**Chapter 15 – Equilibria of Other Reaction Classes**

In the last chapter we talked about acid and base solutions, in particular weak acid and base solutions. That discussion was fine for laboratory work, but it falls short of describing the more general nature of solutions. Many real solutions contain several species in addition to the solute and solvent. We'll talk about three types of equilibria in this chapter: buffers, slightly soluble salts, and complex ions.

15.1    Precipitation and Dissolution

So far, all of the equilibria we have discussed in the past two chapters have been homogeneous equilibria. We will now explore heterogeneous equilibria. Recall that all ionic compounds are strong electrolytes, but some have low solubilities. These slightly soluble salts establish an equilibrium with the solution. For most of the rest of this section, we will use magnesium hydroxide as an example.

$$Mg(OH)_{2\ (s)} \rightleftharpoons Mg^{2+}_{\ (aq)} + 2\ OH^-_{\ (aq)}$$
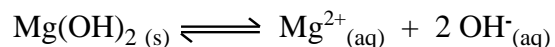
The equilibrium constant for this type of equilibrium bears a special name, the solubility product constant, $K_{sp}$. In this case:

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

Remember the parent magnesium hydroxide does not appear in the equilibrium because it is in a different phase (see Chapter 13.2). Unlike acid and base solutions where everything is soluble, $K_{sp}$ is used to determine the solubility of the salt under a variety of conditions. We'll look at several over the next few pages. At this point, it is important for you to recall that solubility refers to the mass of solute that will dissolve in a given volume of solvent (frequently g/L). Molar solubility is molarity, $M$. Solubility and the solubility product constant are related, but not

necessarily linearly.  Thus, it is **<u>incorrect</u>** to say that because the $K_{sp}$ of some salt is smaller than that of another, it is necessarily less soluble.  We'll come back to this shortly.

Ex.  What is the $K_{sp}$ of magnesium hydroxide if a saturated solution contains $1.65 \times 10^{-4}$ mol of Mg$^{2+}$ ions per liter of solution?

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

if  $[Mg^{2+}] = \dfrac{1.65 \times 10^{-4} \, mol_{Mg2+}}{1.00 \, L} = 1.65 \times 10^{-4} \, M$

then $[OH^-] = (1.65 \times 10^{-4} \, mol_{Mg2+}) \left( \dfrac{1 \, mol_{Mg(OH)2}}{1 \, mol_{Mg2+}} \right) \left( \dfrac{2 \, mol_{OH-}}{1 \, mol_{Mg(OH)2}} \right) \left( \dfrac{1}{1.00 \, L} \right) = 3.30 \times 10^{-4} \, M$

$K_{sp} = (1.65 \times 10^{-4})(3.30 \times 10^{-4})^2 = 1.80 \times 10^{-11}$

Now let's look at the same problem in reverse.

Ex.  What is the molar solubility of a saturated magnesium hydroxide solution?

$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.80 \times 10^{-11}$

Let $[Mg^{2+}] = x$, then $[OH^-] = 2x$   (from stoichiometry)

$x(2x)^2 = 1.80 \times 10^{-11}$

$4x^3 = 1.80 \times 10^{-11}$

$x = 1.65 \times 10^{-4}$

$[Mg(OH)_2] = \left( \dfrac{1.65 \times 10^{-4} \, mol_{Mg2+}}{L_{soln}} \right) \left( \dfrac{1 \, mol_{Mg(OH)2}}{1 \, mol_{Mg2+}} \right) = 1.65 \times 10^{-4} \, M$

It is a very common mistake to forget to multiply the hydroxide "x" by 2 or to square the "2x", but it there is twice as much hydroxide as magnesium ion and it must be taken account of in both places.

Ex.  What is the solubility of magnesium hydroxide?

$$\text{solubility} = \left(\frac{1.65 \times 10^{-4} \text{ mol}_{Mg(OH)2}}{L_{soln}}\right)\left(\frac{58.32 \text{ g}_{Mg(OH)2}}{1 \text{ mol}_{Mg(OH)2}}\right) = 0.00962 \text{ g/L}$$

The Common Ion Effect

Consider a solution of a weak acid, say acetic acid ($CH_3CO_2H$, HOAc).

$$HOAc \rightleftharpoons H^+ + OAc^-$$
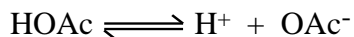
What happens to the equilibrium if we add some NaOAc? Le Châtelier's principle tells us the equilibrium will shift left to remove some of the added ion. What is the effect on pH when this happens? There are fewer hydrogen ions present, so the pH goes up. This should come as no surprise, since we just added a base to the solution. This simple observation can help avoid mistakes when working problems. Try to write out a Le Châtelier's principle argument for the change in pH.

Ex: What is the pH of a solution that is initially 0.500 $M$ in both HOAc and NaOAc?

$[HOAc]_i = 0.500 \ M$ $\qquad\qquad$ $[HOAc]_e = 0.500 - x \ M$

$[H^+]_i = 0 \ M$ $\qquad\qquad\qquad$ $[H^+]_e = x \ M$

$[OAc^-]_i = 0.500 \ M$ $\qquad\quad$ $[OAc^-]_e = 0.500 + x \ M$

$$K_a = \frac{x(0.500 + x)}{0.500 - x} = 1.8 \times 10^{-5}$$

Since $0.500 > 100 K_a$ we can assume x is negligible in the calculation

$$1.8 \times 10^{-5} = \frac{x(0.500)}{0.500}$$

$x = 1.8 \times 10^{-5}$

thus $[H^+]_e = 1.8 \times 10^{-5} \ M \longrightarrow pH = 4.74$

We will see later that, in general for a weak acid, if [HA] = [A$^-$], then [H$^+$] = $K_a$.

As we learned in Chapter 14, mixing an acid and its conjugate base (e.g. acetic acid and

sodium acetate as described above) generates buffer solutions or they may be created by either adding some strong base (e.g. sodium hydroxide) to a weak acid solution or by adding a strong acid to a weak base solution.

$$HOAc_{(aq)} + \tfrac{1}{2}\,NaOH_{(aq)} \rightarrow \tfrac{1}{2}\,HOAc_{(aq)} + \tfrac{1}{2}\,NaOAc_{(aq)}$$
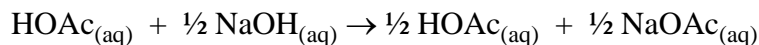
The common ion effect means that if a solution contains both a strong acid and a weak acid, the pH is determined only by the concentration of the strong acid. The strong acid dissociates completely and the hydrogen ions released retard the dissociation of the weak acid. This makes the weak acid a negligible contributor to the hydrogen ion concentration. From pp. 9-10 of the Chapter 14 lecture notes, we know that the pH of a 3.0 $M$ HOAc solution is 2.13. The pH of a 0.1 $M$ HCl solution would be 1.00, since HCl is a strong acid. What is the pH of a solution that is 3.0 $M$ in HOAc and 0.1 $M$ HCl?

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]} = 1.8 \text{ x } 10^{-5}$$

$$1.8 \text{ x } 10^{-5} = \frac{[0.10 + x][x]}{[3.0 - x]}$$

Assume x is negligible, then

$$1.8 \text{ x } 10^{-5} = \frac{[0.10][x]}{[3.0]}$$

x = 5.4 x 10$^{-4}$

$[H^+]$ = 0.10 + 0.00054 ≈ 0.10, so pH of the solution is 1.00. Thus, the hydrochloric acid suppresses the dissociation of the acetic acid and entirely determines the pH of the solution. It is widely, *and incorrectly*, believed that orange juice can cause an upset stomach because of its acidity. While many people have trouble tolerating orange juice, a calculation like the one above shows that a change in pH is not the cause of the distress.

The common ion effect when applied to solubility products looks like this.

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Ex. What is the molar solubility of magnesium hydroxide in a solution which is 1.0 $M$ in

magnesium chloride?

$[Mg^{2+}] = 1.0 + x\ M$      $[OH^-] = 2x\ M$

This is the amount of added $Mg^{2+}$ ion from the $MgCl_2$ plus the amount that dissolves from the $Mg(OH)_2$.

$1.8 \times 10^{-11} = (1.0 + x)(2x)^2$

We can now make an assumption similar to that made for weak acid/base equilibria

Since $1.0 \gg K_{sp}$, we will assume x is negligible in the calculation

$1.8 \times 10^{-11} = (1.0)(2x)^2$

$x = 2.1 \times 10^{-6}$    (the assumption is correct)

$$[Mg(OH)_2] = \left(\frac{2.1 \times 10^{-6}\ mol_{Mg2+}}{L_{soln}}\right)\left(\frac{1\ mol_{Mg(OH)2}}{1\ mol_{Mg2+}}\right) = 2.1 \times 10^{-6}\ M$$

This is much less than the $1.65 \times 10^{-4}\ M$ found when magnesium hydroxide is dissolved in pure

water.

Now, in addition to being a salt, magnesium hydroxide is also a base. Therefore, you'd expect

that if we raised the pH of the water we were dissolving the $Mg(OH)_2$ into, the latter would be less

soluble (another Le Châtelier's principle effect). As a reference point, saturated $Mg(OH)_2$ has a

pH of 10.52

Ex. What is the molar solubility of magnesium hydroxide at pH = 11.00? at pH = 10.00?

pH = 11.00 $\Rightarrow$ pOH = 14.00 – 11.00 = 3.00 $\Rightarrow$ $[OH^-]$ = antilog(-3.00) = $1.00 \times 10^{-3}\ M$

$1.8 \times 10^{-11} = [Mg^{2+}](1.00 \times 10^{-3})^2$

$[Mg^{2+}] = 1.8 \times 10^{-5}\ M$

$$[Mg(OH)_2] = \left(\frac{1.8 \times 10^{-5}\ mol_{Mg2+}}{L_{soln}}\right)\left(\frac{1\ mol_{Mg(OH)2}}{1\ mol_{Mg2+}}\right) = 1.8 \times 10^{-5}\ M$$

pH = 10.00 $\Rightarrow$ pOH = 14.00 – 10.00 = 4.00 $\Rightarrow$ $[OH^-]$ = antilog(-4.00) = $1.00 \times 10^{-4}\ M$
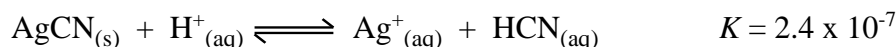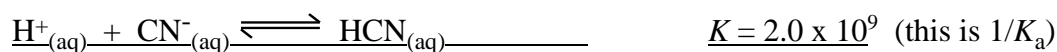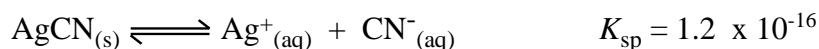
$1.8 \times 10^{-11} = [Mg^{2+}](1.00 \times 10^{-4})^2$

$[Mg^{2+}] = 1.8 \times 10^{-3} \; M$

$$[Mg(OH)_2] = \left(\frac{1.8 \times 10^{-3} \; mol_{Mg2+}}{L_{soln}}\right)\left(\frac{1 \; mol_{Mg(OH)2}}{1 \; mol_{Mg2+}}\right) = 1.8 \times 10^{-3} \; M$$

This calculation shows us that the solubility of magnesium hydroxide drops changes rapidly changing pH. (Not surprisingly, lowering the pH raises the solubility of $Mg(OH)_2$.)

pH can still have an effect even when the common ion effect plays no role. Consider the solubility of silver(I) cyanide in acidic solution.

$$AgCN_{(s)} \rightleftharpoons Ag^+_{(aq)} + CN^-_{(aq)} \qquad\qquad K_{sp} = 1.2 \times 10^{-16}$$

$$\underline{H^+_{(aq)} + CN^-_{(aq)} \rightleftharpoons HCN_{(aq)}} \qquad\qquad \underline{K = 2.0 \times 10^9} \; (\text{this is } 1/K_a)$$

$$AgCN_{(s)} + H^+_{(aq)} \rightleftharpoons Ag^+_{(aq)} + HCN_{(aq)} \qquad\qquad K = 2.4 \times 10^{-7}$$

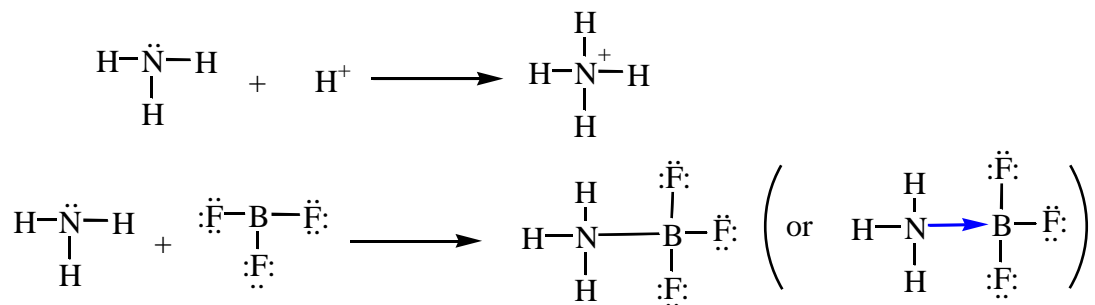$$2.4 \times 10^{-7} = \frac{[Ag^+][HCN]}{[H^+]}$$

We see from the above equilibrium expression that silver(I) cyanide becomes more soluble as pH decreases. This is reasonable because there are two different species competing to bind with the cyanide ion: $Ag^+$ and $H^+$. Silver(I) ions bind more strongly than do hydrogen ions, but as the concentration of hydrogen ions increases, they tie up more and more of the cyanide ions by weight of numbers.

In general, the solubilities of slightly soluble salts that contain the conjugate base of a weak acid increases as pH decreases (the hydrogen ions convert some of the anion to the weak acid).

15.2  Lewis Acids and Bases

It turns out there are many reactions that are similar to Brønsted-Lowry acid/base reactions, but do not involve proton transfer. G.N. Lewis proposed that the common thread between these

reactions is that one reactant donates a pair of electrons to the other. All Brønsted-Lowry acid/base reactions are also Lewis acid/base reactions. Two examples follow:

$$H-\overset{\cdot\cdot}{N}-H \;+\; H^+ \longrightarrow \; H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}\!\!{}^+\!\!-H$$

$$H-\overset{\cdot\cdot}{\underset{\underset{\displaystyle H}{|}}{N}}-H \;+\; :\overset{\cdot\cdot}{F}-B-\overset{\cdot\cdot}{F}: \longrightarrow \; H-N\cdots B-\overset{\cdot\cdot}{F}: \quad \left( or \quad H-N\!\!\longrightarrow\!\!B-\overset{\cdot\cdot}{F}: \right)$$

All nitrogen-hydrogen bonds in the ammonium ion are identical covalent bonds. There is something unusual in the bonding in this ion, however. Begin by looking at ammonia. Here we have three identical bonds. When ammonia reacts with $H^+$ the new bond that results forms when both electrons come from a single atom. This situation is different from a "normal" covalent bond, where each atom contributes one electron to the bond. In cases where one atom contributes both electrons to the bond, the bond is called a <u>coordinate covalent</u> or <u>dative</u> bond. Sometimes an arrow is drawn to show which atom contributes the pair of electrons (see above). It is important to remember that these bonds are not necessarily weaker than standard covalent bonds.

The binding of oxygen to hemoglobin is an example of this type of reaction (a lone pair of electrons on $O_2$ binds to an iron ion in the hemoglobin). This bond is fairly weak; allowing the oxygen bound in the lungs to be released where needed in the body. Carbon monoxide poisoning occurs because it binds much more strongly than oxygen. Thus, relatively small amounts of CO cause trouble, because it so efficiently ties up hemoglobin. Even exposure to a pure oxygen atmosphere only slowly frees the hemoglobin.

Metal ions are Lewis acids. Water, halide ions, cyanide ions, and ammonia are just a few of many Lewis bases. Different metal ions show different levels of affinity for different Lewis bases.
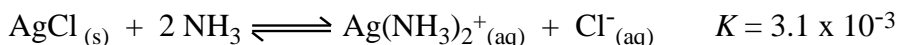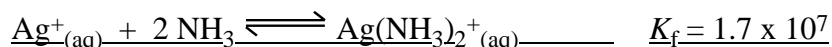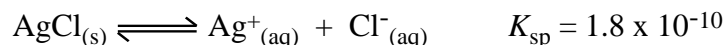
In the presence of halide ions, silver(I) forms a very stable lattice and precipitates from solution as AgX (X = F⁻, Cl⁻, Br⁻, I⁻; we'll discuss this more in the next section). In contrast, in the presence of ammonia, silver(I) quickly binds to two ammonia molecules to form a "complex ion." The term "complex" refers to the contrast with the "simple" elemental ion, $Ag^+$. A <u>complex ion</u> consists of a metal ion to which more than one Lewis base is covalently bound.

$$Ag^+_{(aq)} + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+_{(aq)}$$
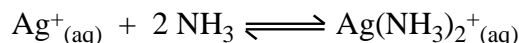
$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$$

where $K_f$ is the "formation constant." Formation constants can be quite large as can be seen in Appendix K (p. 1235) meaning that on mixing a soluble salt with the appropriate Lewis base, the complex ion forms readily. Such equilibria can also be used to dissolve slightly soluble salts. The reverse process is called <u>dissociation</u> and has an equilibrium constant, $K_d$, which equals $1/K_f$.

Ex: How much silver(I) chloride will dissolve in 1.0 L of a solution that is 0.10 $M$ in $NH_3$ at equilibrium? What is the free silver(I) ion concentration?

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)} \qquad K_{sp} = 1.8 \times 10^{-10}$$

$$Ag^+_{(aq)} + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+_{(aq)} \qquad K_f = 1.7 \times 10^7$$

$$AgCl_{(s)} + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+_{(aq)} + Cl^-_{(aq)} \qquad K = 3.1 \times 10^{-3}$$

a) $mol_{AgCl}(\text{dissolved}) = mol_{Cl^-}(\text{in solution})$

We use Cl⁻ because while most of the Ag⁺ is bound in the complex, some exists as free ion.

$$K = 3.1 \times 10^{-3} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

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

$$3.1 \times 10^{-3} = \frac{x^2}{(0.10)^2}$$

$$x = 5.6 \times 10^{-3}$$

$$\text{mass}_{AgCl} = (1.0 \text{ L}_{soln}) \left( \frac{5.6 \times 10^{-3} \text{ mol}_{Cl^-}}{\text{L}_{soln}} \right) \left( \frac{1 \text{ mol}_{AgCl}}{1 \text{ mol}_{Cl^-}} \right) \left( \frac{143.3 \text{ g}_{AgCl}}{1 \text{ mol}_{AgCl}} \right) = 0.80 \text{ g}_{AgCl}$$

b) $K_{sp} = 1.8 \times 10^{-10} = [Ag^+](5.6 \times 10^{-3})$

$[Ag^+] = 3.2 \times 10^{-8} \ M$

Saturated silver(I) chloride solution has $[Ag^+] = 1.3 \times 10^{-5} \ M$, so 99.8% of the silver(I)

ion released into solution is tied up as a complex ion.

Amphoterism was mentioned briefly in Chapter 14, but the most important amphoteric

compounds are metal oxides and hydroxides. Many metal hydroxides and oxides are slightly

soluble in neutral water, but are surprisingly soluble in both acidic and basic solutions.  Since they

are metal hydroxides and oxides their solubility in acidic solutions probably comes as no surprise.

Hydrogen ions protonate the hydroxide and oxide ions to water, leaving the metal ions free in

solution.

$$MOH \ + \ H^+ \ \rightarrow \ M^+ \ + \ H_2O$$

$$M_2O \ + \ 2 \ H^+ \ \rightarrow \ M^+ \ + \ H_2O$$
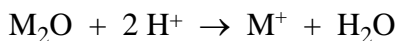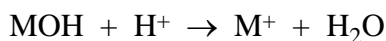
In basic solution, one or more hydroxide ions acts as a Lewis base and coordinates to the metal ion

forming a soluble complex ion.

In general: $\qquad\qquad M(OH)_{n \ (s)} \ + \ OH^-_{(aq)} \ \rightleftharpoons \ M(OH)_{n+1}^-{}_{(aq)}$
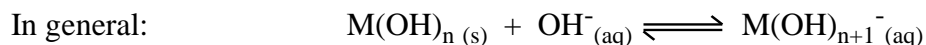
So why does this happen and why to only certain metal oxides and hydroxides?  There are

two parts to the answer: one electronic, the other structural.  First, for a substance to be amphoteric,

the metal ion must bind to oxide/hydroxide much more strongly than to water.  Generally the

interaction of oxides and hydroxides will be stronger because of electrostatic attraction.  If the

cation interacts with water at a comparable level as oxide/hydroxide, the compound will dissolve (e.g. NaOH). Metal ions with large charges or small sizes are more apt to yield amphoteric oxides and hydroxides. The other feature is structural. If metal ions develop Lewis acid/base interactions with neighboring ions, they can crosslink, making a large structure that is difficult to dissolve. Oxide and hydroxide have multiple lone pairs of electrons. It can now bind to several metal ions (i.e. crosslinking). When a solution hydroxide replaces the bridging interactions, monomeric complexes form and they are generally soluble.

### 15.3  Coupled Equilibria

This is a situation where two equilibria are operating at the same time. The problem worked on pp. 8-9 of these notes is an example. These kinds of equilibria are common in general, including biologically.

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