In the last unit we reviewed the common types of equilibrium expressions. The examples typically dealt with relatively simple systems with only a single equilibrium to work with. It is much more common to have two or more simultaneous equilibria. This unit reviews the approaches taken to solve more complex problems.

Steps in solving equilibrium problems

→ List any known values - given in the problem.
→ List what it is you are attempting to solve for.
→ Write balanced equations for all equilibria.
→ Write down all equilibrium expressions along with their constants.
→ Develop mass and/or charge balances.

If you have as many unique equations as unknowns at this point - its solvable.

Steps in solving equilibrium problems

Finding mass and charge balances is often one of the hardest and most important portions of solving a problem. Because they involve addition and subtraction, they are often used to simplify a problem. However, one you have everything in place, its usually just a matter of sequential substitutions that you'll need to work through.

Mass balance equations

Relates species concentrations to the analytical concentration.

Example - 1 M H₃PO₄
Mass balance equation

\[ 1.0 = [H₃PO₄] + [H₂PO₄⁻] + [HPO₄²⁻] + [PO₄^{3-}] \]

Charge balance equations

Conservation of charge
The number of moles of positive charge must equal the moles of negative charge.

Example - dissolution of NaHCO₃

\[ [\text{Na}^+] + [\text{H}_2\text{O}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \]

The best way to learn how to work these problems is to do a series of examples.

We'll attempt to follow each step while covering a range of problems. Solubility, acid-base and complex formation will all be involved at one point or another.
Determine the concentration of silver ion when excess AgCl is added to 0.1M NaBr.

We are adding a relative insoluble material to a solution that contains an anion that also produces a precipitate with silver.

We know that \([\text{Na}^+] = 0.1\ M\)

We want to know \([\text{Ag}^+]\)

Let's write down the equilibria involved.

\[
\begin{align*}
\text{AgCl(s)} & \quad \text{Ag}^+ + \text{Cl}^- \\
\text{AgBr(s)} & \quad \text{Ag}^+ + \text{Br}^- \\
\text{KSP}_{\text{AgBr}} = [\text{Ag}^+][\text{Br}^-] & \quad = 4.9 \times 10^{-13} \\
\text{KSP}_{\text{AgCl}} = [\text{Ag}^+][\text{Cl}^-] & \quad = 1.8 \times 10^{-10}
\end{align*}
\]

It's reasonable to assume that as silver enters the system, some will precipitate as AgBr.

OK, we have 4 species: Na⁺, Ag⁺, Cl⁻, and Br⁻.

We know that Na⁺ = 0.1M since there is no reason for it to change.

We have three unknowns but only two equations so far. We need to consider mass or charge balances.

Let's see what we know about the system.

First, every silver that enters the solution brings a chloride with it.

However, some silver is expected to precipitate as AgBr.

The total charge of the system must equal 0.

so \([\text{Na}^+] + [\text{Ag}^+] = [\text{Cl}^-] + [\text{Br}^-]\)

We know that \([\text{Na}^+] = 0.1\) so

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

So, we now have three equations and three unknowns -- we're ready to solve this thing.

We now need to express a single equation in terms of one unknown.

We'll use our mass balance.

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

Br⁻ and Cl⁻ can be expressed in terms of silver using our KSP expressions:

\[
[\text{Br}^-] = \frac{\text{KSP}_{\text{AgBr}}}{[\text{Ag}^+]} \\
[\text{Cl}^-] = \frac{\text{KSP}_{\text{AgCl}}}{[\text{Ag}^+]}
\]

\[
0.1 + [\text{Ag}^+] = \frac{\text{KSP}_{\text{AgBr}}}{[\text{Ag}^+]} + \frac{\text{KSP}_{\text{AgCl}}}{[\text{Ag}^+]}
\]
We can rearrange this to:

\[ [\text{Ag}^+]^2 + 0.1 [\text{Ag}^+] - K_{\text{sp AgBr}} - K_{\text{sp AgCl}} \]

This quadratic expression can be written as

\[ X^2 + 0.1 X - 1.805 \times 10^{-10} \]

Solve using the quadratic expression.

\[ X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

Solving for \( X \) gives us

\[ [\text{Ag}^+] = 1.081 \times 10^{-9} \text{ M} \]

No approximations were required for this solution.

Let's make things a bit more challenging.

Calculate the equilibrium concentration of silver ion in 1.000 M NH\(_3\) if the solution also contains 0.1 moles of silver nitrate.

You may assume that no conversion of ammonia to ammonium occurs.

This problem stepwise formation constants.

Let's start by setting up the equilibria and seeing what we know about the system.

\[
\begin{align*}
\text{Ag}^+ &\rightleftharpoons \text{Ag(NH}_3\text{)}^+ \\
\text{Ag(NH}_3\text{)}^+ &\rightleftharpoons \text{Ag(NH}_3\text{)}_2^+ \\
\end{align*}
\]

\[ K_1 = 2.34 \times 10^3 = \frac{[\text{Ag(NH}_3\text{)}^+]}{[\text{Ag}^+][\text{NH}_3]} \]

\[ K_2 = 6.90 \times 10^3 = \frac{[\text{Ag(NH}_3\text{)}_2^+]}{[\text{Ag(NH}_3\text{)}^+][\text{NH}_3]} \]

We now have two equations but 4 unknowns - 3 silver species and ammonia.

Time to look a mass/charge balances.

We know that the total silver concentration must be 0.1 M so:

\[ 0.1 = [\text{Ag}^+] + [\text{Ag(NH}_3\text{)}^+] + [\text{Ag(NH}_3\text{)}_2^+] \]

We can also establish a second mass balance based on ammonia:

\[ [\text{NH}_3] = 1.0 - [\text{Ag(NH}_3\text{)}^+] - 2[\text{Ag(NH}_3\text{)}_2^+] \]

since any complex that forms will reduce the ammonia concentration.
Next, can we assume that any species would be insignificant in our mass balances. Here, we can look at our formation constants.

- $K_1 = 2.34 \times 10^3 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]}$
- $K_2 = 6.90 \times 10^3 = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+][NH_3]}$

This shows that there are $2340 [Ag(NH_3)^+]$ for $[Ag^+]$ and $6900 [Ag(NH_3)_2^+]$ for each $[Ag(NH_3)^+]$.

Since almost all of our silver exists as $[Ag(NH_3)_2^+]$, our mass balances become:

- $0.1 = [Ag(NH_3)_2^+]$
- $[NH_3] = 1.0 - 2[Ag(NH_3)_2^+] = 0.8$

So we know the values for two of our species. The other silver species are relatively simple to solve for.

Let's take the last problem and bump it up a level in difficulty.

Determine the solubility of AgCl in a 1 M ammonia solution. Again, you can assume that there is no significant conversion of ammonia to ammonium.

Let's look at our system.

The solubility product constant ($K_{sp}$) for AgCl is:

$K_{sp} = 1.0 \times 10^{-10} = [Ag^+][Cl^-]$
We know from the last example that most of our silver will exist as the diamino complex. We can derive a new expression by combining $K_1$ and $K_2$ which will be easier to work with.

$$K_1K_2 = 1.6 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+] [NH_3]^2}$$

We now need mass or charge balances. One can be developed for chloride:

$$[Cl^-] = [Ag^+] + [Ag(NH_3)_2^+]$$

And another for ammonia:

$$[NH_3] = 1.00 - 2[Ag(NH_3)_2^+]$$

Almost all of our silver exists as $[Ag(NH_3)_2^+]$ so:

$$[NH_3] = 1.00 - 2[Cl^-]$$

Solve for $Cl^-$, it directly reflects the solubility of AgCl.

Need to get one equation in terms of $[Cl^-]$.

Let’s use our chloride mass balance:

$$[Cl^-] = [Ag^+] + [Ag(NH_3)_2^+]$$

First, $[Ag^+] = \frac{K_{sp}}{[Cl^-]}$ so:

$$[Cl^-] = \frac{K_{sp}}{[Cl^-]} + K_1K_2K_{sp}[NH_3]^2$$

Next, we can substitute our combined equilibrium expression for $[Ag(NH_3)_2^+]$.

Finally, we can use our other mass balance to replace ammonia with chloride based expression:

$$[Cl^-] = \frac{K_{sp}}{[Cl^-]} + K_1K_2K_{sp}[NH_3]^2 / [Cl^-]$$

$$[NH_3] = 1.00 - 2[Cl^-]$$

$$[Cl^-] = \frac{K_{sp}}{[Cl^-]} + K_1K_2K_{sp}(1.00-2[Cl^-])^2 / [Cl^-]$$

Now clean this expression up.
\[ [\text{Cl}^-]^2 = K_{SP} + K_{SP}K_1K_2(1-2[\text{Cl}^-])^2 \]

\[ K_{SP} + K_{SP}K_1K_2 \]

\[ [\text{Cl}^-] = 1 + 2K_{SP}K_1K_2 \]

\[ = 0.121 \text{ M} \]

Now for a similar problem that involves weak acids.

Determine the solubility of calcium oxalate at pH 4.00

As with our other examples, we need to start by writing down the entire equilibrium.

\[ \text{CaC}_2\text{O}_4 \rightleftharpoons \text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{H}^+ + \text{HC}_2\text{O}_4^- + \text{H}_2\text{O} \]

Here you can see that we must determine the \([\text{Ca}^+]\) to be able to calculate the solubility.

At least we know the pH.

We’ll use some shorthand. It will make things easier to type.

\[
\begin{align*}
[H^+] &= [H] \\
[\text{Ca}^{2+}] &= [\text{Ca}] \\
[\text{C}_2\text{O}_4^{2-}] &= [\text{Ox}] \\
[\text{HC}_2\text{O}_4^-] &= [\text{HOx}] \\
[\text{H}_2\text{C}_2\text{O}_4] &= [\text{H}_2\text{Ox}] 
\end{align*}
\]

Now to write out our equilibrium expressions.

\[ K_{SP} = [\text{Ca}][\text{Ox}] = 1.6 \times 10^{-6} \]

\[ K_{A_1} = \frac{[\text{H}][\text{HOx}]}{[\text{H}_2\text{Ox}]} = 8.8 \times 10^{-2} \]

\[ K_{A_2} = \frac{[\text{H}][\text{Ox}]}{[\text{HOx}]} = 5.1 \times 10^{-5} \]

\[ [H] = 1.00 \times 10^{-4} \]

On to looking for any mass or charge balances.

We know that the calcium concentration should equal the total of all oxalate species so:

\[ [\text{Ca}] = [\text{H}_2\text{Ox}] + [\text{HOx}] + [\text{Ox}] \]

We now can solve the problem but should attempt to simplify the mass balance to make our life easier.

Let’s look at the oxalate species.
At pH 4.00, we have almost no $H_2Ox$. Both HOx and Ox are present at a ratio of about 2:1 respectively.

Our mass balance becomes:

$$[Ca] = [HOx] + [Ox]$$

We now should attempt to solve for calcium. All we need to do is use a series of substitutions to express our mass balance in terms of a single variable - $[Ca]$ is the best choice since it is a direct measure of our solubility.

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The H3O+ have been omitted from phosphate equilibria for clarity.

There’s obviously more to this than we first thought!

MgNH4PO4

\[
\begin{align*}
\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + \text{OH}^- & \rightleftharpoons \text{Mg(OH)}_2 + \text{NH}_3 + \text{H}_2\text{PO}_4^- + \text{H}_3\text{PO}_4 \\
K_{sp} & \end{align*}
\]

K_{sp} Mg(OH)_2 = 1.2 \times 10^{-11} = [\text{Mg}^{2+}] [\text{OH}^-]^2

K_B NH_4^+ = 1.78 \times 10^{-5} = [\text{OH}^-][\text{NH}_4^+] / [\text{NH}_3]

For phosphate

K_{A1} = 7.5 \times 10^{-3} = [\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-] / [\text{H}_3\text{PO}_4^-]

K_{A2} = 6.0 \times 10^{-8} = [\text{H}_3\text{O}^+][\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]

K_{A3} = 4.8 \times 10^{-13} = [\text{H}_3\text{O}^+][\text{PO}_4^{3-}] / [\text{HPO}_4^{2-}]

What do we already know?

[\text{H}_3\text{O}^+] = 3.98 \times 10^{-11}

[\text{OH}^-] = 2.51 \times 10^{-4}

We also have several mass balances

3.79 \times 10^{-3} = [\text{NH}_4^+] + [\text{NH}_3] = [\text{H}_3\text{PO}_4^-] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]

This actually works out to be three problems in one. We’ll start with Mg^{2+}.

For Mg^{2+} we can see if we’ve exceeded the K_{sp} for Mg(OH)_{2}.

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

[\text{Mg}^{2+}] = K_{sp} / [\text{OH}^-]^2 = 4.7 \times 10^{-4}

We put 3.79 \times 10^{-3} into the solution so some must have precipitated. The [Mg^{2+}] is then based on the K_{sp} for Mg(OH)_{2}.

One down, two to go!

For ammonium, nothing will precipitate out of solution. However, some of it can be expected to be converted to ammonia.

K_B NH_4^+ = 1.78 \times 10^{-5} = [\text{OH}^-][\text{NH}_4^+] / [\text{NH}_3]

K_B [\text{OH}^-] = [\text{NH}_4^+] / [\text{NH}_3] = 0.11
Our mass balance for ammonia species is

\[ 3.79 \times 10^{-3} = [\text{NH}_4^+] + [\text{NH}_3] \]

Substituting for ammonia using

\[ [\text{NH}_4^+] = 0.11 [\text{NH}_3] \]

Gives us

\[ [\text{NH}_4^+] + [\text{NH}_4^+] = 3.79 \times 10^{-3} \]

\[ [\text{NH}_4^+] = 3.8 \times 10^{-4} \text{ M} \]

Two down, one to go!

For phosphate, we need to determine which species exist at significant levels at pH 10.2

\[ K_{a1} = \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{O}^+]} = 1.88 \times 10^6 \]

\[ K_{a2} = \frac{[\text{HPO}_4^{2-}]}{[\text{H}_3\text{O}^+]} = 1.51 \times 10^3 \]

\[ K_{a3} = \frac{[\text{PO}_4^{3-}]}{[\text{H}_3\text{O}^+]} = 0.012 \]

It appears that most of our phosphate exists as \( \text{HPO}_4^{2-} \)

We can now solve for phosphate.

\[ [\text{HPO}_4^{2-}] = 3.79 \times 10^{-3} \text{ M} \]

\[ [\text{PO}_4^{3-}] = 0.012 [\text{HPO}_4^{2-}] = 4.6 \times 10^{-5} \text{ M} \]

\[ K_{SP \ \text{MgNH}_4\text{PO}_4} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^-] = (4.7 \times 10^{-4})(3.8 \times 10^{-4})(4.6 \times 10^{-5}) = 8.2 \times 10^{-12} \]