Equilibrium Calculations

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.

Equilibrium Calculations

Steps in solving equilibrium problems

- → List any know 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

Equilibrium Calculations

Steps in solving equilibrium problems

Finding mass and charge balances is often on 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.

Equilibrium Calculations

Mass balance equations

Relates species concentrations to the analytical concentration.

Example - 1 M H_3PO_4

Mass balance equation

$$1.0 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

Equilibrium Calculations

Charge balance equations

Conservation of charge

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

Example - dissolution of $NaHCO_3$

$$[Na^+] + [H_3O^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

Example one

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 $[Na^+] = 0.1$ M

We want to know $[Ag^+]$

Lets write down the equilibria involved.

Example one

$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

$AgBr_{(s)} \rightleftharpoons Ag^+ + Br^-$

$K_{SP}\ AgBr = [Ag^+][Br^-] = 4.9x10^{-13}$

$K_{SP}\ AgCl = [Ag^+][Cl^-] = 1.8x10^{-10}$

Its reasonable to assume that as silver enters the system, some will precipitate as AgBr.

Example one

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.

Lets see what we know about the system.

Example one

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 $[\mathrm{Na^+}] + [\mathrm{Ag^+}] = [\mathrm{Cl^-}] + [\mathrm{Br^-}]$

Example one

We know that [Na+] = 0.1 so

$$0.1 + [Ag^+] = [Cl^-] + [Br^-]$$

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

Example one

$$0.1 + [Ag^+] = [Cl^-] + [Br^-]$$

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

$$[Br^-] = K_{SP}\ AgBr\ /\ [Ag^+]$$

$$[Cl^-] = K_{SP}\ AgCl\ /\ [Ag^+]$$

$$0.1 + [Ag^+] = K_{SP}AgBr\ /\ [Ag^+] + K_{SP}AgCl\ /\ [Ag^+]$$

Example one

We can rearrange this to:

$$[Ag^{+}]^{2} + 0.1\,[Ag^{+}] - K_{SP}\,AgBr - K_{SP}\,AgCl$$

This quadratic expression can be written as

$$X^{2} + 0.1\,X - 1.805\,x10^{10}$$

Now we can solve using the quadratic expression.

Example one

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

Solving for X gives us

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

No approximations were required for this solution.

Example two

Lets 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.

Lets start by setting up the equilibria and seeing what we know about the system.

Example two

$$Ag^+ + NH_3 \overset{K_1}{\rightleftharpoons} Ag(NH_3)^+$$

$$Ag(NH_3)^+ + NH_3 \overset{K_2}{\rightleftharpoons} Ag(NH_3)_2^+$$

We can see that there are two equilibrium expressions.

Now on to writing out each expression and looking up the various K values.

Example two

$$K_1 = 2.34\text{x}10^3 = \frac{[Ag(NH_3)^+]}{[Ag^+]\,[NH_3]}$$

$$K_2 = 6.90\text{x}10^3 = \frac{[Ag(NH_3)_2{}^+]}{[Ag(NH_3)^+]\,[NH_3]}$$

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

Time to look a mass/charge balances.

Example two

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

$0.1 = [Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+]$

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

$[NH_3] = 1.0 - [Ag(NH_3)^+] - 2\,[Ag(NH_3)_2^+]$

since any complex that forms will reduce the ammonia concentration.

Example two

Next, can we assume that any species would be insignificant in our mass balances.

Here, we can look at our formation constants.

$$K_1 = 2.34\text{x}10^3 = \frac{[Ag(NH_3)^+]}{[Ag^+]\,[NH_3]}$$

$$K_2 = 6.90\text{x}10^3 = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+]\,[NH_3]}$$

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

Example two

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

$$0.1 = [Ag(NH_3)_2^+]$$

$$\begin{aligned}[NH_3] &= 1.0 - 2\,[Ag(NH_3)_2^+] \\ &= 0.8\end{aligned}$$

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

Example two

$$[Ag(NH_3)^+] = \frac{[Ag(NH_3)_2^+]}{6.90\text{x}10^3\ [NH_3]} = \frac{0.1}{6.90\text{x}10^3 \text{ x } 0.8}$$

$$= 1.84\text{x}10^{-5}$$

$$[Ag^+] = \frac{[Ag(NH_3)^+]}{2.34\text{x}10^3\ [NH_3]} = \frac{1.84\text{x}10^{-5}}{2.34\text{x}10^3 \text{ x } 0.8}$$

$$= 9.82\ \text{x}10^{-9}$$

Example three

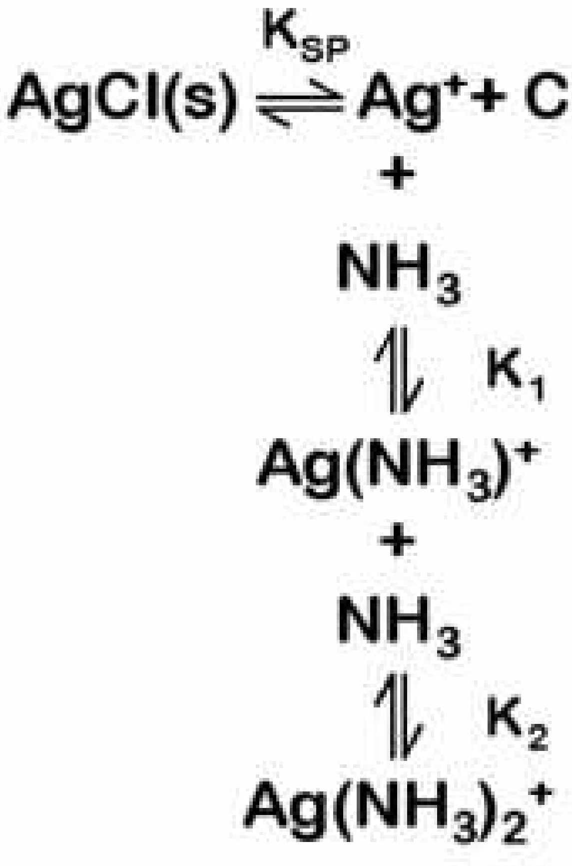
Lets take the last problem and bump it up a level in difficulty.

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.

Lets look at our system.

Example three



$$AgCl(s) \overset{K_{SP}}{\rightleftharpoons} Ag^{+} + Cl^{-}$$

$$\begin{array}{c} Ag^{+} \\ + \\ NH_3 \\ \updownarrow\ K_1 \\ Ag(NH_3)^{+} \\ + \\ NH_3 \\ \updownarrow\ K_2 \\ Ag(NH_3)_2^{+} \end{array}$$

We can see that there are now three equilibrium expressions.

Now on to writing out each expression and looking up the various K values.

Example three

$$K_{SP} = 1.0 \times 10^{-10} = [Ag^+][Cl^-]$$

$$K_1 = 2.34\times10^3 = \frac{[Ag(NH_3)^+]}{[Ag^+]\,[NH_3]}$$

$$K_2 = 6.90\times10^3 = \frac{[Ag(NH_3)_2{}^+]}{[Ag(NH_3)^+]\,[NH_3]}$$

Example three

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.

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

Example three

We now need mass or charge balances.

One can be developed for chloride:

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

And another for ammonia:

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

Example three

Since almost all of our silver exists as $[Ag(NH_3)_2^+]$ then:

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

Lets solve for chloride since it directly reflects the solubility of AgCl.

We just need to get one equation all in terms of $[Cl^-]$.

Example three

Lets use our chloride mass balance:

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

First, $[Ag^+] = K_{SP} / [Cl^-]$ so:

$[Cl^-] = K_{SP} / [Cl^-] + [Ag(NH_3)_2^+]$

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

Example three

$$[Ag(NH_3)_2^+] = K_1K_2[Ag^+]\,[NH_3]^2$$

$$[Cl^-] = K_{SP} / [Cl^-] + K_1K_2[Ag^+]\,[NH_3]^2$$

Again, we can replace $[Ag^+]$ with $K_{SP} / [Cl^-]$.

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

Example three

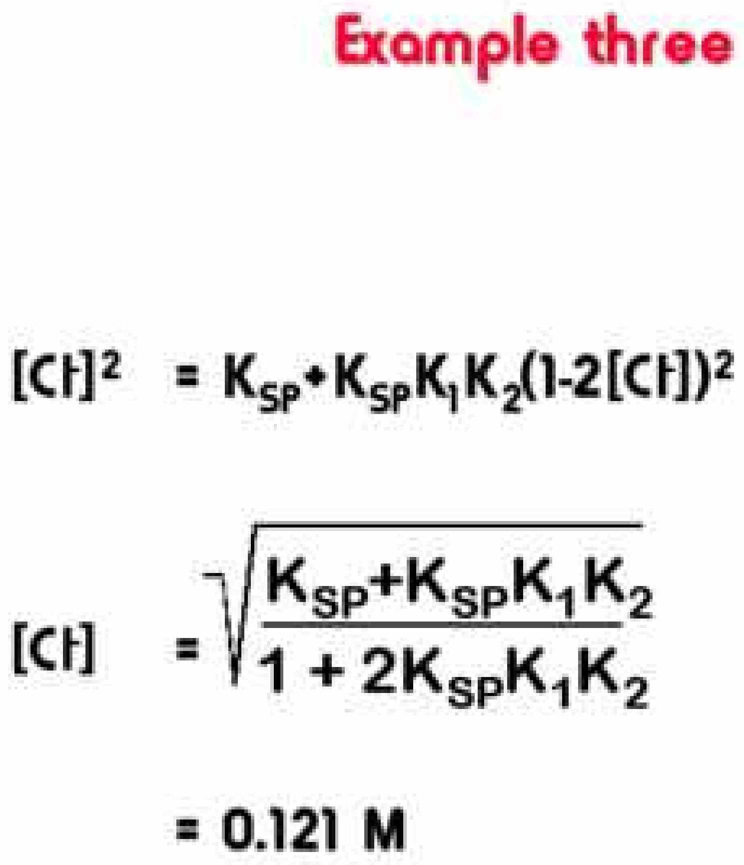
Finally, we can use our other mass balance to replace ammonia with chloride based expression:

$[Cl^-] = K_{SP} / [Cl^-] + K_1K_2K_{SP} [NH_3]^2 / [Cl^-]$

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

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

Now lets clean this expression up.



Example three

$$[Cl^-]^2 = K_{SP} + K_{SP}K_1K_2(1-2[Cl^-])^2$$

$$[Cl^-] = \sqrt{\frac{K_{SP}+K_{SP}K_1K_2}{1+2K_{SP}K_1K_2}}$$

$$= 0.121\ M$$

Extra credit: Prove the relationship.

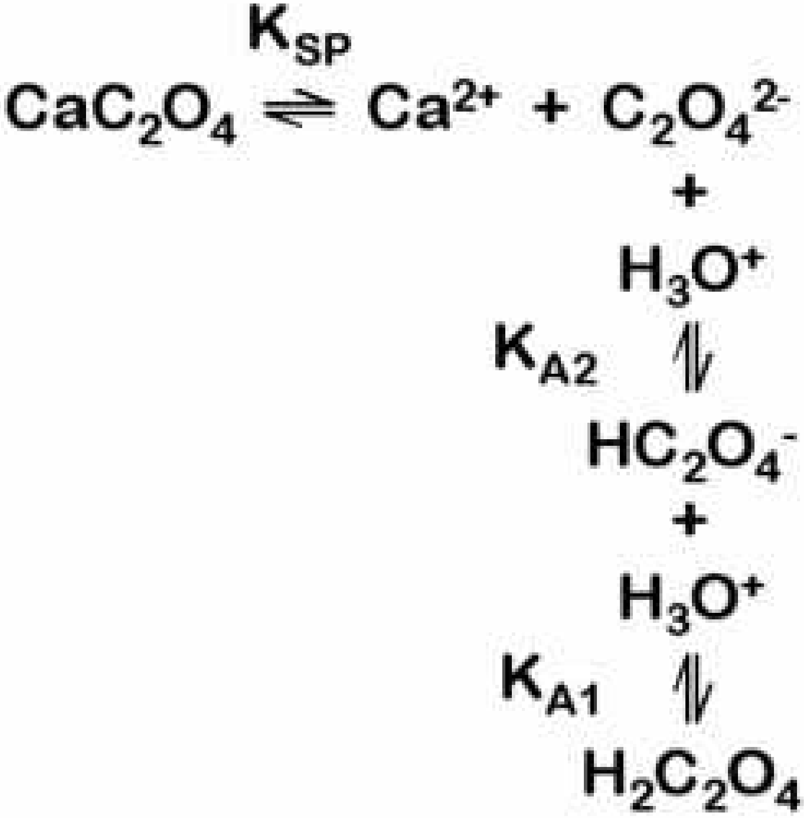
Example four

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.

Example four



$$\mathrm{CaC_2O_4} \overset{K_{SP}}{\rightleftharpoons} \mathrm{Ca^{2+}} + \mathrm{C_2O_4^{2-}}$$

$+$

$\mathrm{H_3O^+}$

K_{A2} $\rightleftharpoons$

$\mathrm{HC_2O_4^-}$

$+$

$\mathrm{H_3O^+}$

K_{A1} $\rightleftharpoons$

$\mathrm{H_2C_2O_4}$

Here you can see that we must determine the [Ca+] to be able to calculate the solubility.

At least we know the pH.

Example four

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

$[H_3O+]$ = $[H]$
$[Ca2+]$ = $[Ca]$
$[C_2O_42-]$ = $[Ox]$
$[HC_2O_4-]$ = $[HOx]$
$[H_2C_2O_4]$ = $[H_2Ox]$

Now to write out our equilibrium expressions.

Example four

$$K_{SP} = [Ca][OX] = 1.6 \times 10^{-8}$$

$$K_{A1} = \frac{[H][HOx]}{[H_2Ox]} = 8.8 \times 10^{-2}$$

$$K_{A2} = \frac{[H][Ox]}{[HOx]} = 5.1 \times 10^{-5}$$

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

On to looking for any mass or charge balances.

Example four

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

$$[Ca] = [H_2Ox] + [HOx] + [Ox]$$

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

Lets look at the oxalate species.

Example four

$$\frac{K_{A1}}{[H]} = \frac{[HOX]}{[H_2Ox]} = 880$$

$$\frac{K_{A2}}{[H]} = \frac{[Ox]}{[HOx]} = 0.51$$

At pH 4.00, we have almost no H_2Ox. Both HOx and Ox are present at a ratio of about 2:1 respectively.

Example four

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.

Example four

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

$[Ox] = K_{SP} / [Ca]$

$[HOx] = [Ox][H] / K_{A2} = 1.96\ [Ox]$

$[Ca] = 1.96\ [Ox] + [Ox]$

$= 2.96\ [Ox]$

$= 2.96 \times K_{SP} / [Ca]$

OK, we now can solve for [Ca].

Example four

$$[Ca]^2 = 2.96 \times K_{SP}$$

$$[Ca] = \sqrt{2.96 \times K_{SP}}$$

$$= 2.18 \times 104 \text{ M}$$

Not too bad!

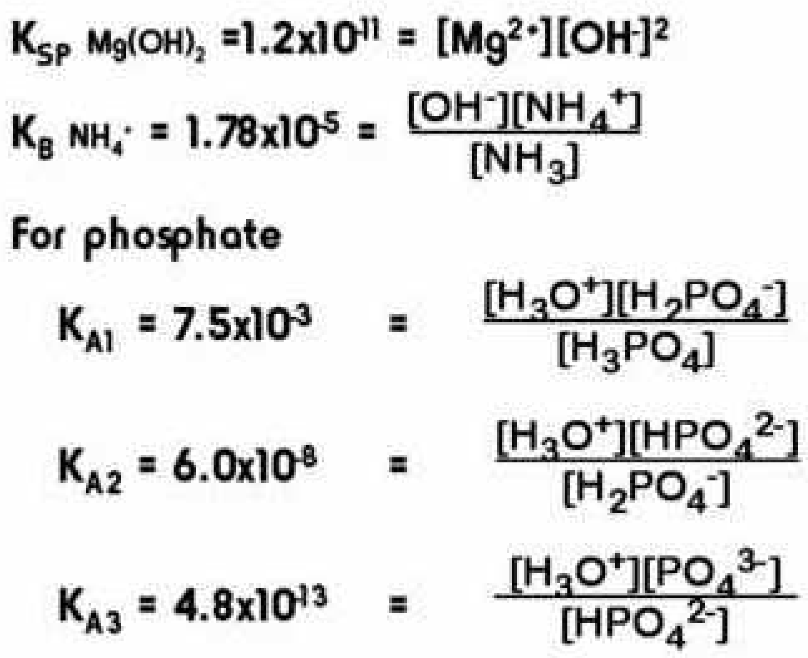
Now you're ready for a really 'fun' problem.

Problem: Calculate the K_{sp} of $MgNH_4PO_4$ if the solubility of the salt at pH = 10.2 is 0.52 g/L.

$MW(MgNH_4PO_4) = 137.32$ g/mol **$K_{sp} = [Mg^{2+}][NH_4^+][PO_4^{3-}]$**

Hint: Set-up the relevant equilibria:

No, the K_{sp} is not 5.44×10^{-8}



$$K_{SP\ Mg(OH)_2} = 1.2x10^{-11} = [Mg^{2+}][OH^-]^2$$

$$K_{B\ NH_4^+} = 1.78x10^{-5} = \frac{[OH^-][NH_4^+]}{[NH_3]}$$

For phosphate

$$K_{A1} = 7.5x10^{-3} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$$

$$K_{A2} = 6.0x10^{-8} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$K_{A3} = 4.8x10^{-13} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$