text{NH}_3]^6 = \frac{x (4.715 + 6x)^6}{(4.75 \times 10^{-2} - x)^4} = \frac{(1.1 \times 10^4)(x)}{4.75 \times 10^{-2}} = \frac{1}{8.3 \times 10^4}
\]

\[
x = 5.2 \times 10^{-11} \ M
\]

37. Calculate the molar solubility of AgCl in 12 M NH₃.

$K_{sp}$ AgCl = $1.8 \times 10^{-10}$, $K_f$ Ag(NH₃)₂⁺ = $1.7 \times 10^7$

\[
\text{AgCl}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \\
K_{sp} = 1.8 \times 10^{-10}
\]

\[
\text{Ag}^{+}(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^{+}(aq) \\
K_f = 1.7 \times 10^7
\]

\[
\text{AgCl}(s) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^{+} + \text{Cl}^{-}(aq)
\]

\[
K = K_{sp} \times K_f = 3.06 \times 10^{-3}
\]

\[
\begin{array}{c|c|c|c|c}
\text{AgCl}(s) & + & 2\text{NH}_3(aq) & \rightleftharpoons & \text{Ag(NH}_3)_2^{+} & + & \text{Cl}^{-}(aq) \\
\hline
\text{Initial} & --- & 12 \ M & 0 \ M & 0 \ M \\
\text{Change} & --- & -2x \ M & +x \ M & +x \ M \\
\text{Equilibrium} & --- & 12-2x \ M & x \ M & x \ M
\end{array}
\]

\[
K = [\text{Ag(NH}_3)_2^{+}][\text{Cl}^{-}] = \frac{x^2}{(12-2x)^2} = 3.06 \times 10^{-3}
\]

\[
x = 6.6 \times 10^{-1} \ M
\]
38. Calculate the concentration of free aluminum ion, \([\text{Al}^{3+}]\), in 1.0 L of solution that contains 0.040 mol \(\text{Al(NO}_3\text{)}_3\), and 2.00 mol \(\text{NaF}\). \(K_f\) for \(\text{AlF}_6^{3-}\) is 7.1 \(\times\) 10^{-9}.

\[
\begin{array}{c|c|c|c}
\text{Initial} & 0.040 \text{ M} & 2.00 \text{ M} & 0 \text{ M} \\
\text{Change} & -0.040 \text{ M} & -6(0.040) \text{ M} & +0.040 \text{ M} \\
\text{Final (NOT equilibrium)} & 0 \text{ M} & 1.76 \text{ M} & 0.040 \text{ M} \\
\end{array}
\]

\[
\begin{array}{c|c|c}
\text{Al}^{3+}\text{(aq)} & + & 6\text{F}^-(\text{aq}) & \rightleftharpoons \text{AlF}_6^{3-}\text{(aq)} \\
\end{array}
\]

\[
K_d=\frac{[\text{Al}^{3+}][\text{F}^-]^6}{[\text{AlF}_6^{3-}]} = \frac{x(1.76+6x)^6}{(0.040-x)^6} = \frac{(2.97 \times 10^1)(x)}{0.040} = \frac{1}{7.1 \times 10^{-9}}
\]

\[
x = 1.9 \times 10^{-23} \text{ M}
\]

39. The \(\text{Cd}^{2+}\) ion forms the complex ion \(\text{CdCl}_4^{2-}\) for which \(K_f = 6.3 \times 10^7\). Determine the equilibrium constant for the solubility of \(\text{CdCO}_3\) in contact with a solution that contains \(\text{Cl}^-\) ion. \(K_{sp}\) for \(\text{CdCO}_3\) is 5.2 \(\times\) 10^{-12}.

\[
\begin{array}{c|c|c|c}
\text{CdCO}_3\text{(s)} & \rightleftharpoons & \text{Cd}^{2+}\text{(aq)} + \text{CO}_3^{2-}\text{(aq)} & \text{K}_{sp}=5.2 \times 10^{-12} \\
\text{Cd}^{2+}\text{(aq)} + 4\text{Cl}^-\text{(aq)} & \rightleftharpoons & \text{CdCl}_4^{2-}\text{(aq)} & \text{K}_f=6.3 \times 10^7 \\
\text{CdCO}_3\text{(s)} + 4\text{Cl}^-\text{(aq)} & \rightleftharpoons & \text{CdCl}_4^{2-}\text{(aq)} + \text{CO}_3^{2-}\text{(aq)} & \text{K} = \text{K}_{sp} \times \text{K}_f = (5.2 \times 10^{-12})(6.3 \times 10^7) = 3.28 \times 10^{-5}
\end{array}
\]

40. Use information from problem 39 to calculate the molar solubility of \(\text{CdCO}_3\) in 3.0 M \(\text{NaCl}\).

\[
\begin{array}{c|c|c|c|c|c}
\text{CdCO}_3\text{(s)} & + & 4\text{Cl}^-\text{(aq)} & \rightleftharpoons & \text{CdCl}_4^{2-}\text{(aq)} & + & \text{CO}_3^{2-}\text{(aq)} \\
\text{Initial} & \text{-----} & 3.0 \text{ M} & 0 \text{ M} & 0 \text{ M} \\
\text{Change} & \text{-----} & -4x \text{ M} & +x \text{ M} & +x \text{ M} \\
\text{Equilibrium} & \text{-----} & 3.0-4x \text{ M} & x \text{ M} & x \text{ M} \\
\end{array}
\]

\[
K=\frac{[\text{CdCl}_4^{2-}][\text{CO}_3^{2-}]}{[\text{Cl}^-]^4} = \frac{x^2}{(3.0-4x)^4} = 3.28 \times 10^{-9}
\]

\[
x = 5.2 \times 10^{-4} \text{ M}
\]

41. The \(\text{Ag}^+\) ion forms the complex ion \(\text{AgCl}_2^{+}\) for which \(K_f = 2.5 \times 10^7\). Determine the equilibrium constant for the solubility of \(\text{AgCl}\) in the presence of excess chloride ion. \(K_{sp}\) of \(\text{AgCl}\) is 1.8 \(\times\) 10^{-10}.

\[
\begin{array}{c|c|c|c|c|c}
\text{AgCl}\text{(s)} & \rightleftharpoons & \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) & \text{K}_{sp}=1.8 \times 10^{-10} \\
\text{Ag}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) & \rightleftharpoons & \text{AgCl}_2^{+}\text{(aq)} & \text{K}_f=2.5 \times 10^7 \\
\text{AgCl}\text{(s)} + \text{Cl}^-(\text{aq}) & \rightleftharpoons & \text{AgCl}_2^{+}\text{(aq)} & \text{K} = \text{K}_{sp} \times \text{K}_f = 4.5 \times 10^{-3}
\end{array}
\]

42. Use the information from problem 41 to calculate the molar solubility of \(\text{AgCl}\) in 8.5 M \(\text{HCl}\).

\[
\begin{array}{c|c|c|c}
\text{AgCl}\text{(s)} & + & \text{Cl}^-(\text{aq}) & \text{AgCl}_2^{+}\text{(aq)} \\
\text{Initial} & \text{-----} & 8.5 \text{ M} & 0 \text{ M} \\
\text{Change} & \text{-----} & -x \text{ M} & +x \text{ M} \\
\text{Equilibrium} & \text{-----} & 8.5-x \text{ M} & x \text{ M} \\
\end{array}
\]


\[ K = [\text{AgCl}_2^-] = \frac{x}{\text{Cl}^-} = 4.5 \times 10^{-5} \]

\[ x = 3.8 \times 10^{-4} \text{M} \]

43. Calculate the concentration of free copper ion, \([\text{Cu}^{2+}]\), in a 1.0 L solution containing \(3.7 \times 10^{-3}\) mol \(\text{Cu}^{2+}\) and 2.5 M \(\text{NH}_3\). \(K_f\) for \(\text{Cu(NH}_3)_4^{2+}\) = \(5 \times 10^{12}\).

\[
\begin{array}{c|c|c|c}
\text{Cu}^{2+}(aq) & + & 4\text{NH}_3(aq) & \rightleftharpoons \text{Cu(NH}_3)_4^{2+}(aq) \\
\hline
\text{Initial} & 3.7 \times 10^{-2} \text{M} & 2.5 \text{M} & 0 \text{M} \\
\text{Change} & -3.7 \times 10^{-2} \text{M} & -4(3.7 \times 10^{-2}) \text{M} & +3.7 \times 10^{-2} \text{M} \\
\text{Final (NOT equilibrium)} & 0 \text{M} & 2.352 \text{M} & 3.7 \times 10^{-2} \text{M} \\
\end{array}
\]

\[
K_d = [\text{Cu}^{2+}][\text{NH}_3]^4 = (x)(2.352 + 4x)^4 = (3.1 \times 10^1)(x) = \frac{1}{3.7 \times 10^{-2}} 5.0 \times 10^{12}
\]

\[ x = 2.4 \times 10^{-16} \text{M} \]

44. What is the concentration of \(\text{Cd}^{2+}\) in a solution that is 0.10 M \(\text{Cd(NH}_3)_4^{2+}\)? \(K_f\) for \(\text{Cd(NH}_3)_4^{2+}\) is \(4.0 \times 10^6\).

\[
\begin{array}{c|c|c|c}
\text{Cd(NH}_3)_4^{2+}(aq) & \rightleftharpoons & \text{Cd}^{2+}(aq) & + & 4\text{NH}_3(aq) \\
\hline
\text{Initial} & 3.7 \times 10^{-2} \text{M} & 0 \text{M} & 2.352 \text{M} \\
\text{Change} & -x \text{M} & +x \text{M} & +4x \text{M} \\
\text{Equilibrium} & 3.7 \times 10^{-2} - x \text{M} & x \text{M} & 2.352 + 4x \text{M} \\
\end{array}
\]

\[
K_d = [\text{Cd}^{2+}][\text{NH}_3]^4 = (x)(4x)^4 = \frac{256x^4}{0.10 - x} = \frac{1}{0.10} 4.0 \times 10^6
\]

\[ x = 1.0 \times 10^{-2} \text{M} \]

45. Calculate the molar solubility of \(\text{ZnS}\) in 2.5 M \(\text{NaOH}\). \(K_{sp}\) \(\text{ZnS} = 3.0 \times 10^{-23}\) \(K_f\) \(\text{Zn(OH)}_2^- = 2.9 \times 10^{15}\).

\[
\begin{array}{c|c|c|c}
\text{ZnS(s)} & \rightleftharpoons & \text{Zn}^{2+}(aq) + \text{S}^2-(aq) \\
\text{Zn}^{2+}(aq) + 4\text{OH}^- (aq) & \rightleftharpoons & \text{Zn(OH)}_2^- (aq) \\
\text{ZnS(s)} + 4\text{OH}^- (aq) & \rightleftharpoons & \text{Zn(OH)}_2^+(aq) + \text{S}^2-(aq) \\
\hline
\text{Initial} & \text{-} & 2.5 \text{M} & 0 \text{M} \\
\text{Change} & \text{-} & -4x \text{M} & +x \text{M} \\
\text{Equilibrium} & \text{-} & 2.5 - 4x \text{M} & x \text{M} \\
\end{array}
\]

\[
K = [\text{Zn(OH)}_2^+] [\text{S}^2-] = \frac{x^2}{(2.5 - 4x)^4} = 8.7 \times 10^{-8}
\]

\[ x = 1.8 \times 10^{-3} \text{M} \]
46. The formation constant, $K_f$, for $\text{Ni(NH}_3\text{)}_6^{2+}$ is $5.5 \times 10^8$. What is the concentration of free nickel ions in a solution that contains 0.045 M Ni$^{2+}$ and 3.0 M NH$_3$ (concentrations refer to the moment before the formation of the complex ion)?

<table>
<thead>
<tr>
<th>Initial</th>
<th>Ni$^{2+}$(aq)</th>
<th>6NH$_3$(aq)</th>
<th>$\text{Ni(NH}_3\text{)}_6^{2+}$(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>-0.045 M</td>
<td>-6(0.045) M</td>
<td>+0.045 M</td>
</tr>
<tr>
<td>Final (NOT equilibrium)</td>
<td>0 M</td>
<td>2.73 M</td>
<td>0.045 M</td>
</tr>
</tbody>
</table>

\[
\text{Ni$^{2+}$(aq)} + 6\text{NH}_3(aq) \rightleftharpoons \text{Ni(NH}_3\text{)}_6^{2+}(aq)
\]

\[
K_d = \frac{[\text{Ni$^{2+}$}(aq)][\text{NH}_3]^{6\text{e}}}{[\text{Ni(NH}_3\text{)}_6^{2+}]} = \frac{2.73 \times 6x}{0.045} = \frac{4.1 \times 10^2}{5.5 \times 10^8}
\]

\[
x = \frac{2.0 \times 10^{-13}}{M}
\]

47. A solution is saturated with silver acetate, $\text{AgC}_2\text{H}_3\text{O}_2$ ($K_{sp} = 1.9 \times 10^{-3}$). Which of the following reagents will increase the solubility of silver acetate?

- NaC$_2$H$_3$O$_2$
- HNO$_3$
- NH$_3$
- AgNO$_3$

For problems like these, first write out the solubility equilibrium expression and see how the various reagents will influence the equilibrium. Remember, a common-ion will decrease solubility, the effect of a change in pH will depend on the particular equilibrium, and formation of a complex ion will increase solubility, trumping both the common-ion and pH effects:

$\text{AgC}_2\text{H}_3\text{O}_2\text{(s)} \rightleftharpoons \text{Ag}^{+}(aq) + \text{C}_2\text{H}_3\text{O}_2^{–}(aq)$

NaC$_2$H$_3$O$_2$- common ion, therefore decreases solubility.

HNO$_3$- $\text{C}_2\text{H}_3\text{O}_2^{–}$ is the conjugate base of a weak acid (HC$_2$H$_3$O$_2$), and is therefore a weak base itself. It can be neutralized by HNO$_3$, a strong acid, thereby decreasing the concentration of $\text{C}_2\text{H}_3\text{O}_2^{–}$ and shifting the equilibrium to the right, increasing solubility.

NH$_3$- Ag$^+$ forms the complex ion Ag(NH$_3$)$_2^+$, increasing solubility.

AgNO$_3$- common ion, therefore decreases solubility.

48. How many of the following salts would be more soluble in acidic solution that in pure water?

- BaC$_2$O$_4$
- CaS
- AuCl$_3$
- PbF$_2$
- ZnCO$_3$

For an acidic solution to increase solubility, it must neutralize a weak base. Therefore the anion must be the conjugate base of a weak acid. Remember, conjugate salts of strong acids/bases are NOT influenced by addition of acids/bases or pH changes:

BaC$_2$O$_4$- $\text{C}_2\text{O}_4^{2–}$ is the conjugate base of the weak acid HC$_2$O$_4$. Solubility increases.

CaS- $\text{S}^{2–}$ is the conjugate base of the weak acid HS. Solubility increases.
AuCl₃- Cl⁻ is the conjugate base of the strong acid HCl. Solubility is NOT affected.

PbF₂- F⁻ is the conjugate base of the weak acid HF. **Solubility increases.**

ZnCO₃- CO₃²⁻ is the conjugate base of the weak acid HCO₃⁻. **Solubility increases.**

49. **Would each of the following reagents increase, decrease, or have no effect on the solubility of Cu(OH)₂?**

<table>
<thead>
<tr>
<th>CuCl₂</th>
<th>HCl</th>
<th>NH₃</th>
<th>NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(OH)₂ (s) ⇌ Cu²⁺(aq) + 2OH⁻(aq)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CuCl₂- common ion, therefore decreases solubility.

HCl- H⁺ neutralizes OH⁻, decreasing the concentration of OH⁻ and shifting the equilibrium to the right, **increasing solubility.**

NH₃- Cu²⁺ forms the complex ion Cu(NH₃)₄²⁺, **increasing solubility.**

NaOH- common ion, therefore decreases solubility.

50. **Which salt solubility would be most sensitive to pH?**

<table>
<thead>
<tr>
<th>Ca(NO₃)₂</th>
<th>CaF₂</th>
<th>CaCl₂</th>
<th>CaBr₂</th>
<th>CaI₂</th>
</tr>
</thead>
</table>

All of the cations are Ca²⁺, the conjugate salt of the strong base Ca(OH)₂. It cannot be neutralized by changes in pH. Of all the anions, only F⁻ is the conjugate base of a weak acid. The rest are conjugate bases of strong acids. Therefore **CaF₂** is most sensitive to pH.

51. **The solubility of which of the listed salts would be unaffected by the presence of a strong acid?**

<table>
<thead>
<tr>
<th>KClO₄</th>
<th>BaF₂</th>
<th>FePO₄</th>
<th>SnI₂</th>
</tr>
</thead>
</table>

Conjugate bases of strong acids will be unaffected by addition of a strong acid. The salts with this type of conjugate base include **KClO₄** (HClO₄ is a strong acid) and **SnI₂** (HI is a strong acid). **BaF₂** and FePO₄ contain conjugate bases of weak acids and are therefore influenced by a strong acid addition.

52. **How many of the following reagents, when added to a solution in contact with solid NiCO₃ would change the solubility of NiCO₃?**

<table>
<thead>
<tr>
<th>HCl</th>
<th>NiCl₂</th>
<th>NaCl</th>
<th>Na₂CO₃</th>
<th>NH₃</th>
</tr>
</thead>
</table>

NiCO₃ (s) ⇌ Ni²⁺(aq) + CO₃²⁻(aq)

HCl- This strong acid can neutralize CO₃²⁻ because this anion is the conjugate base of a weak acid. This removes CO₃²⁻, shifting the reaction to the right and **increasing solubility.**

NiCl₂- common ion, therefore **decreases solubility.**

NaCl- no effect.

Na₂CO₃- common ion, therefore **decreases solubility.**

NH₃- Ni⁺ forms the complex ion Ni(NH₃)₆²⁺, **increasing solubility.**
53. The solubility of how many of the following salts will be affected by strong acid?

<table>
<thead>
<tr>
<th>Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr</td>
</tr>
<tr>
<td>Cu_3(PO_4)_2</td>
</tr>
<tr>
<td>NaNO_3</td>
</tr>
<tr>
<td>BaF_2</td>
</tr>
</tbody>
</table>

Conjugate bases of weak acids will be affected by strong acid. This includes: Cu_3(PO_4)_2 and BaF_2.

54. Zinc oxalate is a slightly soluble salt. How many of the following reagents would be expected to decrease the solubility of ZnC_2O_4?

<table>
<thead>
<tr>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na_2C_2O_4</td>
</tr>
<tr>
<td>NH_3</td>
</tr>
<tr>
<td>NaOH</td>
</tr>
<tr>
<td>HCl</td>
</tr>
<tr>
<td>ZnCl_2</td>
</tr>
</tbody>
</table>

\[ \text{ZnC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \]

Na_2C_2O_4-common ion, therefore decreases solubility.

NH_3- Zn^{2+} forms the complex ion Zn(NH_3)_4^{2+}, increasing solubility.

NaOH- Zn^{2+} forms the complex ion Zn(OH)_4^{2-}, increasing solubility.

HCl- C_2O_4^{2-} is the conjugate base of a weak acid (HC_2O_4^-), and is therefore a weak base itself. It can be neutralized by HCl, a strong acid, thereby decreasing the concentration of C_2O_4^{2-} and shifting the equilibrium to the right and increasing solubility.

ZnCl_2- common ion, therefore decreases solubility.

55. Which of the following reagents would increase the solubility of Ni(OH)_2(s)?

<table>
<thead>
<tr>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(NO_3)_2</td>
</tr>
<tr>
<td>NaOH</td>
</tr>
<tr>
<td>HCl</td>
</tr>
<tr>
<td>NH_3</td>
</tr>
</tbody>
</table>

\[ \text{Ni(OH)}_2(\text{s}) \rightleftharpoons \text{Ni}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \]

Ni(NO_3)_2-common ion, therefore decreases solubility.

NaOH- common ion, therefore decreases solubility.

HCl- H^+ neutralizes OH^-, decreasing the concentration of OH^- and shifting the equilibrium to the right, increasing solubility.

NH_3- Ni^{2+} forms the complex ion Ni(NH_3)_6^{2+}, increasing solubility.

56. The molar solubility of ____________ is not affected by the pH of the solution.

a) MnS  

b) AlCl_3  

c) KNO_3  

d) NaF  

e) Na_3PO_4

To be unaffected by pH, BOTH the cation and anion must be conjugate salts of strong acids/bases. Even if one is the conjugate salt of a weak acid/base, the solubility will be affected by a change in pH. Of the ions, only KNO_3 has both ions as conjugate salts of strong acids/bases (KOH and HNO_3 are a strong base and strong acid, respectively).
57. For which salt should the aqueous solubility be most sensitive to pH?
   a) Ca(NO₃)₂
   b) CaF₂
   c) CaCl₂
   d) CaBr₂
   e) CaI₂

All of the cations are Ca²⁺, the conjugate salt of the strong base Ca(OH)₂. It cannot be neutralized by changes in pH. Of all the anions, only F⁻ is the conjugate base of a weak acid. The rest are conjugate bases of strong acids. Therefore CaF₂ is most sensitive to pH.

Precipitation and Separation of Ions (Section 17.6)

To determine whether or not precipitation occurs, you need to compare \( K_{sp} \) to \( Q \), the reaction quotient. The equation for \( Q \) appears the same as that for \( K_{sp} \):

\[
Q = \frac{[\text{products}]}{[\text{reactants}]}
\]

However, these concentrations can be at any point and do not necessarily correspond to equilibrium concentrations, as they do for \( K_{sp} \). \( K_{sp} \) can be thought of as a specific \( Q \) value that occurs at equilibrium. \( Q \) for given concentrations can be compared to \( K_{sp} \) to determine whether or not precipitation will occur:

**If \( Q < K_{sp} \), there are not enough products. The solution is unsaturated, and the reaction will shift to the right, so NO precipitate is formed. More solid can be dissolved.**

**If \( Q = K_{sp} \), the reaction is at equilibrium. The solution is saturated.**

**If \( Q > K_{sp} \), there are too many products. The solution is supersaturated, and the reaction will shift to the left, so a precipitate will form.**

58. A solution contains Ca²⁺ at a concentration of \( 2.0 \times 10^{-4} \) M. If 40.0 mL of this solution is added to 25.0 mL of \( 5.0 \times 10^{-3} \) M NaF, will a precipitate form? If 40.0 mL of the Ca²⁺ solution is added to 25.0 mL of \( 5.0 \times 10^{-3} \) M Na₃PO₄, will a precipitate form?

For CaF₂,

\[
K_{sp} = 3.9 \times 10^{-11}
\]

For Ca₃(PO₄)₂,

\[
K_{sp} = 2.0 \times 10^{-29}
\]

The concentrations of each ion must be calculated because the volumes change once they are added together:

\[
[\text{Ca}^{2+}] = \frac{(2.0 \times 10^{-4} \text{ mol/L})(0.040 \text{ L})}{0.040 \text{ L} + 0.0250 \text{ L}} = 1.23 \times 10^{-4} \text{ M}
\]

\[
[F^-] = \frac{(5.0 \times 10^{-3} \text{ mol/L})(0.025 \text{ L})}{0.040 \text{ L} + 0.0250 \text{ L}} = 1.92 \times 10^{-3} \text{ M}
\]

\[
Q = [\text{Ca}^{2+}][F^-]^2 = (1.23 \times 10^{-4} \text{ M})(1.92 \times 10^{-3} \text{ M})^2 = 4.55 \times 10^{-10}
\]

\( Q > K_{sp} \), therefore equilibrium will shift left and a precipitate forms.
Ca₃(PO₄)₂(s) ⇌ 3Ca²⁺(aq) + 2PO₄³⁻(aq)

\[
[Ca^{2+}]= \frac{(2.0 \times 10^{-4} \text{ mol/L})(0.040 \text{ L})}{(0.040 \text{ L} + 0.0250 \text{ L})} = 1.23 \times 10^{-4} \text{ M}
\]

\[
[PO_{4}^{3-}]=\frac{(5.0 \times 10^{-3} \text{ mol/L})(0.025 \text{ L})}{(0.040 \text{ L} + 0.0250 \text{ L})} = 1.92 \times 10^{-3} \text{ M}
\]

Q=[Ca²⁺]³[ PO₄³⁻]²=(1.23 \times 10^{-4} \text{ M})³(1.92 \times 10^{-3} \text{ M})²=6.86 \times 10^{-18}

Q>K_{sp}, therefore equilibrium will shift left and a precipitate forms.

59. Will a precipitate form when 4.5 mL of 0.025 M Pb(NO₃)₂ and 1.5 mL of 0.0065 M KF are mixed? How could you tell?

\[
PbF₂(s) ⇌ Pb^{2+}(aq) + 2F^{-}(aq)
\]

\[
[Pb^{2+}]=\frac{(0.025 \text{ mol/L})(0.0045 \text{ L})}{(0.0045 \text{ L} + 0.0015 \text{ L})} = 0.01875 \text{ M}
\]

\[
[F^{-}]=\frac{(0.0065 \text{ mol/L})(0.0015 \text{ L})}{(0.0045 \text{ L} + 0.0015 \text{ L})} = 0.001625 \text{ M}
\]

Q=[Ca²⁺][PO₄³⁻]=0.01875 \times 0.001625^2=4.95 \times 10^{-8}

Q>K_{sp}, therefore equilibrium will shift left and a precipitate forms.

60. Which salt precipitates first and what is the minimum concentration of Ag⁺ necessary to cause this precipitation in a solution containing 7.5 mL of 0.025 M NaCl and 7.5 mL of 0.025 M Na₃PO₄?

\[
K_{sp} \text{ AgCl} = 1.8 \times 10^{-10} \quad \text{K}_{sp} \text{ Ag}_3\text{PO}_4 = 1.3 \times 10^{-20}
\]

To determine which salt precipitates first, we need to look at Q, not K_{sp}, because precipitation occurs when Q>K_{sp}, which is not at equilibrium. We can, however, set Q equal to K_{sp} and solve for the minimum concentration of the ion required for precipitation to occur. Whichever concentration is lower, that solid will precipitate first:

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq)
\]

\[
[\text{Cl}^{-}]=\frac{(0.025 \text{ mol/L})(0.0075 \text{ L})}{(0.0075 \text{ L} + 0.0075 \text{ L})} = 1.25 \times 10^{-2} \text{ M}
\]

\[
Q=[\text{Ag}^{+}][\text{Cl}^{-}]
\]

\[
1.8 \times 10^{-10}=[\text{Ag}^{+}](1.25 \times 10^{-2} \text{ M})
\]

\[
[\text{Ag}^{+}]=1.40 \times 10^{-8} \text{ M needed for AgCl to ppt.}
\]

\[
\text{Ag}_3\text{PO}_4(s) \rightleftharpoons 3\text{Ag}^{+}(aq) + \text{PO}_4^{3-}(aq)
\]

\[
[\text{PO}_4^{3-}]=\frac{(0.025 \text{ mol/L})(0.0075 \text{ L})}{(0.0075 \text{ L} + 0.0075 \text{ L})} = 1.25 \times 10^{-2} \text{ M}
\]

\[
Q=[\text{Ag}^{+}]^3[\text{PO}_4^{3-}]
\]

\[
1.3 \times 10^{-20}=[\text{Ag}^{+}]^3(1.25 \times 10^{-2} \text{ M})
\]

\[
[\text{Ag}^{+}]=1.00 \times 10^{-8} \text{ M needed for Ag}_3\text{PO}_4 to ppt.}
\]

*Since the concentration of Ag⁺ needed for AgCl to precipitate is lower, it will precipitate first.
61. Will a precipitate form when 38 mL of 0.25 M Pb(NO₃)₂ and 12 mL of 0.35 M KBr are mixed? Why or why not?

\[ \text{PbBr}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Br}^-(aq) \]

\[[\text{Pb}^{2+}] = (0.25 \text{ mol/L})(0.038 \text{ L}) = 0.19 \text{ M} \]

\[[\text{Br}^-] = (0.35 \text{ mol/L})(0.012 \text{ L}) = 0.084 \text{ M} \]

\[Q = [\text{Pb}^{2+}][\text{Br}^-]^2 = (0.19 \text{ M})(0.084 \text{ M})^2 = 1.34 \times 10^{-3} \]

\[Q > K_{sp}, \text{ therefore equilibrium will shift left and a precipitate forms.} \]

62. A solution contains 0.10 M Mg(NO₃)₂ and 0.10 M Ca(NO₃)₂. If solid sodium oxalate, Na₂C₂O₄, is added to the solution, what is \([Ca^{2+}] \text{ (M)}\) when MgC₂O₄ begins to precipitate? (Assume no volume changes.) At 25 °C, \(K_{sp}\) of CaC₂O₄ is \(2.3 \times 10^{-9}\) and \(K_{sp}\) of MgC₂O₄ is \(8.6 \times 10^{-5}\).

First, calculate the concentration of C₂O₄²⁻ when MgC₂O₄ begins to precipitate:

\[ \text{MgC₂O₄(s) } \rightleftharpoons \text{Mg}^{2+}(aq) + \text{C₂O₄}^{2-}(aq) \]

\[Q = [\text{Mg}^{2+}][\text{C₂O₄}^{2-}] = 8.6 \times 10^{-5} = (0.10 \text{ M})[\text{C₂O₄}^{2-}] \]

\[\text{[C₂O₄}^{2-}] = 8.6 \times 10^{-4} \text{ M needed for MgC₂O₄ to ppt} \]

Now, use this concentration of C₂O₄²⁻ in the \(K_{sp}\) expression for CaC₂O₄ to determine the concentration of Ca²⁺ at this point:

\[ \text{CaC₂O₄(s) } \rightleftharpoons \text{Ca}^{2+}(aq) + \text{C₂O₄}^{2-}(aq) \]

\[K_{sp} = [\text{Ca}^{2+}][\text{C₂O₄}^{2-}] = 2.3 \times 10^{-9} = [\text{Ca}^{2+}](8.6 \times 10^{-4} \text{ M}) \]

\[\text{[Ca}^{2+}] = 2.7 \times 10^{-6} \text{ M} \]

63. The \(K_{sp}\) for BaF₂ is \(1.0 \times 10^{-6}\). When 10 mL of 0.010 M NaF is mixed with 10 mL of 0.01 M Ba(NO₃)₂ will a precipitate form? Why or why not?

\[ \text{BaF}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{F}^-(aq) \]

\[[\text{Ba}^{2+}] = (0.01 \text{ mol/L})(0.010 \text{ L}) = 0.005 \text{ M} \]

\[[\text{F}^-] = (0.01 \text{ mol/L})(0.010 \text{ L}) = 0.005 \text{ M} \]

\[Q = [\text{Ba}^{2+}][\text{F}^-]^2 = (0.005 \text{ M})(0.005 \text{ M})^2 = 1.25 \times 10^{-7} \]

\[Q < K_{sp}, \text{ therefore equilibrium will shift right and no precipitate forms.} \]
64. A solution contains 0.005 M AsO$_4^{3-}$, 0.005 M I$^-$, and 0.005 M CO$_3^{2-}$. If AgNO$_3$ is slowly added, in what order would the silver salts precipitate?

For Ag$_3$AsO$_4$,

$K_{sp} = 1.0 \times 10^{-22}$

For AgI,

$K_{sp} = 8.3 \times 10^{-17}$

For Ag$_2$CO$_3$,

$K_{sp} = 8.1 \times 10^{-12}$

Ag$_3$AsO$_4$(s) $\rightleftharpoons$ 3Ag$^+$ (aq) + AsO$_4^{3-}$ (aq)

$Q = [Ag^+]^3[AsO_4^{3-}]$

$1.0 \times 10^{-22} = [Ag^+]^3(0.005 \text{ M})$

$[Ag^+] = 2.71 \times 10^{-7} \text{ M needed for Ag}_3\text{AsO}_4 \text{ to ppt}$

AgI(s) $\rightleftharpoons$ Ag$^+$ (aq) + I$^-$ (aq)

$Q = [Ag^+][I^-]$

$8.3 \times 10^{-17} = [Ag^+](0.005 \text{ M})$

$[Ag^+] = 1.66 \times 10^{-14} \text{ M needed for AgI to ppt}$

Ag$_2$CO$_3$(s) $\rightleftharpoons$ 2Ag$^+$ (aq) + CO$_3^{2-}$ (aq)

$Q = [Ag^+]^2[CO_3^{2-}]$

$8.1 \times 10^{-12} = [Ag^+]^2(0.005 \text{ M})$

$[Ag^+] = 4.02 \times 10^{-5} \text{ M needed for Ag}_2\text{CO}_3 \text{ to ppt}$

*Lowest concentration will precipitate first: AgI precipitates first, then Ag$_3$AsO$_4$, then Ag$_2$CO$_3$.

65. Three beakers contain the following solutions:

1) 40.0 mL of 0.020 M Ca(NO$_3$)$_2$
2) 40.0 mL of 0.020 M Fe(NO$_3$)$_2$
3) 40.0 mL of 0.020 M Pb(NO$_3$)$_2$

If 10.0 mL of 0.050 M NaF is added to each beaker, in which beakers will a precipitate form?

For CaF$_2$, $K_{sp} = 1.5 \times 10^{-10}$, FeF$_2$ $K_{sp} = 2.4 \times 10^{-6}$, PbF$_2$ $K_{sp} = 7.1 \times 10^{-7}$

MF$_2$(s) $\rightleftharpoons$ M$^{2+}$ (aq) + 2F$^-$ (aq)

$[M^{2+}] = (0.020 \text{ mol/L})(0.040 \text{ L}) = 0.016 \text{ M}$

$(0.040 \text{ L} + 0.010 \text{ L})$

$[F^-] = (0.050 \text{ mol/L})(0.010 \text{ L}) = 0.010 \text{ M}$

$(0.040 \text{ L} + 0.010 \text{ L})$

$Q = [M^{2+}][F^-]^2 = (0.016 \text{ M})(0.010 \text{ M})^2 = 1.6 \times 10^{-6}$

$Q = 1.6 \times 10^{-6}$ for each equilibrium because the concentrations are the same. Compare the Q value to the individual $K_{sp}$ values:

CaF$_2$: $Q > K_{sp}$, therefore equilibrium will shift left and a precipitate forms.
FeF$_2$: $Q < K_{sp}$, therefore equilibrium will shift right and no precipitate forms.
PbF$_2$: $Q > K_{sp}$, therefore equilibrium will shift left and a precipitate forms.
66. A solution contains 0.010 M Al\(^{3+}\) and 0.010 M Ag\(^+\). Solid Na\(_3\)PO\(_4\) is slowly added to separate the two cations. 
\(K_{sp}\) for AlPO\(_4\) is \(1.3 \times 10^{-20}\) and \(K_{sp}\) for Ag\(_3\)PO\(_4\) is \(1.3 \times 10^{-20}\). Which cation would precipitate first, and after it precipitates, what concentration of PO\(_4^{3-}\) ion should be obtained in the solution for the best separation?

\[
\begin{align*}
\text{AlPO}_4(s) & \rightleftharpoons \text{Al}^{3+}(aq) + \text{PO}_4^{3-}(aq) \\
Q &= \left[\text{Al}^{3+}\right]\left[\text{PO}_4^{3-}\right] \\
1.3 \times 10^{-20} &= (0.010 \text{ M})\left[\text{PO}_4^{3-}\right]
\end{align*}
\]

\([\text{PO}_4^{3-}] = 1.3 \times 10^{-18} \text{ M needed for AlPO}_4 \text{ to ppt}\)

\[
\begin{align*}
\text{Ag}_3\text{PO}_4(s) & \rightleftharpoons 3\text{Ag}^+(aq) + \text{PO}_4^{3-}(aq) \\
Q &= \left[\text{Ag}^+\right]^3\left[\text{PO}_4^{3-}\right] \\
1.3 \times 10^{-20} &= (0.010 \text{ M})^3\left[\text{PO}_4^{3-}\right]
\end{align*}
\]

\([\text{PO}_4^{3-}] = 1.3 \times 10^{-14} \text{ M needed for Ag}_3\text{PO}_4 \text{ to ppt}\)

*Since the concentration of PO\(_4^{3-}\) needed for AlPO\(_4\) to precipitate is lower, it will precipitate first. To ensure the best separation, [PO\(_4^{3-}\)] should be as close to the higher concentration (1.3 \times 10^{-14} \text{ M}) WITHOUT going over that concentration. This ensures that virtually all of AlPO\(_4\) will be solid, but no Ag\(^+\) will have precipitated yet into Ag\(_3\)PO\(_4\).*

67. A solution of NaF is added dropwise to a solution that is 0.0144 M in Ba\(^{2+}\). BaF\(_2\) (\(K_{sp} = 1.7 \times 10^{-6}\)) will begin to precipitate when the concentration of F\(^-\) ions reaches what value? Neglect volume changes associated with the addition of NaF solution.

\[
\begin{align*}
\text{BaF}_2(s) & \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{F}^-(aq) \\
Q &= \left[\text{Ba}^{2+}\right]\left[\text{F}^\text{-}\right]^2 \\
1.7 \times 10^{-6} &= (0.0144 \text{ M})\left[\text{F}^\text{-}\right]^2
\end{align*}
\]

\([\text{F}^-] = 0.011 \text{ M needed for BaF}_2 \text{ to ppt}\)

68. AgNO\(_3\) is slowly added to a solution containing the following anions:

- 0.02 M AsO\(_4^{2-}\)
- 0.02 M I\(^-\)
- 0.02 M CO\(_3^{2-}\)

In what order will these salts precipitate? \(K_{sp}\) for Ag\(_3\)AsO\(_4\) = \(1.0 \times 10^{-22}\) AgI = \(8.3 \times 10^{-17}\) Ag\(_2\)CO\(_3\) = \(8.1 \times 10^{-12}\)

\[
\begin{align*}
\text{Ag}_3\text{AsO}_4(s) & \rightleftharpoons 3\text{Ag}^+(aq) + \text{AsO}_4^{3-}(aq) \\
Q &= \left[\text{Ag}^+\right]^3\left[\text{AsO}_4^{3-}\right] \\
1.0 \times 10^{-22} &= [\text{Ag}^+]^3(0.02 \text{ M})
\end{align*}
\]

\([\text{Ag}^+] = 1.7 \times 10^{-7} \text{ M needed for Ag}_3\text{AsO}_4 \text{ to ppt}\)

\[
\begin{align*}
\text{AgI(s)} & \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq) \\
Q &= \left[\text{Ag}^+\right]\left[\text{I}^\text{-}\right] \\
8.3 \times 10^{-17} &= [\text{Ag}^+]\left[\text{I}^\text{-}\right](0.02 \text{ M})
\end{align*}
\]

\([\text{Ag}^+] = 4.2 \times 10^{-15} \text{ M needed for AgI to ppt}\)

\[
\begin{align*}
\text{Ag}_2\text{CO}_3(s) & \rightleftharpoons 2\text{Ag}^+(aq) + \text{CO}_3^{2-}(aq) \\
Q &= \left[\text{Ag}^+\right]^2\left[\text{CO}_3^{2-}\right] \\
8.1 \times 10^{-12} &= [\text{Ag}^+]^2(0.02 \text{ M})
\end{align*}
\]

\([\text{Ag}^+] = 2.0 \times 10^{-5} \text{ M needed for Ag}_2\text{CO}_3 \text{ to ppt}\)

*Lowest concentration will precipitate first: AgI precipitates first, then Ag\(_3\)AsO\(_4\), then Ag\(_2\)CO\(_3\).*
69. A solution contains three anions with the following concentrations, 0.20 M CrO$_4^{2-}$, 0.10 M CO$_3^{2-}$ and 0.01 M Cl$^-$. If a dilute AgNO$_3$ solution is slowly added to the solution what precipitate forms first?

Ag$_2$CrO$_4$ ($K_{sp} = 1.2 \times 10^{-12}$), Ag$_2$CO$_3$ ($K_{sp} = 8.1 \times 10^{-12}$), AgCl ($K_{sp} = 1.8 \times 10^{-10}$)?

\[
\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq) \\
Q = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \\
1.2 \times 10^{-12} = [\text{Ag}^+]^2(0.20 \text{ M}) \\
[\text{Ag}^+] = 2.45 \times 10^{-6} \text{ M needed for Ag}_2\text{CrO}_4 \text{ to ppt.}
\]

\[
\text{Ag}_2\text{CO}_3(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{CO}_3^{2-}(aq) \\
Q = [\text{Ag}^+]^2[\text{CO}_3^{2-}] \\
8.1 \times 10^{-12} = [\text{Ag}^+]^2(0.10 \text{ M}) \\
[\text{Ag}^+] = 9.0 \times 10^{-6} \text{ M needed for Ag}_2\text{CO}_3 \text{ to ppt.}
\]

\[
\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \\
Q = [\text{Ag}^+][\text{Cl}^-] \\
1.8 \times 10^{-10} = [\text{Ag}^+](0.01 \text{ M}) \\
[\text{Ag}^+] = 1.8 \times 10^{-8} \text{ M needed for AgCl to ppt.}
\]

*Lowest concentration will precipitate first: AgCl precipitates first, then Ag$_2$CrO$_4$, then Ag$_2$CO$_3$.

70. In which one of the following solutions is silver chloride the most soluble?

a) 0.181 M HCl solution
b) 0.0176 M NH$_3$ solution
c) Pure water
d) 0.744 M LiNO$_3$ solution
e) 0.181 M NaCl solution

\[
\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \\
Q = [\text{Ag}^+][\text{Cl}^-]
\]

a) HCl: common-ion effect, decreases solubility
b) NH$_3$: Ag$^+$ forms the complex ion Ag(NH$_3$)$_2^+$, increasing solubility.
c) Water: no change in solubility
d) LiNO$_3$: both ions are conjugate salts of strong base/acid (LiOH and HNO$_3$) and therefore do not affect solubility.
e) NaCl: common-ion effect, decreases solubility.

71. Given the following $K_{sp}$ values, which statement about solubility in water is correct?

\[
\begin{align*}
\text{PbCrO}_4 &= 2.0 \times 10^{-16} \\
\text{Zn(OH)}_2 &= 4.5 \times 10^{-17} \\
\text{Pb(OH)}_2 &= 1.2 \times 10^{-15} \\
\text{MnS} &= 2.3 \times 10^{-13}
\end{align*}
\]

a) PbCrO$_4$, Zn(OH)$_2$, and Pb(OH)$_2$ have the same solubilities in water.
b) PbCrO$_4$ has the lowest solubility in water.
c) The solubility of MnS in water will not be pH dependant
d) MnS has the highest molar solubility in water.
e) A saturated PbCrO$_4$ solution will have a higher [Pb$^{2+}$] that a saturated Pb(OH)$_2$ solution.
a) Because the cation-to-anion ratios are the same for Zn(OH)_2 and Pb(OH)_2, we can directly compare their K_{sp} values. Because they differ, their solubilities in water cannot be the same, 
**making this statement FALSE.**

b) Because the cation-to-anion ratios are the same for PbCrO_4 and MnS, we can directly compare their K_{sp} values. Because K_{sp} is lower for PbCrO_4, we know it is less soluble than MnS. However, to compare the solubility of PbCrO_4 to those of Zn(OH)_2 and Pb(OH)_2, we must use ICE tables to calculate molar solubilities:

<table>
<thead>
<tr>
<th>PbCrO_4(s)</th>
<th>Pb^{2+}(aq) + CrO_4^{2-}(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0 M</td>
</tr>
<tr>
<td>Change</td>
<td>+1x M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>+x M</td>
</tr>
</tbody>
</table>

K_{sp}=[ Pb^{2+}] [CrO_4^{2-}]= (x)(x)= x^2= 2.0 \times 10^{-16}

x = 1.4 \times 10^{-8} M

<table>
<thead>
<tr>
<th>Zn(OH)_2(s)</th>
<th>Zn^{2+}(aq) + 2OH^{-}(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0 M</td>
</tr>
<tr>
<td>Change</td>
<td>+1x M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>+x M</td>
</tr>
</tbody>
</table>

K_{sp}=[ Zn^{2+}] [OH^{-}]^2= (x)(2x)^2= 4x^3= 4.5 \times 10^{-17}

x = 2.2 \times 10^{-6} M

<table>
<thead>
<tr>
<th>Pb(OH)_2(s)</th>
<th>Pb^{2+}(aq) + 2OH^{-}(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0 M</td>
</tr>
<tr>
<td>Change</td>
<td>+1x M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>+x M</td>
</tr>
</tbody>
</table>

K_{sp}=[ Pb^{2+}] [OH^{-}]^2= (x)(2x)^2= 4x^3= 1.2 \times 10^{-15}

x = 6.7 \times 10^{-6} M

*PbCrO_4 has the lowest x-value (molar solubility) in water, **making this statement TRUE.**

c) MnS(s) \rightleftharpoons Mn^{2+}(aq) + S^{2-}(aq)

*Both ions are the conjugate acid/base of a WEAK base/acid, making them both subject to the effects of pH, **making this statement FALSE.**

d) Because the cation-to-anion ratios are the same for PbCrO_4 and MnS, we can directly compare their K_{sp} values. Because K_{sp} is higher for MnS, we know it is more soluble than PbCrO_4. However, to compare the solubility of MnS to those of Zn(OH)_2 and Pb(OH)_2, we must use ICE tables to calculate molar solubilities:

<table>
<thead>
<tr>
<th>MnS(s)</th>
<th>Mn^{2+}(aq) + S^{2-}(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0 M</td>
</tr>
<tr>
<td>Change</td>
<td>+1x M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>+x M</td>
</tr>
</tbody>
</table>
\[
K_{sp} = [Mn^{2+}][S^{2-}] = (x)(x) = x^2 = 2.3 \times 10^{-13}
\]
\[
x = 4.8 \times 10^{-7}M
\]

*The molar solubilities of Zn(OH)\(_2\) and Pb(OH)\(_2\) were calculated in statement C, and they are both higher than that of MnS. Thus MnS does NOT have the highest molar solubility in water, making this statement FALSE.*

e) From the molar solubilities calculated in statement C, we can calculate the concentration of Pb\(^{2+}\) in each solution. Since the coefficient of Pb\(^{2+}\) in both equilibria is one, the molar solubility equals [Pb\(^{2+}\)]. Pb(OH)\(_2\) has the higher molar solubility, and therefore also the higher [Pb\(^{2+}\)], making this statement FALSE.

**Qualitative Analysis Group II & III (Section 17.7 & “Isolation and Characterization of Metal Ions: Exploitation of Differences in Solubility” Lab)**

72. A solution contains 0.015 M Cu\(^{2+}\) and 0.015 M Ni\(^{2+}\). The solution is saturated with H\(_2\)S (0.10M) and adjusted to pH = 2.00. Which of the metal sulfides will precipitate?

K\(_{sp}\) of NiS is 3 \times 10^{-20}, K\(_{sp}\) of CuS is 6 \times 10^{-37}.

For these type of problems, we need to consider two different equilibria that influence the solubility of these metal sulfides:

\[
\text{MS(s)} \rightleftharpoons M^{2+}(aq) + S^{2-}(aq)
\]
\[
S^{2-}(aq) + H_2O (l) \rightleftharpoons HS(aq) + OH(aq)
\]
\[
MS(s) + H_2O (l) \rightleftharpoons M^{2+}(aq) + HS(aq) + OH(aq)
\]

From this overall equilibrium, we can set up an expression for Q:
\[
Q = [M^{2+}][HS^\cdot][OH^\cdot]
\]

[M\(^{2+}\)] is given in the problem. We can calculate [OH\(^-\)] from the given pH:
\[
\text{pH} = -\log[H^+] = 2.00
\]
\[
[H^+] = 1.0 \times 10^{-2} M
\]
\[
[H^+][OH^-] = 1.0 \times 10^{-14} \quad \text{(always true)}
\]
\[
(1.0 \times 10^{-2} M)^{-1} [OH^-] = 1.0 \times 10^{-14}
\]
\[
[OH^-] = 1.0 \times 10^{-12} M
\]

To get [HS\(^-\)], we need to consider yet another equilibrium, that of the weak acid H\(_2\)S:
\[
H_2S(aq) \rightleftharpoons H^+(aq) + HS(aq) \quad K_a = 9.5 \times 10^{-8}
\]
\[
K_s = [H^+][HS^-] / [H_2S]
\]

Rearrange to find [HS\(^-\)]:
\[
[HS^-] = [H_2S] \cdot K_s / [H^+]
\]

We know K\(_s\), we are given [H\(_2\)S], and we calculated [H\(^+\)] earlier from the given pH:
\[
[HS^-] = (0.10 M)(9.5 \times 10^{-8}) = 9.5 \times 10^{-7} M
\]
\[
(1.0 \times 10^{-2} M)
\]

Plugging these values into the expression for Q, we have:
\[
Q = M^{2+} [HS^-][OH^-] = (0.015 M)(9.5 \times 10^{-7} M)(1.0 \times 10^{-12} M) = 1.43 \times 10^{-20}
\]

Compare Q to K\(_{sp}\) for each salt:

NiS: Q<<K\(_{sp}\), therefore equilibrium will shift right and **no precipitate forms.**

CuS: Q>K\(_{sp}\), therefore equilibrium will shift left and a **precipitate forms.**
73. Solutions were prepared using 0.03 M metal ion, 0.10 M H₂S and a pH of 5.25. Which metal sulfides will precipitate? Kᵢ, H₂S = \(9.5 \times 10^{-6}\)

\[ K_\text{sp} : \text{MnS} = 3 \times 10^{-14} \quad \text{NiS} = 3 \times 10^{-21} \quad \text{PbS} = 7 \times 10^{-29} \]

\[
\text{MS(s)} \rightleftharpoons \text{M}^{2+}(aq) + \text{S}^{2-}(aq)
\]

\[
\text{S}^{2-}(aq) + \text{H}_2\text{O (l)} \rightleftharpoons \text{HS}^{-}(aq) + \text{OH}^{-}(aq)
\]

\[
\text{MS(s)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{M}^{2+}(aq) + \text{HS}^{-}(aq) + \text{OH}^{-}(aq)
\]

\[ Q = [\text{M}^{2+}] [\text{HS}^{-}] [\text{OH}^{-}] \]

\[
\text{pH} = -\log[\text{H}^+] = 5.25
\]

\[
[\text{H}^+] = 5.6 \times 10^{-6} \text{ M}
\]

\[
[\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \quad \text{(always true)}
\]

\[
(5.6 \times 10^{-6} \text{ M}) [\text{OH}^-] = 1.0 \times 10^{-14}
\]

\[
[\text{OH}^-] = 1.8 \times 10^{-9} \text{ M}
\]

\[
\text{H}_2\text{S(aq)} \rightleftharpoons \text{H}^+(aq) + \text{HS}^{-}(aq) \quad K_a = 9.5 \times 10^{-8}
\]

\[
K_a = \frac{[\text{H}^+] [\text{HS}^-]}{[\text{H}_2\text{S}]} \quad [\text{HS}^-] = 9.5 \times 10^{-8} \text{ M}
\]

\[
[\text{HS}^-] = 0.10 \text{ M} \times 9.5 \times 10^{-8} = 1.7 \times 10^{-3} \text{ M}
\]

\[
Q = [\text{M}^{2+}] [\text{HS}^-] [\text{OH}^-] = (0.03 \text{ M})(1.7 \times 10^{-3} \text{ M})(1.8 \times 10^{-9} \text{ M}) = 9.2 \times 10^{-14}
\]

MnS: \(Q < K_\text{sp}\), therefore equilibrium will shift right and a precipitate forms.

NiS: \(Q < K_\text{sp}\), therefore equilibrium will shift right and a precipitate forms.

PbS: \(Q > K_\text{sp}\), therefore equilibrium will shift left and a precipitate forms.

74. Which of the following metal sulfides would form a precipitate from a solution of pH = 3.75 containing 0.10 M H₂S (Kᵢ, H₂S = \(9.5 \times 10^{-6}\)) and 0.01 M metal ion?

\[ K_\text{sp for MnS} = 3 \times 10^{-14}, \text{FeS} = 6 \times 10^{-19}, \text{CoS} = 5 \times 10^{-22} \]

\[
\text{MS(s)} \rightleftharpoons \text{M}^{2+}(aq) + \text{S}^{2-}(aq)
\]

\[
\text{S}^{2-}(aq) + \text{H}_2\text{O (l)} \rightleftharpoons \text{HS}^{-}(aq) + \text{OH}^{-}(aq)
\]

\[
\text{MS(s)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{M}^{2+}(aq) + \text{HS}^{-}(aq) + \text{OH}^{-}(aq)
\]

\[ Q = [\text{M}^{2+}] [\text{HS}^-] [\text{OH}^-] \]

\[
\text{pH} = -\log[\text{H}^+] = 3.75
\]

\[
[\text{H}^+] = 1.8 \times 10^{-4} \text{ M}
\]

\[
[\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \quad \text{(always true)}
\]

\[
(1.8 \times 10^{-4} \text{ M}) [\text{OH}^-] = 1.0 \times 10^{-14}
\]

\[
[\text{OH}^-] = 5.6 \times 10^{-11} \text{ M}
\]
\[
\text{H}_2\text{S(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{HS}^-(\text{aq}) \quad K_a = 9.5 \times 10^{-8}
\]

\[
K_a = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \quad \text{[Equation 1]}
\]

\[
[\text{HS}^-] = \frac{[\text{H}_2\text{S}]^*K_a}{[\text{H}^+]} \quad \text{[Equation 2]}
\]

\[
[\text{HS}^-] = (0.10 \text{ M}) \times (9.5 \times 10^{-8}) = 5.3 \times 10^{-5} \text{ M}
\]

\[
Q = [\text{M}^{2+}][\text{HS}^-][\text{OH}^-] = (0.01 \text{ M}) \times (5.3 \times 10^{-5} \text{ M}) \times (5.6 \times 10^{-11} \text{ M}) = 3.0 \times 10^{-17} \text{ M}
\]

MnS: \( Q < K_{sp} \), therefore equilibrium will shift right and no precipitate forms.
FeS: \( Q > K_{sp} \), therefore equilibrium will shift left and a precipitate forms.
CoS: \( Q > K_{sp} \), therefore equilibrium will shift left and a precipitate forms.

75. A solution containing \( \text{Zn}^{2+}, \text{Co}^{2+}, \text{Pb}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Sn}^{2+}, \text{Fe}^{2+}, \text{Sb}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+}, \text{and Bi}^{3+} \) ions is treated with HNO\(_3\) and H\(_2\)S. What is the identity of the precipitate(s) that form and which ions remain in solution?

The answer for this question comes from the lab manual and involves the separation of Group II and Group III ions: Group II ions form precipitates as sulfides, while Group III ions remain in solution:

Form precipitate (Group II): \( \text{PbS(s)}, \text{Bi}_2\text{S}_3(s), \text{CuS(s)}, \text{Sb}_2\text{S}_5(s), \text{SnS}_2(s) \)
Remain in solution (Group III): \( \text{Fe}^{2+/3+}, \text{Al}^{3+}, \text{Cr}^{3+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+} \)

76. Aqua regia is a commonly used reagent in experiment #25. What is the identity of aqua regia and what purpose does each component serve?

This, again, comes from the lab manual. Aqua regia is a combination of concentrated HCl and HNO\(_3\) in a ratio of 3:1. The nitric acid serves as an oxidizing agent, putting each cation in its highest oxidation state (i.e. \( \text{Sn}^{2+} \rightarrow \text{Sn}^{4+} \) and \( \text{Sb}^{3+} \rightarrow \text{Sb}^{5+} \)), and the hydrochloric acid serves as a complexing agent.

77. For the sulfide equilibrium of the type:

\[
\text{MS(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{M}^{2+}(\text{aq}) + \text{HS}^-(\text{aq}) + \text{OH}^-(\text{aq})
\]

<table>
<thead>
<tr>
<th>( \text{MS(s)} )</th>
<th>( K_{sp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CdS} )</td>
<td>( 8.0 \times 10^{-28} )</td>
</tr>
<tr>
<td>( \text{CoS} )</td>
<td>( 5.0 \times 10^{-24} )</td>
</tr>
<tr>
<td>( \text{CuS} )</td>
<td>( 6.0 \times 10^{-27} )</td>
</tr>
<tr>
<td>( \text{FeS} )</td>
<td>( 6.0 \times 10^{-19} )</td>
</tr>
<tr>
<td>( \text{PbS} )</td>
<td>( 3.0 \times 10^{-28} )</td>
</tr>
<tr>
<td>( \text{MnS} )</td>
<td>( 3.0 \times 10^{-34} )</td>
</tr>
<tr>
<td>( \text{NiS} )</td>
<td>( 1.1 \times 10^{-21} )</td>
</tr>
<tr>
<td>( \text{SnS} )</td>
<td>( 1.0 \times 10^{-26} )</td>
</tr>
<tr>
<td>( \text{ZnS} )</td>
<td>( 2.0 \times 10^{-35} )</td>
</tr>
</tbody>
</table>

In the laboratory the following experimental conditions were observed: \( [\text{M}^{2+}] = 0.01 \text{ M}, [\text{H}_2\text{S}] = 0.10 \text{ M}, [\text{HNO}_3] = 0.3 \text{ M} \). Which of the following metal ions from the chart will precipitate under these conditions?
\[
\begin{align*}
\text{MS(s)} & \rightleftharpoons M^{2+}(aq) + S^{2-}(aq) \\
S^{2-}(aq) + H_2O (l) & \rightleftharpoons HS(aq) + OH(aq) \\
\text{MS(s) + H}_2\text{O (l)} & \rightleftharpoons M^{2+}(aq) + HS^{-}(aq) + OH^{-}(aq) \\
Q = [M^{2+}][HS^{-}][OH^{-}] \\
[H^+] = 0.3 \text{ M} (*\text{from HNO}_3) \\
[H^+][OH^-] &= 1.0 \times 10^{-14} \text{ (always true)} \\
(0.3 \text{ M})^{-1}[OH^-] &= 1.0 \times 10^{-14} \\
[OH^-] &= 3.3 \times 10^{-14} \text{ M} \\
H_2S(aq) & \rightleftharpoons H^+(aq) + HS^{-}(aq) \quad K_a = 9.5 \times 10^{-8} \\
K_a &= \frac{[H^+][HS^-]}{[H_2S]} \\
[HS^-] &= \frac{[H_2S] \times K_a}{[H^+]} \\
[HS^-] &\approx (0.01 \text{ M}) (9.5 \times 10^{-8}) = 3.2 \times 10^{-8} \text{ M} \\
Q = [M^{2+}][HS^{-}][OH^{-}] &\approx (0.01 \text{ M})(3.2 \times 10^{-8} \text{ M})(3.3 \times 10^{-14} \text{ M}) = 1.0 \times 10^{-23}
\end{align*}
\]

A precipitate will form if the above Q-value is greater than $K_{sp}$. This is true for: Cds, Cus, PbS, Sns, Zns.

**78. At what pH will each of the nine sulfides begin to precipitate?**

To find the pH at which precipitation begins, we need to solve for [H\(^+\)]:

\[
\begin{align*}
\text{MS(s)} & \rightleftharpoons M^{2+}(aq) + S^{2-}(aq) \\
S^{2-}(aq) + H_2O (l) & \rightleftharpoons HS(aq) + OH(aq) \\
\text{MS(s) + H}_2\text{O (l)} & \rightleftharpoons M^{2+}(aq) + HS^{-}(aq) + OH^{-}(aq) \\
Q = [M^{2+}][HS^{-}][OH^{-}] \\
[H^+] = 0.3 \text{ M} (*\text{from HNO}_3) \\
[H^+][OH^-] &= 1.0 \times 10^{-14} \\
[OH^-] &= 3.3 \times 10^{-14} \text{ M} \\
H_2S(aq) & \rightleftharpoons H^+(aq) + HS^{-}(aq) \quad K_a = 9.5 \times 10^{-8} \\
K_a &= \frac{[H^+][HS^-]}{[H_2S]} \\
[HS^-] &= \frac{[H_2S] \times K_a}{[H^+]} \\
[HS^-] &\approx (0.01 \text{ M}) (9.5 \times 10^{-8}) = 3.2 \times 10^{-8} \text{ M} \\
Q = [M^{2+}][HS^{-}][OH^{-}] &\approx (0.01 \text{ M})(3.2 \times 10^{-8} \text{ M})(3.3 \times 10^{-14} \text{ M}) = 1.0 \times 10^{-23}
\end{align*}
\]
Substitute the bolded expressions into the expression for Q and set Q equal to $K_{sp}$ in order to solve for $[H^+]$. Use $[M^{2+}]$ and $[H_2S]$ from problem 76:

$$Q = \frac{[M^{2+}] \cdot [H_2S] \cdot K_{sp} \times 1.0 \times 10^{-14}}{[H^+]^2}$$

$$K_{sp} = \frac{(0.01 \ M) \times (0.1 \ M) \times (9.5 \times 10^{-8}) \times 1.0 \times 10^{-14}}{[H^+]^2}$$

$$[H^+]^2 = \frac{9.5 \times 10^{-25}}{K_{sp}}$$

**CdS:** $[H^+]^2 = 9.5 \times 10^{-25}$
- $8.0 \times 10^{-28}$
- $[H^+] = 34.5 \ M$
- $pH = -\log[H^+] = -\log(34.5) = 1.5$

**CoS:** $[H^+]^2 = 9.5 \times 10^{-25}$
- $5.0 \times 10^{-22}$
- $[H^+] = 0.044 \ M$
- $pH = -\log[H^+] = -\log(0.044) = 1.4$

**CuS:** $[H^+]^2 = 9.5 \times 10^{-25}$
- $6.0 \times 10^{-37}$
- $[H^+] = 1.26 \times 10^6 \ M$
- $pH = -\log[H^+] = -\log(1.26 \times 10^6) = 6.1$

**FeS:** $[H^+]^2 = 9.5 \times 10^{-25}$
- $6.0 \times 10^{-19}$
- $[H^+] = 1.26 \times 10^{-3} \ M$
- $pH = -\log[H^+] = -\log(1.26 \times 10^{-3}) = 2.9$

**PbS:** $[H^+]^2 = 9.5 \times 10^{-25}$
- $3.0 \times 10^{-28}$
- $[H^+] = 56.3 \ M$
- $pH = -\log[H^+] = -\log(56.3) = 1.8$

**MnS:** $[H^+]^2 = 9.5 \times 10^{-25}$
- $3.0 \times 10^{-14}$
- $[H^+] = 5.6 \times 10^{-6} \ M$
- $pH = -\log[H^+] = -\log(5.6 \times 10^{-6}) = 5.2$

**NiS:** $[H^+]^2 = 9.5 \times 10^{-25}$
- $1.1 \times 10^{-21}$
- $[H^+] = 0.029 \ M$
- $pH = -\log[H^+] = -\log(0.029) = 1.5$
SnS: \[ [H^+] \text{=} 9.5 \times 10^{-25} \]
\[ 1.0 \times 10^{-26} \]
\[ [H^+] \text{=} 9.7 \text{ M} \]
\[ \text{pH} \text{=} -\log[H^+] \text{=} -\log(9.7) \text{=} -1.0 \]

ZnS: \[ [H^+] \text{=} 9.5 \times 10^{-25} \]
\[ 2.0 \times 10^{-25} \]
\[ [H^+] \text{=} 2.18 \text{ M} \]
\[ \text{pH} \text{=} -\log[H^+] \text{=} -\log(2.18) \text{=} -0.3 \]

79. Notice that CdS is not a part of the Group II or Group III analysis. If we were to include Cd\(^{2+}\) in the qualitative scheme in the laboratory which group would it be included in? Give a valid reason to support your answer.

According to problem 77, CdS begins to precipitate at a pH of -1.5. Because it is a precipitate at such a low pH, it will be insoluble under the acidic conditions presented in problem 76, and thus it would be included in Group II. **If you look at pg. 757 in the textbook, CdS is included in Group II, but we do not use in lab it because of its toxicity.**

80. A solution containing Al\(^{3+}\), Cr\(^{3+}\), and Fe\(^{3+}\) was treated with NH\(_3\) to precipitate out Al(OH)\(_3\), Cr(OH)\(_3\), and Fe(OH)\(_3\). The solids were treated with NaOH and H\(_2\)O which dissolved Al(OH)\(_3\) and Cr(OH)\(_3\) and left Fe(OH)\(_3\) as a solid. What chemical principle is responsible for this difference in solubility?

**Amphoterism:** This is a special case of the complex ion effect on solubility when the anion in the precipitate is also a complexing agent. This is the case for amphoteric hydroxides of Al\(^{3+}\), Cr\(^{3+}\), Zn\(^{2+}\), Sn\(^{2+}\). Thus, when treated with NaOH, Al(OH)\(_3\) and Cr(OH)\(_3\) form complex ions and therefore dissolve. Fe(OH)\(_3\) forms no such ion and remains as a solid.

81. How would each of the following reagents affect the solubility of Fe(OH)\(_3\) in the following reaction:

\[ \text{Fe(OH)}_3(s) + 3 \text{ H}^+(aq) \leftrightarrow \text{Fe}^{3+}(aq) + 3\text{H}_2\text{O}(l) \]

a.) NaOH
b.) NH\(_3\)
c.) HNO\(_3\)
d.) HCl
e.) aqua regia

a) NaOH- OH\(^-\) would neutralize H\(^+\), removing it from the equilibrium and shifting the reaction to the left, therefore decreasing solubility.

b) NH\(_3\)- no complex ion forms; but remember that NH\(_3\) is a base and produces OH\(^-\) in solution, which neutralizes H\(^+\), removing it from the equilibrium and shifting the reaction to the left, therefore decreasing solubility.

c) HNO\(_3\)- produces H\(^+\), shifting the equilibrium to the right (away from the added ion), therefore increasing solubility.

d) HCl- produces H\(^+\), shifting the equilibrium to the right (away from the added ion), therefore increasing solubility.
e) aqua regia - this is a mixture of HNO₃ and HCl, and therefore has the same effect as C and D, therefore increasing solubility.

82. Why is H₂O₂ an effective oxidizing agent?
In H₂O₂, oxygen is in an oxidation state of -1. It is highly electronegative and really wants to be reduced to an oxidation state of -2 by removing electrons from something else, therefore oxidizing that other molecule.

83. Consider the following reaction:

\[ \text{M}^{n+}(aq) + x \text{NH}_3(aq) \leftrightarrow \text{M(NH}_3)_x^{n+} (aq) \]

where M^{n+} = Al^{3+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}.

(a) Upon addition of NH₃ which complex ions will form?
(b) NH₃ was added and was also buffered with NH₄Cl. Which complex ions will form?

a) Look at a K_f table. ***Remember, NH₃ is also a base, so it produces OH⁻. Any cation that complexes with EITHER NH₃ or OH⁻ will form a complex ion.
Ni(NH₃)_6^{2+}, Co(NH₃)_6^{2+}, Zn(NH₃)_4^{2+}, Al(OH)_4⁻

b) Buffers resist changes in pH, so with a buffer, no OH⁻ forms. Therefore, only cations that complex with NH₃ will form a complex ion.
Ni(NH₃)_6^{2+}, Co(NH₃)_6^{2+}, Zn(NH₃)_4^{2+}

84. You will be responsible for all the chemical separations that were mentioned in class. Be sure to look over your notes and know everything that was discussed.

See class notes.