Separation Science - Equilibrium Unit

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The following textual material is designed to accompany a series of in-class problem sets that develop many of the fundamental aspects of chemical equilibrium calculations.

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OVERVIEW: SIGNIFICANCE OF CHEMICAL EQUILIBRIUM

Suppose you are a chemist involved in developing a new product for a small manufacturing company. Part of the process leads to the formation of the compound lead phosphate. The lead phosphate will end up in the wastewater from the process. Since you are a small facility, instead of having your own wastewater treatment plant, you will discharge the wastewater to the local municipal wastewater treatment plant. The municipal wastewater treatment plant faces strict requirements on the amount of lead that is permitted in their end products. A wastewater treatment plant ends up with "clean" water and a solid sludge. Most lead ends up in the sludge, and the Environmental Protection Agency has set a limit on how much lead is permitted in the sludge. Most municipalities will require you to enter into a pre-treatment agreement, under which you will need to remove the lead before discharging to the plant. For example, the City of Lewiston, Maine will require you to discharge a material that contains no more than 0.50 mg of total lead per liter.

Lead phosphate is a sparingly soluble material so most of it will actually be a solid in your waste, thereby allowing you to filter it out before discharge to the treatment plant.

What is the concentration of total dissolved lead in the discharge from your facility?

What we need to consider here is the reaction that describes the solubility of lead phosphate. Lead phosphate has the formula $Pb_3(PO_4)_2$, and the accepted practice for writing the solubility reaction of a sparingly soluble compound that will dissociate into a cation and anion is shown. The solid is always shown on the left, or reactant, side. The dissolved ions are always shown on the product side.

$$Pb_3(PO_4)_2(s) \leftrightarrow 3Pb^{2+}(aq) + 2PO_4^{3-}(aq)$$

Next, we can write the equilibrium constant expression for this reaction, which is as follows:

$$K_{sp} = [Pb^{2+}]^3[PO_4^{3-}]^2$$

This general equilibrium constant expression for a sparingly soluble, ionic compound is known as the **solubility product**, or $\mathbf{K_{sp}}$. Note that there is no term for the solid lead phosphate in the expression. One way to view this is that a solid really cannot have variable concentrations (moles/liter) and is therefore not important to the expression. K_{sp} values have been measured for many substances and tables of these numbers are available. The K_{sp} for lead phosphate is known and is 8.1×10^{-47}. What this means is that any solution that is in contact with solid lead phosphate will have a solubility product ($[Pb^{2+}]^3[PO_4^{3-}]^2$) that exactly equals its K_{sp} (8.1×10^{-47}).

There is a complication to this process though. It turns out that the phosphate ion is a species that appears in the dissociation reactions for a substance known as phosphoric acid (H_3PO_4). Acids and their corresponding conjugate bases are very important in chemistry and the properties of many acids and bases have been studied. What can happen in this case is that the phosphate ion can undergo a set of stepwise protonations, as shown below.

$$\begin{array}{ccccc} Pb_3(PO_4)_2 & \leftrightarrow & 3Pb^{2+} & + & 2PO_4^{3-} \\ &&&& \Updownarrow \\ &&&& HPO_4^{2-} \\ &&&& \Updownarrow \\ &&&& H_2PO_4^{-} \\ &&&& \Updownarrow \\ &&&& H_3PO_4 \end{array}$$

If we wanted to calculate the solubility of lead phosphate in water, we would need to consider the effect of protonation of the phosphate on the solubility. Remember, the K_{sp} expression only includes terms for Pb^{2+} and PO_4^{3-}, and it is the product of these two that must always equal K_{sp} if some solid lead phosphate is in the mixture. Protonation of the phosphate will reduce the concentration of PO_4^{3-}. If the concentration of PO_4^{3-} is reduced, more of the lead phosphate must dissolve to maintain K_{sp}.

We can look up relevant equilibrium constants for the dissociation of phosphoric acid. There is an accepted practice in chemistry for the way in which these reactions are written, and the series for phosphoric acid is shown below. This describes the chemistry of an acid and the equilibrium constant expressions are known as **K_a** values, or **acid dissociation constants**.

$$H_3PO_4 + H_2O \leftrightarrow H_2PO_4^{-} + H_3O^{+} \qquad K_{a1}$$

$$H_2PO_4^{-} + H_2O \leftrightarrow HPO_4^{2-} + H_3O^{+} \qquad K_{a2}$$

$$HPO_4^{2-} + H_2O \leftrightarrow PO_4^{3-} + H_3O^{+} \qquad K_{a3}$$

$$K_{a1} = \frac{[H_2PO_4^{-}][H_3O^{+}]}{[H_3PO_4]} \qquad\qquad K_{a2} = \frac{[HPO_4^{2-}][H_3O^{+}]}{[H_2PO_4^{-}]}$$

$$K_{a3} = \frac{[PO_4^{3-}][H_3O^{+}]}{[HPO_4^{2-}]}$$

But before we can proceed, there is still one other complication to this process. It turns out that the lead cation has the possibility of forming complexes with other anions in solution. One such anion that is always present in water is hydroxide (OH^{-}). The hydroxide complex could be another insoluble one with lead. More important, though, is whether lead can form water-soluble complexes with the hydroxide ion. A species that complexes with a metal ion is known as a **ligand**. It turns out that hydroxide can form water-soluble complexes with lead ions, and that there are three of them that form in a stepwise manner. The equations to represent this are always written with the metal ion and ligand on the reactant side and the complex on the product side, as shown below.

$$Pb^{2+}(aq) + OH^-(aq) \leftrightarrow Pb(OH)^+(aq) \qquad K_{f1}$$

$$Pb(OH)^+(aq) + OH^-(aq) \leftrightarrow Pb(OH)_2(aq) \qquad K_{f2}$$

$$Pb(OH)_2(aq) + OH^-(aq) \leftrightarrow Pb(OH)_3^-(aq) \qquad K_{f3}$$

The equilibrium constant expressions are shown below, and these are known as **formation constants (K_f)**.

$$K_{f1} = \frac{[Pb(OH)^+]}{[Pb^{2+}][OH^-]} \qquad K_{f2} = \frac{[Pb(OH)_2]}{[Pb(OH)^+][OH^-]}$$

$$K_{f3} = \frac{[Pb(OH)_3^-]}{[Pb(OH)_2][OH^-]}$$

The important thing to realize is that any complexation of lead ions by hydroxide will lower the concentration of Pb^{2+}. Since $[Pb^{2+}]$ is the concentration in the K_{sp} expression, complexation of lead ions by hydroxide will cause more lead phosphate to dissolve to maintain K_{sp}. Since all soluble forms of lead are toxic, this increase in lead concentration is a potential problem. We can now couple these reactions into our scheme that describes the solubility of lead phosphate in this solution.

$$\begin{array}{ccccc}
Pb_3(PO_4)_2 & \leftrightarrow & 3Pb^{2+} & + & 2PO_4^{3-} \\
 & & \Updownarrow & & \Updownarrow \\
 & & Pb(OH)^+ & & HPO_4^{2-} \\
 & & \Updownarrow & & \Updownarrow \\
 & & Pb(OH)_2 & & H_2PO_4^- \\
 & & \Updownarrow & & \Updownarrow \\
 & & Pb(OH)_3^- & & H_3PO_4
\end{array}$$

This is now quite a complicated set of simultaneous reactions that take place. Our goal in the equilibrium unit of this course will be to develop the facility to handle these types of complicated problems.

Before we get started into this process, there are a couple of other general things to know about chemical equilibrium. Consider the general reaction shown below.

$$aA + bB \Leftrightarrow cC + dD$$

One way of describing equilibrium is to say that the concentrations do not change. The concentrations of the species in this solution represent a macroscopic parameter of the system, and so at the **macroscopic level**, this system is **static**.

Another way of describing equilibrium is to say that for every forward reaction there is a corresponding reverse reaction. This means at the microscopic level that As and Bs are constantly converting to Cs and Ds and vice versa, but that the rate of these two processes are equal. At the **microscopic level**, a system at equilibrium is **dynamic**.

Unless you have taken physical chemistry, I am fairly certain that everything you have learned until this point has taught you that the following expression can be used to describe the equilibrium state of this reaction.

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Well it turns out that this expression is not rigorously correct. Instead of the concentrations of reagents, the actual terms we need in an equilibrium constant expression are the **activities** of the substances. The expression shown below is the correct form of the equilibrium constant, in which a_A represents the activity of substance A.

$$K = \frac{[a_C]^c[a_D]^d}{[a_A]^a[a_B]^b}$$

If you examine the group of As and Bs below, hopefully you can appreciate that the A shown in boldface is "inactive". For that A species to react with a B, another A species must move out of the way.

A B A **A** A B B A

If the correct form of the equilibrium constant expression uses the activities of the chemicals, why have you always been taught to use concentrations? It turns out that in most situations we do not have reliable procedures to accurately calculate the activities of substances. If we did, we would almost certainly use the correct form of the expression. Since we do not know how to evaluate the activities of substances under most circumstances, we do the next best thing and use concentrations as an approximation. This means that all equilibrium calculations are at best approximations (some better than others). In other words, equilibrium calculations usually provide estimations of the situation, but not rigorously correct answers. Because the entire premise is based on an approximation, this will often allow us to make other approximations when we perform equilibrium calculations. These approximations will usually involve ignoring the contributions of minor constituents of the solution.

One last thing we ought to consider is when the approximation of using concentration instead of activity is most valid. Perhaps a way to see this is to consider a solution that has lots of A (the concentration of A is high) and only a small amount of B (the concentration of B is low). Inactivity results if a similar species is in the way of the two reactants getting together. Since the concentration of B is low, there is very little probability that one B would get in the way of another and prevent it from encountering an A. For A, on the other hand, there are so many that they are likely to get in each other's way from being able to encounter a B. **Concentration is a better approximation of activity at low concentrations.** The example I have shown with A and B implies there is no solvent, but this trend holds as well if the substances are dissolved in a solvent. Notice as well that the activity can never be higher than the concentration, but only lower.

How low a concentration do we need to feel fully comfortable in using the approximation of concentrations for activities? A general rule of thumb is if the concentrations are less than 0.01 M then the approximation is quite a good one. Many solutions we will handle this term will have concentrations lower than 0.01 M, but many others will not. We do not need to dwell excessively on this point, but it is worth keeping in the back of one's mind that calculations of solutions with relatively high concentrations are always approximations. We are getting a ballpark figure that lets us know whether a particular process we want to use or study is viable.

IN-CLASS PROBLEM SET #1

Unless specifically told otherwise, whenever a problem lists a concentration, that is the value of material added to solution prior to any reactions occurring to achieve equilibrium. So in the first problem below, 0.155 moles of ammonia were dissolved in 1 liter of solution. The final concentration of ammonia would be something less than 0.155 moles/liter provided some form of equilibration occurred.

1. Calculate the pH of a solution that is 0.155 M in ammonia.

The first step in any equilibrium problem is an assessment of the relevant chemical reactions that occur in the solution. To determine the relevant reactions, one must examine the specie(s) given in the problem and determine which types of reactions might apply. In particular, we want to consider the possibility of acid-base reactions, solubility of sparingly soluble solids, or formation of water-soluble metal complexes.

When given the name of a compound (e.g., ammonia), it is essential that we know or find out the molecular formula for the compound, and often times we have to look this up in a book or table. The molecular formula for ammonia is NH_3. Ammonia can be viewed as the building block for a large family of similar compounds called amines in which one or more of the hydrogen atoms are replaced with other functional groups (a functional group is essentially a cluster of atoms - most of these are carbon-containing clusters). For example, the three compounds below result from replacing the hydrogen atoms of ammonia with methyl (CH_3) groups.

CH_3NH_2	Methyl amine
$(CH_3)_2NH$	Dimethyl amine
$(CH_3)_3N$	Trimethyl amine

Amines and many other organic, nitrogen-containing compounds constitute one of the major families of bases. Ammonia is therefore a base.

Bases undergo a very specific reaction with water to produce the hydroxide ion. The appropriate reaction needed to describe what will happen when ammonia is mixed with water is shown below.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

We can describe this reaction by saying that ammonia reacts with water to produce the ammonium cation and hydroxide anion.

Now that we know the reaction that describes the system, we have to ask what K expression is used to represent that particular reaction. For the reaction of a base, we need an equilibrium constant known as K_b. The expression for K_b is shown below.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

If we examine the tables of equilibrium constants, though, we observe that the table does not list K_b values, but instead only lists K_a values for substances. A species that is in the reaction that we do find a K_a value for in the table is the ammonium cation. It is important to note that the species ammonia and ammonium differ by only a hydrogen ion.

$$NH_3/NH_4^+$$

Species that differ from each other by only a hydrogen ion are said to be a **conjugate pair**. A conjugate pair always contains a base (ammonia in this case) and an acid (ammonium in this case). The acid is always the form with the extra hydrogen ion. The base is the form without the extra hydrogen ion.

The K_a reaction is that of the ammonium ion acting as an acid.

$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$$

The equilibrium constant expression for K_a is shown below.

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Furthermore, the K_b and K_a values for the base and acid form respectively of a conjugate pair have a very specific relationship that is shown below.

$$K_b \times K_a = K_w = 1\times10^{-14}$$

Remember, K_w is the equilibrium expression that describes the autoprotolysis of water.

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

$$K_w = [H_3O^+][OH^-] = 1\times10^{-14}$$

The expression below shows that the result of multiplying K_b times K_a is actually K_w

$$K_b \times K_a = \frac{[NH_4^+][OH^-]}{[NH_3]} \times \frac{[NH_3][H_3O^+]}{[NH_4^+]} = [OH^-][H_3O^+] = K_w$$

Now that the K_b value is known, it is finally possible to solve for the pH of the solution of ammonia. A useful way to keep track of such problems is to use the reaction as the headings for columns of values that describe the concentrations of species under certain conditions. The first set of numbers represents the initial concentrations in solution prior to any equilibration.

	NH_3	+	H_2O	$\Leftrightarrow$	NH_4^+	+	OH^-
Initial	0.155				0		10^{-7}

We do not need an initial value for water since it's the solvent. The hydroxide is given a value of 10^{-7} M because of the autoprotolysis of the water. The second set of numbers are expressions for the equilibrium concentrations of the species. In this case, we want to keep in mind that the value for K_b is small, meaning we do not expect that much product to form.

	NH_3	+	H_2O	$\Leftrightarrow$	NH_4^+	+	OH^-
Initial	0.155				0		10^{-7}
Equilibrium	$0.155 - x$				x		$10^{-7} + x$

If we wanted, these values could now be plugged into the K_b expression and it could be solved using a quadratic. There may be a way to simplify the problem, though, if we keep in mind that K_b is so small. In this case, we expect the value of x to be small and we can make two approximations.

The first is that $x \ll 0.155$ so that $(0.155 - x) = 0.155$

The second is that $x \gg 10^{-7}$ so that $(10^{-7} + x) = x$

	NH_3	+	H_2O	$\Leftrightarrow$	NH_4^+	+	OH^-
Initial	0.155				0		10^{-7}
Equilibrium	$0.155 - x$				x		$10^{-7} + x$
Approximation	0.155				x		x

Now we can plug the approximations in the K_b expression and solve for the value of x.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{0.155} = 1.76\times10^{-5}$$

$$x = [OH^-] = 1.65\times10^{-3}$$

Before we can use this to calculate the concentration of H_3O^+ and solve for pH, we first must check the two approximations to make sure they are both valid.

$$\frac{1.65\times10^{-3}}{0.155} \times 100 = 1.1\% \qquad \frac{10^{-7}}{1.65\times10^{-3}} \times 100 = 0.0061\%$$

It is worth noting that the assumption that the initial hydroxide or hydronium ion can be ignored is almost always made in these problems. The only two instances in which this approximation would break down are if:

1) the acid or base is exceptionally weak so that so little dissociation occurs that the initial amount is significant or

2) the acid or base is so dilute that very little dissociation occurs.

Since both approximations are less than 5%, the concentration of H_3O^+ can be calculated using the K_w expression and the pH can be calculated.

$$[H_3O^+] = 6.31\times10^{-12}$$

$$pH = 11.2$$

NOMENCLATURE

Before continuing on to more problems, it is useful to consider some general rules for the nomenclature of species common to acid-base systems.

The names of species with a positive charge (**cations**) almost always end with an **"ium"** ending.

> NH_3 was ammonia. Its protonated ion (NH_4^+) is called the ammonium ion.
>
> Earlier the species methyl amine (CH_3NH_2) was mentioned. The protonated form of this ($CH_3NH_3^+$) would be the methyl ammonium ion.
>
> When you name the protonated form of a base, the scheme is to remove the last vowel (which is usually an"e") and replace it with "ium".
>
> The protonated form of aniline, a base, would be anilinium.
>
> The elements sodium and calcium are found in nature as the Na^+ and Ca^{2+} ion respectively.
>
> We can therefore state that the protonated form of "wenzel" would be "wenzelium".

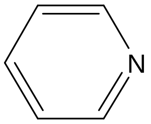
The names of most species with a negative charge (**anions**) end with an **"ate"** ending.

> H_2SO_4 is sulfuric acid, whereas SO_4^{2-} is the sulfate ion.
>
> Butyric acid ($CH_3CH_2CH_2COOH$) has the smell of dirty socks. $CH_3CH_2CH_2COO^-$ is the butyrate ion.
>
> The general rule is to drop the "ic" ending of the name of the acid and replace it with "ate".
>
> When in doubt, if you need the name of the anion, add an "ate" ending. The anion of "wenzel" is therefore "wenzelate".

There are other endings in the nomenclature for **anions** besides the "ate" ending. For example, we are quite familiar with the **"ide"** ending that occurs with the halides (e.g., fluoride, chloride, bromide, and iodide). There are other anions that are named using an **"ite"** ending (e.g., nitrite, sulfite).

2. Calculate the pH of a solution that is 0.147 M in pyridine and 0.189 M in pyridinium chloride.

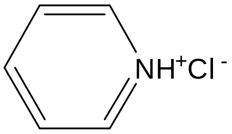
The first step in any equilibrium problem is to determine a reaction that describes the system. This system has appreciable quantities of both pyridine (Py) and pyridinium chloride. The structure of pyridine is shown below and is a base.



As a base it could undergo the following reaction (note that this is the K_b reaction).

$$Py + H_2O \Leftrightarrow PyH^+ + OH^-$$

The structure of pyridinium chloride is shown below. It is important to realize that when added to water, the pyridinium and chloride ions will separate from each other such that the ions will be solvated by water (the pyridinium ion will have the negative oxygen atoms directed toward it, the chloride ion will have the positive hydrogen atoms of the water directed toward it)



We can write potential reactions for both the pyridinium and chloride ions reacting with water as follows.

$$PyH^+ + H_2O \Leftrightarrow Py + H_3O^+$$

Note that this is the K_a reaction for pyridinium. Looking in the table of values shows a pK_a of 5.22. This means that pyridinium is a weak acid.

$$Cl^- + H_2O \Leftrightarrow HCl + OH^-$$

Note that this is the K_b reaction for chloride. Chloride is the conjugate base of hydrochloric acid. Looking up hydrochloric acid in the table shows that hydrochloric acid is a strong acid, meaning that it reacts essentially 100% in water to produce Cl^- and H_3O^+. Because of this, the reaction above of chloride with water to produce HCl and hydroxide ion will not occur and can be ignored.

At this point it seems we have two reactions (the K_b reaction for pyridine producing pyridinium and hydroxide being one, the K_a reaction for pyridinium producing pyridine and hydronium being the other) that describe the system. As a test, lets do the calculation using both possible reactions.

Using pyridine acting as a base ($pK_b = 8.78$, $K_b = 1.66\times10^{-9}$):

	Py + H_2O ↔	PyH^+ +	OH^-
Initial	0.147	0.189	0
Equilibrium	0.147 – x	0.189 + x	x
Approximation	0.147	0.189	x

Note that the initial amount of hydroxide, which is set at 0, assumes that the amount that will be produced is significant compared to 10^{-7} M. Also, the approximations can be attempted since the value of K_b is small.

The approximations can now be plugged into the K_b expression and x evaluated.

$$K_b = \frac{[PyH^+][OH^-]}{[Py]} = \frac{(0.189)(x)}{0.147} = 1.66\times10^{-9}$$

$$x = [OH^-] = 1.29\times10^{-9}$$

However, we must first check the approximation before calculating the pH.

$$\frac{1.29\times10^{-9}}{0.147}\times 100 = 8.77\times10^{-7}\% \qquad \frac{1.29\times10^{-9}}{0.189}\times 100 = 6.83\times10^{-7}\%$$

These approximations are both valid. However, if you consider that we ignored the initial amount of hydroxide present from the autoprotolysis of water (10^{-7} M), this would seem to be in error because of the low level of hydroxide (1.29×10^{-9} M). For the moment, let's just move ahead assuming it was okay to ignore the autoprotolysis of water, and more will be said later about the appropriateness of this decision. The concentration of hydronium ion and pH can be calculated.

$$[H_3O^+] = 7.75\times10^{-6} \qquad pH = 5.11$$

Using pyridinium acting as an acid ($pK_a = 5.22$, $K_a = 6.03\times10^{-6}$):

	PyH^+ + H_2O ↔	Py +	H_3O^+
Initial	0.189	0.147	0
Equilibrium	0.189 – x	0.147 + x	x
Approximation	0.189	0.147	x

The approximations can now be plugged into the K_a expression and x evaluated.

$$K_a = \frac{[Py][H_3O^+]}{[PyH^+]} = \frac{(0.147)(x)}{0.189} = 6.03\times10^{-6}$$

$$x = [H_3O^+] = 7.75\times10^{-6}$$

However, we must first check the approximation before calculating the pH.

$$\frac{7.75\times10^{-6}}{0.147}\times100 = 0.00527\% \qquad \frac{7.75\times10^{-6}}{0.189}\times100 = 0.00410\%$$

In this case, we can also examine whether it was appropriate to ignore the hydronium ion concentration from the autoprotolysis of water.

$$\frac{1.0\times10^{-7}}{7.75\times10^{-6}}\times100 = 1.29\%$$

In this case (unlike with the pyridine acting as a base), ignoring the autoprotolysis of water is appropriate.

Since all of the approximations are valid, we can use the hydronium ion concentration to calculate the pH.

$$[H_3O^+] = 7.75\times10^{-6} \qquad pH = 5.11$$

What is important to realize that we get the same pH (5.11) using either the K_a or K_b equation. These two answers are reassuring but also problematic. The reassuring part is that a solution can only have one pH. If either of the two reactions can be used to describe the system, then both ought to give the same answer for the pH. But one reaction has pyridine acting as a base, another pyridinium acting as an acid. Which one is actually correct? The way to assess that is to examine the relative values of K_a for the conjugate acid and K_b for the conjugate base. In this case, the K_a for the acid is about 1,000 times larger than the K_b for the base. Because of that, a small amount of the acid would dissociate to the base. And note, we did get a pH that was acidic for the answer in each case. But it really does not matter since the amount of change is so small that it can be ignored.

However, there is something very important to realize about this system. **A solution with appreciable concentrations of both members of a conjugate pair is known as a buffer**. Buffers are solutions that resist changes in pH. This resistance is created by having both members of the conjugate pair.

If acid is added, the base component of the conjugate pair reacts to form the conjugate acid.

If base is added, the acid component of the conjugate pair reacts to form the conjugate base.

As long as the concentration of the buffer components are not excessively dilute (on the order of 10^{-6} M or lower), a buffer controls the pH of the system and in buffer solutions we can always ignore the initial concentration of hydronium or hydroxide ion from the autoprotolysis of water. A convenient way to calculate the pH of a buffer is to use what is known as the Henderson-Hasselbalch equation. This equation can be derived from the K_a expression.

K_a expression:

$$K_a = \frac{[Py][H_3O^+]}{[PyH^+]}$$

Take the negative logarithm of both sides:

$$-\log K_a = -\log\left(\frac{[Py][H_3O^+]}{[PyH^+]}\right)$$

Rearrange the right hand side using the properties of logs:

$$-\log K_a = -\log\left(\frac{[Py]}{[PyH^+]}\right) - \log[H_3O^+]$$

Remember that:

$$-\log(K_a) = pK_a$$

$$-\log[H_3O^+] = pH$$

Substituting these in gives:

$$pK_a = -\log\left(\frac{[Py]}{[PyH^+]}\right) + pH$$

Rearranging gives the final form of the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[Py]}{[PyH^+]}\right)$$

If we substitute in the values for this problem (and note, with a buffer we will be able to ignore any redistribution of the appreciable amount of the two species), we get:

$$pH = pK_a + \log\left(\frac{[Py]}{[PyH^+]}\right) = 5.22 + \log\left(\frac{0.147}{0.189}\right) = 5.11$$

This is the same answer we got using either the K_a or K_b expressions.

We can also write two generalized forms of the Henderson-Hasselbalch equation for the two generalized types of weak acid/weak base buffer solutions (the generalized formulas for a weak acid, HA and BH^+).

$$HA + H_2O \leftrightarrow A^- + H_3O^+$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

$$BH^+ + H_2O \leftrightarrow B + H_3O^+$$

$$pH = pK_a + \log\left(\frac{[B]}{[BH^+]}\right)$$

Earlier we said that a buffer is effective at controlling the pH because the acid form of the conjugate pair can neutralize bases and the base form can neutralize acids. Examining the Henderson-Hasselbalch equation also allows us to appreciate from a quantitative sense how buffers are able to control the pH of a solution. If you look at this equation, you notice that the pH is expressed as a constant (pK_a) that then varies by the log of a ratio. One thing to note about log terms is that they change rather slowly. Someone who offers you the log of a million dollars is not being very generous with their money. It takes a very large change in the ratio of the two concentrations to make a large difference in the log term. This large change will only occur when one of the two components of the buffer gets used up by virtue of the acid or base that is being added.

3. Calculate the pH of a solution that is 0.332 M in anilinium iodide.

The anilinium ion is in the table of K_a values and is a weak acid ($pK_a = 4.596$). Anilinium iodide could be formed by the reaction between aniline (the conjugate base of anilinium) and hydrogen iodide, as shown below.

$$\text{An} + \text{HI} \leftrightarrow \text{AnH}^+\text{I}^-$$

In water, anilinium iodide will dissociate to produce the anilinium cation and the iodide anion. What must now be assessed is whether either of these ions will react with water. The two possible reactions that could occur are shown below.

$$\text{AnH}^+ + H_2O \leftrightarrow \text{An} + H_3O^+$$

$$\text{I}^- + H_2O \leftrightarrow \text{HI} + OH^-$$

The anilinium ion is behaving as an acid and since it has a pK_a value in the table (4.596), this reaction will occur. The iodide ion is acting as a base. To see if this reaction occurs, we would need to look up hydroiodic acid (HI) in the table, and see that it is a strong acid. The important feature of strong acids is that, for all practical purposes, strong acids go 100% to completion. This means that HI in water will dissociate 100% to H_3O^+ and I^-. Actually, some amount of undissociated HI must remain, but it is so small that we never need to consider it under normal circumstances in water. Regarding I^- acting as a base, this means that it will all stay as I^- and no HI will form as shown above. We can therefore solve the answer to this problem by only using the reaction of the anilinium ion.

The procedure is rather analogous to what we have already used in problems 1 and 2 above. We ought to write a table for initial values, equilibrium values, and then examine whether any assumptions can be made. If x is the amount of AnH^+ that reacts, there are two important assumptions that can be made in this problem. One is that, because K_a is so small, very little of the AnH^+ reacts so that $0.332 \gg x$. However, enough AnH^+ reacts to produce a much larger concentration of H_3O^+ than was initially in solution such that $x \gg 10^{-7}$ M.

	AnH^+	+	H_2O	$\leftrightarrow$	An	+ H_3O^+
Initial amount	0.332				0	10^{-7}
Equilibrium	$0.332 - x$				x	$x + 10^{-7}$
Assumption	$0.332 \gg x$					$x \gg 10^{-7}$
Approximation	0.332				x	x

These values can now be plugged into the equilibrium constant expression for the reaction.

$$K_a = \frac{[An]\left[H_3O^+\right]}{\left[AnH^+\right]} = \frac{(x)(x)}{0.332} = 2.54\times10^{-5}$$

$$x = [H_3O^+] = 2.9\times10^{-3}$$

$$pH = 2.54$$

Both approximations must now be checked for validity.

$$\frac{2.93\times10^{-3}}{0.332} \times 100 = 0.88\% \qquad \frac{10^{-7}}{2.93\times10^{-3}} \times 100 = 0.0034\ \%$$

Both are okay, so the pH we calculated above is correct.

4. Calculate the pH of a solution that is prepared by mixing 45 ml of 0.224 M 3-chlorobenzoic acid with 30 ml of 0.187 M ethylamine.

Chlorobenzoic acid (Hcba) is a weak acid with a pK_a value of 3.824. Ethylamine is not in the table, but ethylammonium, its conjugate acid, is ($pK_a = 10.63$). Therefore ethylamine (EA) is a weak base ($pK_b = 3.37$). This solution consists of a mixture of a weak acid and a weak base.

What happens when we mix an acid with a base? From prior material we should know that an acid and a base react with each other in what is known as a **neutralization reaction**. The neutralization reaction between chlorobenzoic acid and ethylamine is shown below.

$$\text{Hcba} + \text{EA} \leftrightarrow \text{cba}^- + \text{EAH}^+ \qquad K_n$$

We can calculate initial amounts of Hcba and EA that exist in solution, but some of these will react according to the neutralization reaction. What we need to know is the extent of the neutralization reaction, in other words the value of K for this reaction. There are no tables of K_n values so what we need to do is see if there is a way to come up with the K_n expression by adding up a series of reactions that we do have K values for.

We do have reactions for Hcba and EA that we can look up in the table. These are as follows:

$$\text{Hcba} + H_2O \leftrightarrow \text{cba}^- + H_3O^+ \qquad K_a \text{ of Hcba}$$

$$\text{EA} + H_2O \leftrightarrow \text{EAH}^+ + OH^- \qquad K_b \text{ of EA}$$

Adding these two together produces the following reaction:

$$\text{Hcba} + \text{EA} + 2H_2O \leftrightarrow \text{cba}^- + \text{EAH}^+ + H_3O^+ + OH^- \qquad K = K_a(\text{acid}) \times K_b(\text{base})$$

This almost looks like K_n but it is not exactly the same. The reactant side has two water molecules, and the product side has the hydronium and hydroxide ion. Note that these species do not show up in the neutralization reaction above. As tempting as it might be to say hydronium and hydroxide will react to produce the water molecules (thereby just cancelling these out and ignoring them), they are real species in the reaction that need to be accounted for in the final form of K_n. The way to eliminate these would be to add in the following reaction:

$$H_3O^+ + OH^- \leftrightarrow 2H_2O \qquad K = {}^1/_{K_w}$$

This reaction is the reverse of K_w, a reaction we have seen before. If the direction of a reaction is reversed, its equilibrium constant is just the inverse or reciprocal value, 1/ K_w in this case.

The final expression to calculate the value of K_n then is the following:

$$K_n = \frac{K_a(\text{acid}) \times K_b(\text{base})}{K_w} = K_a(\text{acid}) \times K_b(\text{base}) \times 10^{14}$$

If we evaluate the value of K_n for the reaction in the problem, we get the following value.

$$\begin{array}{ll} pK_a\ (\text{Hcba}) = 3.824 & K_a = 1.5\times10^{-4} \\ pK_b\ (\text{EA}) = 3.37 & K_b = 4.27\times10^{-4} \end{array}$$

$$K_n = (1.5\times10^{-4})(4.27\times10^{-4})(10^{14}) = 6.4\times10^{6}$$

This K_n value of slightly more than six million is very large. That says that this reaction, for all practical purposes, will go to completion.

Before solving this problem, it would be worth a digression to examine more generally what we might expect for the value of K_n. Can we always expect K_n to be large such that neutralization reactions always go to completion? Or are there occasions when K_n might be relatively small such that the reaction will not go to completion?

One thing to keep in mind is a solution with excessively dilute concentrations of an acid or base. For example, suppose the concentrations of the acid and base are on the order of 10^{-10} M. In this case, there is so little acid and base, that even if the K_n value were large, the actual extent of reaction could still be small. It is not that common that we would encounter such solutions in a laboratory setting where we usually use much higher concentrations. But this could occur in environmental samples for some species.

Assuming solutions with appreciable concentrations of acid and base, would we ever have a small value of K_n? Recollecting back, we talked about weak acids as having K_a values on the order of, from strongest to weakest, 10^{-3}, 10^{-5}, 10^{-7}, and 10^{-9}. Similarly weak bases had K_b values from strongest to weakest on the same scale (10^{-3} to 10^{-9}). Remembering the equation for K_n:

$$K_n = K_a \times K_b \times 10^{14}$$

We can see that it will take a mixture of an excessively weak acid and base to get a small value for K_n. For example, mixing an extremely weak acid with a K_a of 10^{-9} with an extremely weak base with a K_b of 10^{-9} will give a K_n of 10^{-4}, a small number. This neutralization reaction would not proceed much at all. If the acid had a K_a value of 10^{-7} and the base a K_b value of 10^{-7}, the value of K_n would be 1, an intermediate value. This neutralization reaction would proceed to some extent.

If we considered a neutralization reaction in which either the acid or base was strong (a strong acid or base might have a K_a or K_b value on the order of 10^{6} or higher), you would need the other species to have a K value of 10^{-20} or lower to get a small value of K_n. Since this is an unreasonably low value for the weak acid or base, any acid-base reaction that involves either a strong acid or a strong base will go to completion.

The first step is to calculate the initial concentrations of Hcba and EA, remembering that mixing the two solutions dilutes each of the species.

$$[\text{Hcba}]\text{: } (0.224\text{ M}) \times \frac{45\text{ ml}}{75\text{ ml}} = 0.1344\text{ M}$$

$$[\text{EA}]\text{: } (0.187\text{ M}) \times \frac{30\text{ ml}}{75\text{ ml}} = 0.0748\text{ M}$$

The next step, since K_n is large, is to allow the reaction to go to completion. This is a one-to-one reaction, so the species with the lower concentration will be used up and limit the amount of product that forms.

	Hcba	+	EA	⇔	cba^-	+	EAH^+
Initial	0.1344		0.0748		0		0
Completion	0.0596		0		0.0748		0.0748

Of course, the amount of EA cannot really be zero, since K_n is a finite value and there needs to be some finite amount of EA. The next step in this problem is to think that some small amount of back reaction occurs.

	Hcba	+	EA	⇔	cba^-	+	EAH^+
Initial	0.1344		0.0748		0		0
Completion	0.0596		0		0.0748		0.0748
Back reaction	$0.0596 + x$		x		$0.0748 - x$		$0.0748 - x$

And we can now consider whether there are any approximations that can be made. Considering that K_n is so large, the extent of back reaction is very small. This means that it is likely that x is very small compared to 0.0596 and 0.0748, such that $0.0596 \gg x$ and $0.0748 \gg x$.

	Hcba	+	EA	⇔	cba^-	+	EAH^+
Initial	0.1344		0.0748		0		0
Completion	0.0596		0		0.0748		0.0748
Back reaction	$0.0596 + x$		x		$0.0748 - x$		$0.0748 - x$
Assumption	$0.0596 \gg x$				$0.0748 \gg x$		$0.0748 \gg x$
Approximation	0.0596		x		0.0748		0.0748

Before we go on, it is worth examining these final concentrations. One interesting thing to note is that we have appreciable quantities of Hcba and cba^-. These two are conjugate pairs, and we know that a solution with appreciable quantities of both members of a conjugate pair represents a buffer. We can therefore use the appropriate Henderson-Hasselbalch equation for chlorobenzoic acid to solve for the pH of this solution.

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{cba}^-]}{[\mathrm{Hcba}]}\right) = 3.824 + \log\left(\frac{0.0748}{0.0596}\right) = 3.92$$

Before assuming that this answer is the correct one, we ought to check our assumptions. Using the K_n expression, we can calculate the value of x.

$$K_n = \frac{[\mathrm{cba}^-][\mathrm{EAH}^+]}{[\mathrm{Hcba}][\mathrm{EA}]} = \frac{(0.0748)(0.0748)}{(0.0596)(x)} = 6.4\times10^6$$

$$x = 1.46\times10^{-8}$$

This number is very small and obviously less than 5% of 0.0596 and 0.0748. If we assume that 1.46×10^{-8} is the final value of EA after back reaction, and that 0.0748 is the final value of EAH^+, we have final values for both members of a conjugate pair. If we substitute these into the Henderson-Hasselbalch equation of ethylammonium we ought to get the same pH as above. (Note, the EA and EAH^+ are not a buffer since the amount of EA is not appreciable. But if you know the concentration of both members of a conjugate pair, you can still use the Henderson-Hasselbalch equation to solve for the pH, since it is just a rearrangement of the K_a expression.)

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{EA}]}{[\mathrm{EAH}^+]}\right) = 10.63 + \log\left(\frac{1.46\times10^{-8}}{0.0748}\right) = 3.92$$

It should not be a surprise that the two values are identical.

5. **Calculate the pH of a solution that is prepared by mixing 75 ml of 0.088 M aniline with 50 ml of 0.097 M 2-nitrophenol.**

From the table, we can determine that aniline (An) is a base and nitrophenol (HNp) is an acid. This solution consists of a mixture of an acid and a base, so the first thing we must consider is that a neutralization reaction takes place. In this case we also note that aniline is a very weak base ($K_b = 3.94\times10^{-10}$) and nitrophenol is a very weak acid ($K_a = 5.83\times10^{-8}$). The value of K_n is calculated below.

$$K_n = K_a \times K_b \times 10^{14} = (5.83\times10^{-8})(3.94\times10^{-10})(10^{14}) = 2.3\times10^{-3}$$

This value is fairly small, so we cannot assume that this neutralization reaction will go to completion. Instead we anticipate that this reaction will go to a small extent. Since it goes to only a small extent, we can try making the assumption that x is small compared to the initial concentrations of the aniline ($0.0528 \gg x$) and nitrophenol ($0.0388 \gg x$).

	An	+	HNp	⇔	AnH^+	+	Np^-
Initial	0.0528		0.0388		0		0
Equilibrium	0.0528 – x		0.0388 – x		x		x
Assumption	$0.0528 \gg x$		$0.0388 \gg x$				
Approximation	0.0528		0.0388		x		x

These values can be plugged into the K_n expression to solve for x:

$$K_n = \frac{[AnH^+][Np^-]}{[An][HNp]} = \frac{(x)(x)}{(0.0528)(0.0388)} = 2.3\times10^{-3}$$

$$x = 2.17\times10^{-3}$$

Now we could solve the two Henderson-Hasselbalch equations for each of the conjugate pairs, since we know the concentrations of both members of each pair.

$$pH = pK_a + \log\left(\frac{[An]}{[AnH^+]}\right) = 4.596 + \log\left(\frac{0.0528}{0.00217}\right) = 5.98$$

$$pH = pK_a + \log\left(\frac{[Np^-]}{[HNp]}\right) = 7.234 + \log\left(\frac{0.00217}{0.0388}\right) = 5.98$$

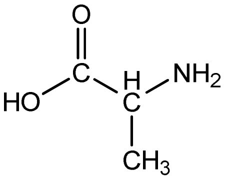
The two identical values suggest that the pH of the solution will be 5.98. It is interesting to check the assumptions that were used in calculating the values.

$$\frac{0.00217}{0.0388} \times 100 = 5.6\% \qquad \frac{0.00217}{0.0528} \times 100 = 4.1\%$$

One does meet the 5% rule, the other is just a little over. This might suggest that solving a quadratic is in order, however, if you solve the quadratic and substitute in the values, you will still get a pH of 5.98.

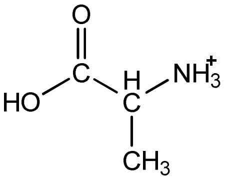
AMINO ACIDS

It is worth highlighting the acid-base properties of amino acids, since these are so important in biochemistry. The structure of the amino acid alanine, as you would typically see if written, is shown below.



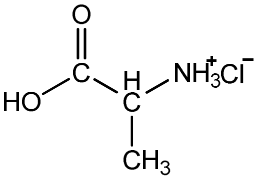
alanine

If you look in our chart of pKa values, you would find that two values are given for alanine (pK_{a1} = 2.34; pK_{a2} = 9.69), which might surprise you at first. As you look at the structure, remember that the -COOH group is an acid, but also that an amine group (NH_2) is a base. There are two pK_a values because we can protonate the amine group, as shown below.



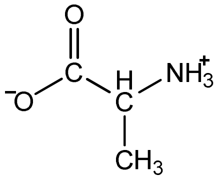
alaninium ion

Usually the protonated form is prepared by reaction with hydrogen chloride, so instead of referring to the alaninium ion, we would call it alanine hydrochloride.



alanine hydrochloride

One last thing to consider about the neutral amino acid. If we have a substance that has an acid (-COOH) and base ($-NH_2$) within the same molecule, we could ask whether this could undergo an internal acid-base neutralization reaction (realize that we would have many of these molecules in solution so we could also view the acid and base functionalities of different alanine molecules neutralizing each other). It turns out that this actually occurs with amino acids in water, leading to an alanine species with two charges that is called a **zwitterion**.



alanine (zwitterion notation)

Note that the zwitterion still has a net neutral charge, so we do not need to distinguish whether its written form is neutral or zwitterionic in equilibrium calculations.

IN-CLASS PROBLEM SET # 2

1. Starting with 30 ml of a solution that is 0.1 M in butylamine, calculate the original pH, and then the pH as 5 ml increments of 0.1 M hydrochloric acid are added. Continue the series of calculations until 40 ml of acid have been added. Plot the data (pH on the y axis, volume of added acid on the x).

Has 99.9% of the butylamine been titrated at the equivalence point?

Butylamine is a base ($K_b = 3.98\times10^{-4}$). Hydrochloric acid is a strong acid, so it will convert the butylamine into the butylammonium ion by a neutralization reaction. Remember, the K_n of a neutralization reaction will always be large if one of the species is strong.

Calculating the initial pH of a weak base is something we have done before.

	BNH_2 + H_2O	⇔ BNH_3^+	+ OH^-
Initial	0.1	0	0
Equilibrium	0.1 – x	x	x
Approximation	0.1	x	x

$$K_b = \frac{[BNH_3^+][OH^-]}{[BNH_2]} = \frac{(x)(x)}{0.1} = 3.98\times10^{-4}$$

$$x = [OH^-] = 6.31\times10^{-3}$$

If we check the approximation:

$$\frac{6.31\times10^{-3}}{0.1}\times 100 = 6.31\%$$

It’s not quite valid, but we’ll still use this value. Solving the quadratic would only lead to a small change in the initial value, and this is close enough for our purposes now.

$$pOH = 2.2$$

$$pH = 11.8$$

First thing we ought to ask is whether we think this is a reasonable number. Remembering that it is a base, a pH of 11.8 is basic, so that seems good.

Now we can examine the first 5 ml increment of hydrochloric acid that's added. Remember that the HCl (shown as H_3O^+ in the reaction below since all of it is dissociated in water) will convert butylamine to butylammonium as shown below.

$$BNH_2 + H_3O^+ \leftrightarrow BNH_3^+ + H_2O$$

There is something else important to consider about this reaction. If we start with 30 ml of 0.1 M butylamine, that corresponds to 0.0030 moles. If we add 5 ml of 0.1 M hydrochloric acid, that corresponds to 0.0005 moles. The amounts of these initial reagents before and after the reaction are listed below

	BNH_2	+	H_3O^+	↔	BNH_3^+	+	H_2O
Initial	0.0030 mol		0.0005 mol		0		
After neutralization	0.0025 mol		0		0.0005 mol		

There is something very interesting to note about this solution. There are appreciable amounts of butylamine and butylammonium in the final solution. These two are a conjugate pair, so this solution is a buffer. We can solve for the pH of this solution by using the Henderson-Hasselbalch equation for butylamine.

But there is also something else that is interesting about this when you try to solve for the pH using the Henderson-Hasselbalch equation. If we examine the form of the Henderson-Hasselbalch equation, we note that the final term consists of the ratio of the concentrations of the two components of the buffer. Remember that we started with 30 ml of butylamine and added 5 ml of hydrochloric acid. This causes the final solution to have a volume of 35 ml. If we write out the terms in the equation as shown:

$$pH = pK_a + \log\left(\frac{[BNH_2]}{[BNH_3^+]}\right) = 10.6 + \log\left(\frac{0.0025\text{ mol}/\cancel{35\text{ ml}}}{0.0005\text{ mol}/\cancel{35\text{ ml}}}\right) = 11.3$$

What you note is that the two volume terms in the concentration ratio cancel each other out. In other words, the pH of a buffer solution can be calculated either by determining the ratio of the concentrations of the two components, or by determining the ratio of the moles of the two components.

There is another very important outcome of this. The pH of a buffer does not change if the solution is diluted. In other words, suppose we just added 5 ml of water to the above solution. The final volume would now be 40 ml, but the moles of each component would still be 0.0025 and 0.0005. The pH would remain the same because the volumes cancel. Now, does this hold under all circumstances? At some point if we diluted the solution too much, we may start to promote a significant redistribution of the two species in the buffer and this observation would break down. But generally, we find that the pH of a buffer solution stays fixed under dilution with water.

Before we go on to the next increment of hydrochloric acid, let's consider one other aspect of this initial addition of 5 ml of acid. If we reconsider the initial solution, we found that x, which was the concentration of BNH_3^+, was 6.31×10^{-3} M. If we calculate the moles of that we find out that it is:

$$[BNH_3^+] = (6.31\times10^{-3}\ \text{mol/L})(0.030\ \text{L}) = 0.0002\ \text{moles}$$

We could write these as the approximate amounts in the initial solution at equilibrium.

$$\begin{array}{lllllll} BNH_2 & + & H_2O & \leftrightarrow & BNH_3^+ & + & OH^- \\ 0.0028\ \text{mol} & & & & 0.0002\ \text{mol} & & 0.0002\ \text{mol} \end{array}$$

When we thought about adding the first 0.0005 moles of acid, we thought of it converting butylamine to butylammonium. Does that mean we should have removed 0.0005 moles of the 0.0028 moles that are listed under the reaction above? If so, that would alter the pH we got after the first addition. NO IT DOESN'T. We have to remember that 0.0002 moles of hydroxide are produced by this initial reaction. Hydroxide is a strong base and the first 0.0002 moles of hydrochloric acid will react with the hydroxide ion. The remaining 0.0003 moles of the acid will then start reacting with the butylamine.

The best way to proceed through the other increments of added hydrochloric acid is to construct a chart of the species in solution. This is shown in Table 1 with the first two pH values included.

Table 1. Moles of butylamine and butylammonium in the titration of butyl amine (0.1 M, 30 ml) with hydrochloric acid (0.1 M).

Step #	Added HCl (ml)	BNH_2 (moles)	BNH_3^+ (moles)	pH
1	0	0.0030	0	11.8
2	5	0.0025	0.0005	11.3
3	10	0.0020	0.0010	
4	15	0.0015	0.0015	
5	20	0.0010	0.0020	
6	25	0.0005	0.0025	
7	30	0	0.0030	
8	35	0	0.0030	
9	40	0	0.0030	

Examine the table and consider steps 3 through 6 (10 to 25 ml of acid added). In each of these cases, we have an appreciable amount of each of the two components of the conjugate pair and each of these solutions is a buffer. That means we can use the Henderson-Hasselbalch equation to solve for the pH. It is also sufficient to use the mole ratio of the two and not worry about the dilution of the molar concentrations that would occur.

10 ml: $$\text{pH} = 10.6 + \log\left(\frac{0.0020\ \text{mol}}{0.0010\ \text{mol}}\right) = 10.9$$

15 ml: $$\mathrm{pH} = 10.6 + \log\left(\frac{0.0015\ \mathrm{mol}}{0.0015\ \mathrm{mol}}\right) = 10.6$$

Note an important point about this one. Here we have equal concentrations, or equal moles of the two components of the buffer, and the log of 1 is 0. At the point at which the concentrations of both members of the conjugate pair are equal, the pH of a buffer equals the pK_a.

20 ml: $$\mathrm{pH} = 10.6 + \log\left(\frac{0.0010\ \mathrm{mol}}{0.0020\ \mathrm{mol}}\right) = 10.3$$

25 mL: $$\mathrm{pH} = 10.6 + \log\left(\frac{0.0005\ \mathrm{mol}}{0.0025\ \mathrm{mol}}\right) = 9.9$$

The situation at 30 mL of acid deserves some attention. First note, that this is called the equivalence point. The equivalence point is the point in a titration where the moles of titrant (hydrochloric acid) that have been added exactly equal the moles of analyte (butylamine) that were in the initial solution. It might be tempting to think that, since there are equal moles of acid and base, that the pH of a solution at the equivalence point of an acid-base titration must be 7. Let's examine the solution that we have at the equivalence point of this titration.

To a first approximation, all of the butylamine has been used up and converted to butylammonium ion. This is the equivalent to saying what would be the pH of a solution prepared by adding some amount of butylammonium to water. If we think about the nature of butylammonium, we realize that it is a weak acid. So the solution at the equivalence point of this titration is a solution of a weak acid. If that's the case, the pH at the equivalence point ought to be slightly acidic. Also note, that at this point we now have to account for the effects of dilution since we no longer have appreciable amounts of both members of the conjugate pair (we have 0.0030 moles of BNH_3^+ in a total volume of 60 ml or 0.060 L).

$$(0.0030\ \mathrm{mol}/0.060\ \mathrm{L}) = 0.050\ \mathrm{M}$$

	BNH_3^+	+	H_2O	⇔	BNH_2	+	H_3O^+
Initial	0.05				0		0
Equilibrium	0.05 – x				x		x
Approximation	0.05				x		x

$$K_a = \frac{[BNH_2][H_3O^+]}{[BNH_3^+]} = \frac{(x)(x)}{0.05} = 2.51\times10^{-11}$$

$$x = [H_3O^+] = 1.12\times10^{-6}$$

$$\mathrm{pH} = 5.9$$

Checking the approximation shows that it is valid.

$$\frac{1.12\times 10^{-6}}{0.05}\times 100 = 0.00224\%$$

Note that the pH at this point, the equivalence point, is slightly acidic, just as we would expect for a solution of a weak acid. However, one other thing to note is that the true initial value of H_3O^+ at the equivalence point (10^{-7} M) is more than 5% of the final concentration of H_3O^+ (1.12×10^{-6}). So if we wanted to be rigorously correct, we would need to account for that in determining the true pH at the equivalence point.

If we now consider the solution where 35 ml of acid have been added, we note that the butylamine/butylammonium system is used up and no more changes can occur here. Instead, what we now have is an excess of strong acid. So this solution consists of a mixture of a weak acid (butylammonium) with some strong acid (hydrochloric). It should seem reasonable that the extra strong acid will be the critical part in determining the pH of the solution. Remember that every mole of HCl will be converted to H_3O^+.

5 ml of extra acid adds 0.0005 moles of H_3O^+.

$$(0.0005 \text{ mol}/0.065 \text{ L}) = 7.69\times 10^{-3} \text{ M} \quad [H_3O^+]$$

$$\text{pH} = 2.1$$

And for 40 ml: 10 ml of extra acid adds 0.0010 moles of H_3O^+.

$$(0.0010 \text{ mol}/0.070 \text{ L}) = 1.4\times 10^{-2} \text{ M} = [H_3O^+]$$

$$\text{pH} = 1.8$$

It's worthwhile at this point to compile a complete table (Table 2) of this process and examine some of the general trends that occur.

Table 2. Calculated pH values for the titration of butyl amine (0.1 M, 30 ml) with hydrochlorid acid (0.1 M).

Step #	Added HCl (ml)	BNH_2 (moles)	BNH_3^+ (moles)	pH
1	0 ml	0.0030	0	11.8
2	5	0.0025	0.0005	11.3
3	10	0.0020	0.0010	10.9
4	15	0.0015	0.0015	10.6
5	20	0.0010	0.0020	10.3
6	25	0.0005	0.0025	9.9
7	30	0	0.0030	5.9
8	35	0	0.0030	2.1
9	40	0	0.0030	1.8

First, note the large drop in pH between 25 and 30 ml of added acid. At this point we have exhausted the buffer and so it should not be surprising that a small amount of extra acid causes a large drop in pH. Also note, that the pH of 0.1 M hydrochloric acid is 1.0, so that the pH would slowly approach a limit of 1.0 if we continued to add more acid to the solution.

It is also worth examining a plot of the pH during the course of the titration as shown in Figure 1. The relatively flat portion of the plot between 5 ml and 25 ml of acid is known as the buffer region. Notice how the center of the buffer region corresponds to the pK_a value. So the butylammonium/butylamine system would be a useful buffer at a pH of around 10.6.

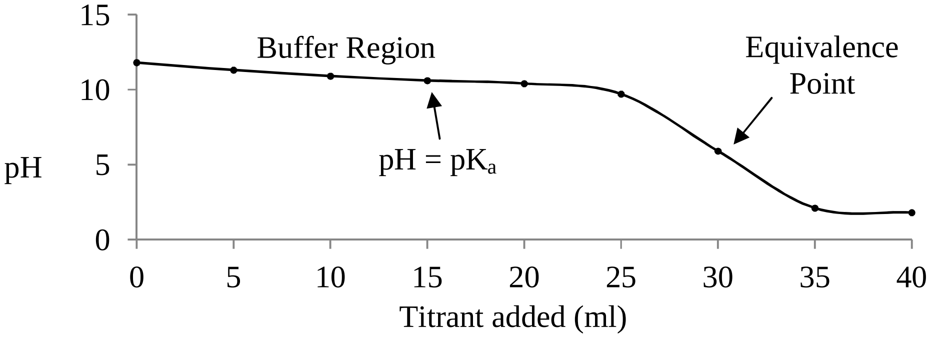


Figure 1. Plot of pH versus ml titrant for titration of butylamine (0.1 M, 30 ml) with hydrochloric acid (0.1 M).

Suppose we had used an identical situation (30 ml of 0.1 M base, add 5 ml increments of HCl) but had a base whose conjugate acid had a pK_a of 8. What would that plot look like? The plot is shown in Figure 2 and compared to what we observed with butylamine. Note how the initial pH would be a little less basic, how the buffer region is now centered around 8, how the equivalence point still occurs at 30 ml of acid, but how the pH at the equivalence point is a little more acidic because the weak acid is a little stronger than the butylammonium ion. If we then showed a plot for a species where the acid form had a pK_a of 6, we start to note that it becomes more difficult to distinguish the equivalence point in the plot. A concentration of a species like butylamine can be analyzed using an acid-base titration. The concentration of a base whose conjugate acid has a pK_a value of 6 could not be analyzed using an acid-base titration.

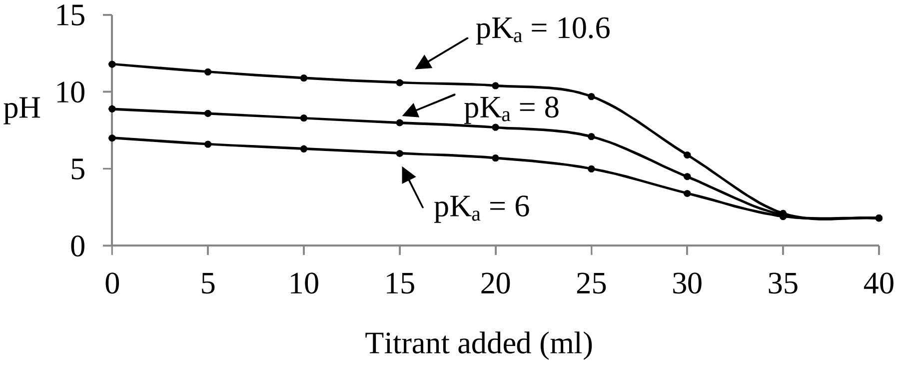


Figure 2. Plot of pH versus ml titrant for the titration of weak bases (0.1 M, 30 mL, pKa values of 6, 8 and 10.6) with hydrochloric acid (0.1 M).

We can also talk about the qualities that define a "good" buffer. The term that is used here is **buffer capacity** (a measure of how much acid or base a buffer can neutralize without an appreciable change in pH), and we want a high buffer capacity.

Presumably there is a particular pH that you want to buffer your solution at. The first criteria is to select a buffer that has a pK_a close to the pH that you want to buffer at. The "official standard" is that the pK_a of the acid must be within +/– one unit of the pH you want to buffer at, but the closer the better. Note from the Henderson-Hasselbalch equation that one unit of change from pK_a would correspond to either a 1/10 or 10/1 ratio of the two members of the conjugate pair. If you look at the plots above, note that ratios of 1/10 or 10/1 are out on the extreme end of the buffer region. At these extremes, there is a lot of buffer capacity in one direction, but almost none in the other. It would be risky to use such a solution as a buffer and much better to use a species with a pK_a much closer to the pH you need to buffer at.

The second criterion is to have a high concentration of both components of the conjugate pair so that the buffer will neutralize more acid or base. A good buffer therefore is one in which both components of the conjugate pair are highly soluble in water. So buffers usually have high concentrations of species relative to the other species you are studying in solution. The actual concentration of components you use for a buffer depend on the nature of your investigation. In biochemistry, where the concentrations of proteins and nucleic acids are usually quite low, the concentrations of buffer components are relatively low. In chemical analysis procedures where the concentrations of reagents might be fairly high, the concentration of buffer needs to be high as well.

The last criteria in selecting a buffer is to ensure that the buffer components do not interfere in any way with the process being studied. For example, if you want to determine the amount of a substance in solution by measuring its absorption of light, it's essential that the buffer not absorb at that wavelength. If your procedure involves the formation of a metal complex, it's essential that the components of the buffer do not complex with the metal ion.

The criteria used in selecting a buffer can be summarized as follows:

1. The buffer substance needs a pK_a value as close as possible to the desired pH.
2. The buffer components must have high solubility.
3. The buffer components cannot interfere in any way with the other species in solution or the measurement you want to make.

Now, there is one other component to the question that we have not addressed yet. The question asks whether 99.9% of the butylamine has been titrated at the equivalence point (in other words, has 99.9% of the butylamine been converted to butylammonium). This is an important question in analysis procedures. If we used this titration to determine the concentration of butylamine in the solution, the assumption is that "all" of the butylamine has been converted to butylammonium so that we are getting an accurate measurement. Of course, we can never convert all of the butylamine, since the K values are finite and so there must always be a little bit of butylamine in the solution, but if we can convert at least 99.9%, that's a high enough degree of accuracy for most purposes. The way we assess this is to compare the concentrations of the two species at the equivalence point. Going back to our pH calculation at 30 ml of acid, we have the following values:

$$[BNH_2] = 1.12\times10^{-6}\ M$$

$$[BNH_3^+] = 0.05\ M$$

Admittedly, the BNH_3^+ is a little less than 0.05 M, but the approximation we made when solving the problem can still be used. If we evaluate the ratio of BNH_2 to BNH_3^+, as shown below, we find that 0.002% is BNH_2 and 99.998% is BNH_3^+ at the equivalence point. That says that this titration procedure would be an effective way to analyze the concentration of butylamine in the initial solution.

$$\frac{1.12\times10^{-6}}{0.05}\times 100 = 0.00224\%$$

IN-CLASS SET #3

1. Calculate the pH of a 0.127 M solution of ascorbic acid (H_2asc).

This is a new situation that we have not encountered before, since ascorbic acid (which is vitamin C by the way) has two dissociable hydrogen ions. We can find this out by looking in the table and seeing that two pK_a values (4.30 and 11.82) are provided. The relevant reactions needed to describe what happens in a solution of ascorbic acid in water are shown below.

$$H_2asc + H_2O \Leftrightarrow Hasc^- + H_3O^+ \qquad K_{a1}$$

$$Hasc^- + H_2O \Leftrightarrow asc^{2-} + H_3O^+ \qquad K_{a2}$$

The problem we have is that there are two reactions that can cause production of H_3O^+. Remember that there is a small amount of H_3O^+ in solution to begin with (10^{-7} M from the dissociation of water), but like in other problems of weak acids, we can assume that the H_3O^+ produced by the dissociation of ascorbic acid will be much larger than the amount there from the dissociation of water.

The first step in understanding how to do this problem is to write an expression for H_3O^+ in terms of the other species that are produced when the ascorbic acid dissociates. In other words, we ought to be able to write an expression that equates the concentration of H_3O^+ to the concentrations of $Hasc^-$ and asc^{2-}.

First consider the $Hasc^-$ species. If we look at the first reaction above, it should be apparent that one H_3O^+ occurs for each $Hasc^-$ found in solution. If this was the only reaction that took place in solution, we could therefore write:

$$[H_3O^+] = [Hasc^-]$$

Next consider the asc^{2-} species. One way to think about this is to envision a situation in which all of the ascorbic acid dissociated into the asc^{2-} form. Under this situation, we could write the following reaction to describe this process.

$$H_2asc = asc^{2-} + 2\ H_3O^+$$

The important thing to note here is that two H_3O^+ occur for each asc^{2-} found in solution. Similarly, if only a small amount of asc^{2-} is found in solution, as would occur in this solution of ascorbic acid given the pK_a values, it would still be the case that two H_3O^+ ions must occur for each asc^{2-} species found in solution.

$$[H_3O^+] = 2[asc^{2-}]$$

Note, there are two H_3O^+ for every asc^{2-}. Substitute a "1" in for asc^{2-} in the equation above and you will get "2" for the H_3O^+.

We can combine these two into one equation that describes the total concentration of H_3O^+ in a solution of ascorbic acid as follows:

$$[H_3O^+] = [Hasc^-] + 2[asc^{2-}]$$

What this means is that for each $Hasc^-$ in solution we have one H_3O^+, and for each asc^{2-} in solution, we have two corresponding H_3O^+ ions.

The next critical step is to consider the relative magnitudes of these two terms. If we examine the two pK_a values for the ascorbic acid reactions, and convert them to K_a values, note that the second reaction has a K_a value that is about 10^7 times smaller than the first. This means that the extent of the second reaction is minimal compared to that of the first. In other words, the amount of H_3O^+ formed by the second reaction is insignificant compared to how much H_3O^+ is produced by the first. This means that:

$$[Hasc^-] \gg 2[asc^{2-}]$$

and we can use the following approximation to describe this solution:

$$[H_3O^+] = [Hasc^-]$$

In other words, we only need to consider the first reaction to determine the pH of a solution of ascorbic acid. Even though this looked initially like it might be a complicated system, if we only need to consider the first reaction, solving this problem is identical to what we have done earlier when solving for the pH of a solution of a monoprotic acid. This raises the question of whether we can always simplify such a problem down to only one reaction. The answer depends in part on the relative magnitudes of the two pK_a values. If these two differed by two units ($pK_{a1} = 3$, $pK_{a2} = 5$), this represents a 100-fold difference in the extent of reaction and we can ignore the second reaction. If you were to examine the typical pK_a values in the table for polyprotic acids, you would notice that the relative values would almost always allow you to treat this comparable to a monoprotic system. Only in a few instances when the two pK_a values are almost identical would you need to treat this in a more complex manner by including both reactions in the problem.

What we will find in general with polyprotic acid/base systems is that we can almost always find one reaction that is significant and ignore the other reactions in the series. As we examine more problems of this variety, we will see how this will apply to other situations.

Now we can solve for the pH of this solution. Note, that there are two important assumptions. Because K_{a1} is small, the value of x is small compared to the starting concentration of H_2asc ($0.0127 \gg x$). Also, since H_2asc is a weak acid, the amount of H_3O^+ produced by dissociation of the acid will be much larger than the starting concentration of H_3O^+ that exists due to the autoprotolysis of water ($x \gg 10^{-7}$)

	H_2asc	+	H_2O	⇔	$Hasc^-$	+	H_3O^+
Initial	0.127				0		10^{-7}
Equilibrium	$0.127 - x$				x		x
Assumption	$0.127 \gg x$						$x \gg 10^{-7}$
Approximation	0.127				x		x

$$K_{a1} = \frac{[Hasc^-][H_3O^+]}{[H_2asc]} = \frac{(x)(x)}{0.127} = 5.0\times10^{-5}$$

$$x = [H_3O^+] = 2.52\times10^{-3}$$

$$pH = 2.6$$

Checking the approximation shows that this is valid.

$$\frac{2.52\times10^{-3}}{0.127} \times 100 = 1.98\%$$

As one final check that it was reasonable to ignore the second reaction, we can plug in the values of $[Hasc^-]$ and $[H_3O^+]$ calculated above into the K_{a2} expression. That leads to an interesting finding as seen below that $[asc^{2-}]$ equals K_{a2}. Note how small this is, and therefore how little extra H_3O^+ would come from the second reaction. Ignoring this reaction in the calculation of pH was a valid thing to do.

$$K_{a2} = \frac{[asc^{2-}][H_3O^+]}{[Hasc^-]} = \frac{[asc^{2-}](2.52\times10^{-3})}{(2.52\times10^{-3})} = 1.51\times10^{-12}$$

$$[asc^{2-}] = 1.51\times10^{-12}$$

2. Calculate the pH of a 0.089 M solution of sodium carbonate.

The carbonate ion is part of the carbonic acid system. If we look up carbonic acid in the table, we find that it is a diprotic acid. The two equilibria are as follows. Also, looking at the two pK_a values (6.35 and 10.33) we notice that there is an appreciable difference between the two, suggesting that it may well be necessary to consider one of the two reactions in this problem.

$$H_2CO_3 + H_2O \leftrightarrow HCO_3^- + H_3O^+ \qquad K_{a1}$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \qquad K_{a2}$$

Before continuing, we need to know whether sodium carbonate refers to $NaHCO_3$ or Na_2CO_3. We will adopt a particular system in this course for naming these types of species, but in this case note that sodium carbonate refers to Na_2CO_3. The HCO_3^- ion is known as the bicarbonate ion and the species $NaHCO_3$ is known as sodium bicarbonate (also known as baking soda). The name bicarbonate for HCO_3^- is not a systematic name, but a common name for this ion.

The naming system we will adopt can be demonstrated for the phosphoric acid (H_3PO_4) series of reactions. Phosphoric acid has three dissociable hydrogen ions, leading to the following possible species.

H_3PO_4 – phosphoric acid
NaH_2PO_4 – sodium dihydrogen phosphate
Na_2HPO_4 – disodium hydrogen phosphate
Na_3PO_4 – sodium phosphate

Note that the species sodium phosphate refers to the one in which all the dissociable hydrogen ions have been replaced with sodium cations. The others contain a prefix that tells you how many hydrogen atoms or sodium ions are involved in the salt. You must be careful when using or purchasing species like the intermediate ones since the names given above may not be used. Sometimes these are referred to as sodium phosphate monobasic and sodium phosphate dibasic. Presumably the label actually gives the formula so that you can be certain which species you actually have.

If we go back to our solution of sodium carbonate, this means that we have the CO_3^{2-} species in solution. Remember, if you add sodium carbonate to water, the ions will dissociate to produce sodium ions and carbonate ions. Since the sodium ion is the cation of a strong base (sodium hydroxide – NaOH), this species won't form and the sodium ion is what we call a **spectator ion** (it effectively watches things but does not get involved in any important reactions). Since the carbonate ion is the anion of a weak acid, it's actually a base and we can write the following reactions to describe what will occur in this solution.

$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^- \qquad K_b \text{ of } K_{a2}$$

$$HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^- \qquad K_b \text{ of } K_{a1}$$

Because of the significant distinction between the two K_b values, we only need to consider the first reaction in the series above to calculate the pH. The amount of hydroxide produced by the second reaction will be insignificant.

We can then treat this as a monobasic base, a process we have seen before.

	CO_3^{2-}	+	H_2O	$\leftrightarrow$	HCO_3^-	+	OH^-
Initial	0.089				0		0
Equilibrium	0.089 – x				x		x
Approximation	0.089				x		x

Plugging this into the appropriate K_b expression gives:

$$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{(x)(x)}{0.089} = 2.14\times10^{-4}$$

$$x = [OH^-] = 4.36\times10^{-3}$$

$$pOH = 2.37$$

$$pH = 11.63$$

The pH value of 11.63 seems reasonable since this is a solution of a base. Checking the approximation shows that this was just under our 5% rule.

$$\frac{4.36\times10^{-3}}{0.089}\times 100 = 4.9\%$$

3. Calculate the pH of a solution prepared by adding 30 ml of 0.1 M hydrochloric acid to 60 ml of 0.080 M potassium malonate.

The first key to solving this problem is to identify the nature of potassium malonate. If we look in the table we will find the species malonic acid (H_2mal), a diprotic acid. Potassium malonate is therefore the species K_2mal. When you add this to water, you would get two potassium cations and the malonate ion (mal^{2-}). Since potassium is the cation of a strong base (potassium hydroxide – KOH), it does not react in any way and is a spectator ion.

$$H_2mal + H_2O \leftrightarrow Hmal^- + H_3O^+ \qquad K_{a1} = 1.40\times10^{-3}$$

$$Hmal^- + H_2O \leftrightarrow mal^{2-} + H_3O^+ \qquad K_{a2} = 2.01\times10^{-6}$$

So the malonate ion is a base. We have added hydrochloric acid, a strong acid to the solution. The hydrochloric acid will therefore undergo a neutralization reaction with the malonate ion to produce $Hmal^-$. If it turns out that all the mal^{2-} gets used up in producing $Hmal^-$ and there is still an excess of hydrochloric acid, the additional hydrochloric acid will then convert $Hmal^-$ to H_2mal. Remember, a strong acid will always lead to the neutralization of a base. $Hmal^-$ can act as a base and accept another hydrogen ion to product H_2mal.

Next we need to calculate the moles of mal^{2-} and hydrochloric acid that we have in solution.

Moles of mal^{2-}: (0.08 mol/L)(0.060 L) = 0.0048 moles

Moles of HCl: (0.10 mol/L)(0.030 L) = 0.0030 moles

The reaction that describes what will occur is as follows:

	mal^{2-}	+ H_3O^+	$\leftrightarrow$ $Hmal^-$
Initial	0.0048 mol	0.0030 mol	0
Neutralization	0.0018 mol	0	0.0030 mol

Note that there are appreciable amounts of both members of a conjugate pair, which constitutes a buffer. The only remaining question is whether we need to consider the other reaction that can occur for the $Hmal^-$.

$$Hmal^- + H_2O \leftrightarrow H_2mal + OH^-$$

It turns out that just like the case of ascorbic acid or sodium carbonate, there is so much distinction between the K values for the two reactions that we can ignore the second one and only consider the $mal^{2-}/Hmal^-$ reaction in determining the pH. Since we have a buffer, we can now use the appropriate Henderson-Hasselbalch expression for K_{a2}.

$$pH = pK_{a2} + \log\left(\frac{[mal^{2-}]}{[Hmal^-]}\right) = 5.696 + \log\left(\frac{0.0018}{0.0030}\right) = 5.47$$

If you go ahead and substitute the amount of $Hmal^-$ and OH^- into the K_{a1} expression, as shown below, you see that the amount of H_2mal that forms is insignificant compared to the $Hmal^-$ concentration and can be ignored.

$$[Hmal^-] = (0.0030\ mol/0.090\ L) = 0.0333\ M$$

$$[H_3O^+] = 3.39\times10^{-6}$$

$$K_{a1} = \frac{[Hmal^-][H_3O^+]}{[H_2mal]} = \frac{(0.0333)(3.39\times10^{-6})}{[H_2mal]} = 1.40\times10^{-3}$$

$$[H_2mal] = 8.06\times10^{-5}$$

4. Calculate the pH of a solution prepared by adding 55 ml of 0.098 M sodium phosphate to 65 ml of 0.136 M phosphoric acid.

Phosphoric acid	– H_3PO_4
Sodium phosphate	– Na_3PO_4 (which dissociates to PO_4^{3-})

Both of these species are in the phosphoric acid system shown below. The two species in appreciable quantities are shown in boldface.

$$\mathbf{H_3PO_4} + H_2O \Leftrightarrow H_2PO_4^- + H_3O^+ \qquad K_{a1}$$

$$H_2PO_4^- + H_2O \Leftrightarrow HPO_4^{2-} + H_3O^+ \qquad K_{a2}$$

$$HPO_4^{2-} + H_2O \Leftrightarrow \mathbf{PO_4^{3-}} + H_3O^+ \qquad K_{a3}$$

What we need to realize here is that H_3PO_4 is an acid, and PO_4^{3-} is a base. As such they will react with each other according to the following neutralization reaction.

$$H_3PO_4 + PO_4^{3-} \Leftrightarrow H_2PO_4^- + HPO_4^{2-}$$

If we use the K_a for H_3PO_4 (7.11×10^{-3}) and the K_b for PO_4^{3-} (2.4×10^{-2}) and solve for K_n using our established equation ($K_n = (K_a\times K_b)/K_w$) we get a value of 1.7×10^{10}, a very large number. This neutralization will go to completion.

We can also take this a step further. In almost all cases for a multistep equilibria system such as this, we can anticipate that only one reaction of the series will be important in determining the pH. This does not happen in every situation (a little later in the course we will see an example where this does not rigorously work), but it does most of the time. One expectation is that eventually we will wind up with appreciable amounts of both members of a conjugate pair, which constitutes a buffer. The most straight forward way of working with this problem is to consider the moles of different chemicals that are present.

Moles of phosphate:	(0.098 mol/L)(0.055 L) = 0.00539 moles
Moles of phosphoric acid:	(0.136 mol/L)(0.065 L) = 0.00884 moles

	H_3PO_4	+	PO_4^{3-}	$\Leftrightarrow$	$H_2PO_4^-$	+	HPO_4^{2-}
Initial	0.00884		0.00539		0		0
Neutralization	0.00345		0		0.00539		0.00539

As seen by the data, all of the phosphate ion (PO_4^{3-}) has been used up in the solution. At this point, which is still an intermediate one, it can be helpful to put in boldface the three species that are present in appreciable quantities in the solution.

$$\mathbf{H_3PO_4} + H_2O \leftrightarrow \mathbf{H_2PO_4^-} + H_3O^+ \qquad K_{a1}$$

$$\mathbf{H_2PO_4^-} + H_2O \leftrightarrow \mathbf{HPO_4^{2-}} + H_3O^+ \qquad K_{a2}$$

$$HPO_4^{2-} + H_2O \leftrightarrow PO_4^{3-} + H_3O^+ \qquad K_{a3}$$

What we now need to examine is the possibility for neutralization between H_3PO_4 and HPO_4^{2-}. Note that the product consists of two equivalents of the species $H_2PO_4^-$.

$$H_3PO_4 + HPO_4^{2-} \leftrightarrow 2H_2PO_4^-$$

Evaluation of the K_n for this reaction involves the K_a value of H_3PO_4 (7.11×10^{-3}) and the K_b value for HPO_4^{2-} (K_b of $K_{a2} = 1.578\times10^{-7}$). Using our established equation for evaluating K_n, we get a value of 1.12×10^{5}, which is a large number. This neutralization will essentially go to completion.

We can now assess the moles of material produced in the reaction.

	H_3PO_4 +	HPO_4^{2-} ↔	$2H_2PO_4^-$
Initial	0.00345	0.00539	0.00539
Neutralization	0	0.00194	0.01229

Be careful when calculating the amount of $H_2PO_4^-$ in the final solution. There is an amount already present (0.00539 moles) and we produce two equivalents in the reaction above (2 × 0.00345 moles), hence the total of 0.01229 moles of $H_2PO_4^-$.

Once again, it is helpful to boldface the species in the series of reactions that are present in appreciable quantities.

$$H_3PO_4 + H_2O \leftrightarrow H_2PO_4^- + H_3O^+ \qquad K_{a1}$$

$$\mathbf{H_2PO_4^-} + H_2O \leftrightarrow \mathbf{HPO_4^{2-}} + H_3O^+ \qquad K_{a2}$$

$$HPO_4^{2-} + H_2O \leftrightarrow PO_4^{3-} + H_3O^+ \qquad K_{a3}$$

Note that we now have appreciable quantities of a conjugate pair. Since the distribution of the species in a conjugate pair will not change (these two cannot neutralize each other since they will simply reform each other), we can now calculate the pH using the appropriate Henderson-Hasselbalch equation.

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}\right) = 7.198 + \log\left(\frac{0.00194}{0.01229}\right) = 6.4$$

It might be useful to check and make sure that ignoring the other two reactions was a reasonable thing to do.

We can calculate the concentration of H_3PO_4 using the expression for K_n. We first need to convert the moles of the different species to molarity for the subsequent calculations.

$$[H_2PO_4^-] = \frac{0.01229\text{ mol}}{0.120\text{ L}} = 0.102\text{ M}$$

$$[HPO_4^{2-}] = \frac{0.00194\text{ mol}}{0.120\text{ L}} = 0.016\text{ M}$$

$$K_n = \frac{[H_2PO_4^-]^2}{[H_3PO_4][HPO_4^{2-}]} = \frac{(0.102)^2}{(x)(0.016)} = 1.12\times10^5$$

$$x = [H_3PO_4] = 5.8\times10^{-6}$$

This is a very small quantity of H_3PO_4, so ignoring the K_{a1} reaction was justified. We can calculate the amount of PO_4^{3-} using K_{a3}.

$$K_{a3} = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]} = \frac{(x)(3.98\times10^{-7})}{(0.016)} = 4.17\times10^{-13}$$

$$x = [PO_4^{3-}] = 1.68\times10^{-8}$$

Once again, we see that this is an exceptionally small quantity that can be ignored. As has been the pattern so far, in problems involving polyprotic acids or bases, we see that only one reaction is significant in determining the pH of the solution. This situation will occur in almost all cases for these reactions. The approach to these problems is to identify the important reaction and solve for the pH using only that one, then use the values that are obtained to check that we could ignore the other ones. Of course, if the pK_a values for the reactions are appreciably different (value of 10 or greater), we would know ahead of time that only one reaction will be important.

5. Calculate the pH of a 0.240 M solution of sodium bicarbonate ($NaHCO_3$).

This will dissociate to produce the HCO_3^- ion, which is in the carbonic acid system.

$$H_2CO_3 + H_2O \Leftrightarrow HCO_3^- + H_3O^+ \qquad K_{a1}$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+ \qquad K_{a2}$$

What we observe in this case is that the HCO_3^- is an intermediate and we essentially have "all" of an intermediate. Some small amount of H_2CO_3 and CO_3^{2-} will form, since the two equilibrium constants have finite values, but not enough of either one will form to constitute a buffer. The bicarbonate ion has the ability to react as an acid (reaction 2) or a base (reaction 1), and it might be tempting to determine whether it's a stronger acid or base (by comparing the relative magnitude of K_{a2} to the K_b of K_{a1}) and use that reaction to calculate the pH. The situation is complicated by the fact that any H_2CO_3 and CO_3^{2-} that are formed can neutralize each other.

What we need to do in this case is write an expression for $[H_3O^+]$ in terms of species in the carbonate system. Remember, there is some H_3O^+ around from dissociation of water, however, this value will be overcome by the carbonate system and can be ignored in this calculation.

We need to realize that we have a lot of HCO_3^- in solution and consider what each of the reactions above does to the concentration of H_3O^+ in solution. At the start, before the system equilibrates, there is no H_2CO_3 or CO_3^{2-}.

If we look at the second reaction (K_{a2}), we see that for every CO_3^{2-} that is produced we need to produce one equivalent of H_3O^+. If this was the only reaction that occurred, it would allow us to write the following expression:

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

If we look at the first reaction (K_{a1}), we see that in order to produce a molecule of H_2CO_3, we actually need to remove an H_3O^+ species. Therefore, every H_2CO_3 that we find in the final solution subtracts an H_3O^+. This would allow us to write:

$$[H_3O^+] = -[H_2CO_3]$$

Both CO_3^{2-} and H_2CO_3 will be present in the final solution, so we can combine these two equations and come up with the following expression for the concentration of H_3O^+ in the final solution:

$$[H_3O^+] = [CO_3^{2-}] - [H_2CO_3]$$

Now we need to do some algebra. First, rearrange the above expression into the following:

$$[H_3O^+] + [H_2CO_3] = [CO_3^{2-}] \qquad (1)$$

Now rearrange the K_{a1} and K_{a2} expressions to solve them for $[H_2CO_3]$ and $[CO_3^{2-}]$ respectively.

$$K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} \qquad [H_2CO_3] = \frac{[HCO_3^-][H_3O^+]}{K_{a1}} \tag{2}$$

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} \qquad [CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H_3O^+]} \tag{3}$$

Substitute the expressions for $[H_2CO_3]$ and $[CO_3^{2-}]$ into equation (1).

$$[H_3O^+] + \frac{[HCO_3^-][H_3O^+]}{K_{a1}} = \frac{K_{a2}[HCO_3^-]}{[H_3O^+]} \tag{4}$$

Multiply each side through by $K_{a1}[H_3O^+]$ to remove all terms from the denominator.

$$K_{a1}[H_3O^+]^2 + [HCO_3^-][H_3O^+]^2 = K_{a1}K_{a2}[HCO_3^-] \tag{5}$$

Pull out an $[H_3O^+]^2$ term from the left-hand side of the equation.

$$[H_3O^+]^2(K_{a1} + [HCO_3^-]) = K_{a1}K_{a2}[HCO_3^-] \tag{6}$$

Divide both sides by $(K_{a1} + [HCO_3^-])$ to give the following:

$$[H_3O^+]^2 = \frac{K_{a1}K_{a2}[HCO_3^-]}{K_{a1} + [HCO_3^-]} \tag{7}$$

Now comes a critical assessment of the terms in the denominator, as we want to compare the magnitude of K_{a1} to $[HCO_3^-]$. Usually, we would anticipate that K_{a1} is a fairly small number since this is a weak acid. For example, in the current problem, K_{a1} is 4.47×10^{-7}. Usually the concentration of the intermediate (HCO_3^- in this case) is fairly high (0.240 M in this case). In many situations the concentration of the intermediate is a lot larger than the K_a value.

$$[HCO_3^-] \gg K_{a1}$$

In this case, we can ignore the K_{a1} in the term $(K_{a1} + [HCO_3^-])$. That simplifies equation (7) to the following:

$$[H_3O^+]^2 = \frac{K_{a1}K_{a2}[HCO_3^-]}{[HCO_3^-]} \tag{8}$$

Notice how the $[HCO_3^-]$ terms now cancel out of the equation leaving:

$$[H_3O^+]^2 = K_{a1}\,K_{a2} \tag{9}$$

Using the properties of logs, this expression can be rewritten as follows:

$$\mathrm{pH} = \frac{\mathrm{p}K_{a1} + \mathrm{p}K_{a2}}{2} \qquad (10)$$

There is a certain way in which this outcome seems to make sense. We stated at the onset that one of the problems was that the bicarbonate ion could act as an acid and a base. The $\mathrm{p}K_{a1}$ value represents bicarbonate acting as a base, and $\mathrm{p}K_{a2}$ represents bicarbonate acting as an acid. This equation essentially represents an average of these two values. That average will also reflect whether the intermediate is more likely to act as an acid or base, as the pH of the final solution will either be acidic or basic depending on the magnitudes of the two $\mathrm{p}K_a$ values. One other wonderful aspect of the pH of this solution is that it is independent of the concentration of bicarbonate. Of course, we need to remember that we made an approximation to come up with this simple form to get the pH. At very dilute concentrations of intermediate, that approximation breaks down and then the calculation becomes more complicated. We would need to use equation (7) in that case.

In this case, we can now substitute in the two $\mathrm{p}K_a$ values for the carbonic acid system and determine the pH:

$$\mathrm{pH} = \frac{\mathrm{p}K_{a1} + \mathrm{p}K_{a2}}{2} = \frac{6.35 + 10.33}{2} = 8.34$$

The value of 8.34 is slightly basic. Perhaps it is not surprising then that we could use a solution of sodium bicarbonate as an antacid if a night of pizzas, tacos, jalapeno poppers, and tequila sunrises (including the worm at the bottom of the bottle) left our stomach with excess acid.

It turns out that the generalized expression we derived in this case, in which the pH was equal to (pK_{a1} + pK_{a2})/2, can be applied to any intermediate in a polyprotic acid system. For example, consider the series of equations for phosphoric acid.

$$H_3PO_4 + H_2O \Leftrightarrow H_2PO_4^- + H_3O^+ \qquad K_{a1}$$

$$H_2PO_4^- + H_2O \Leftrightarrow HPO_4^{2-} + H_3O^+ \qquad K_{a2}$$

$$HPO_4^{2-} + H_2O \Leftrightarrow PO_4^{3-} + H_3O^+ \qquad K_{a3}$$

Suppose we had a solution that to a first approximation was “all” sodium dihydrogen phosphate (NaH_2PO_4). This would dissolve to produce $H_2PO_4^-$, the first intermediate in this series of reactions. We can ignore the third reaction because it will be insignificant. We can perform a derivation analogous to what we did for bicarbonate and would come up with the following expression for the pH:

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

Suppose instead we had a solution that to a first approximation was “all” disodium hydrogen phosphate (Na_2HPO_4). This would dissolve to produce HPO_4^{2-}, the second intermediate in this series of reactions. In this case, we can ignore the first reaction and, doing a derivation analogous to what we did for bicarbonate, we would come up with the following expression for the pH:

$$pH = \frac{pK_{a2} + pK_{a3}}{2}$$

Something to note in this case is that if we examined the comparable equation to equation (7), it would look as follows:

$$[H_3O^+]^2 = \frac{K_{a2}K_{a3}[HPO_4^{2-}]}{K_{a2} + [HPO_4^{2-}]}$$

Note that in this case, we are comparing the magnitude of [HPO_4^{2-}] to K_{a2}. Since K_{a2} is always smaller than K_{a1} (and usually much smaller), the likelihood that we can ignore the magnitude of K_{a2} relative to the concentration of [HPO_4^{2-}] is improved, allowing us to use this very straight forward way of calculating the pH.

OUT OF CLASS ASSIGNMENT #4, PROBLEM 2

Starting with 30 ml of 0.1 M citric acid, calculate the initial pH and the pH at each 5 ml increment of 0.1 M NaOH until you are 10 ml past the last equivalence point. Plot the data and determine whether 99.9% of the citric acid has been neutralized at the last equivalence point. Also calculate the concentration of all species in solution at the second equivalence point.

It is worth examining this problem in some detail since we have not done anything exactly like it in class. Essentially it consists of the titration of a polyprotic acid using a strong base. Citric acid is a common buffer but is an interesting example because the first two pK_a values are fairly close to each other.

If we look in the table we find out that citric acid (H_3cit) is a triprotic acid. The following three equilibrium reactions define the system.

$$H_3cit + H_2O \Leftrightarrow H_2cit^- + H_3O^+ \qquad K_{a1} = 7.45\times10^{-4}$$

$$H_2cit^{2-} + H_2O \Leftrightarrow Hcit^{2-} + H_3O^+ \qquad K_{a2} = 1.73\times10^{-5}$$

$$Hcit^- + H_2O \Leftrightarrow cit^{3-} + H_3O^+ \qquad K_{a3} = 4.02\times10^{-7}$$

Even though the first two K_a values are fairly close to each other, we can still use only the K_{a1} expression to solve for the initial pH.

	H_3cit	+	H_2O	$\Leftrightarrow$	H_2cit^-	+	H_3O^+	K_{a1}
Initial	0.1				0		0	
Equilibrium	0.1 – x				x		x	
Approximation	0.1				x		x	

$$K_{a1} = \frac{[H_2cit^-][H_3O^+]}{[H_3cit]} = \frac{(x)(x)}{0.1} = 7.45\times10^{-4}$$

$x = [H_3O^+] = 0.00863$ pH = 2.06

If we check the approximation, it actually turns out that the value is too high and that we should have used a quadratic if we wanted the exact answer. But the value of 2.06 will suffice for now.

The next step is to consider what happens when we start adding sodium hydroxide to the solution. This will convert H_3cit into the other forms, and we can start the process by assuming it will occur in a stepwise manner (in other words, H_3cit will be converted into H_2cit^- by the base until all the H_3cit is used up, then H_2cit^- will be converted into $Hcit^{2-}$, etc.). This would allow us to construct the chart shown in Table 3 of the moles of each species that would occur over the course of the titration.

Table 3. Moles of each species in the titration of citric acid (0.1 M, 30 ml) with NaOH (0.1M).

ml NaOH	H_3cit	H_2cit^-	$Hcit^{2-}$	cit^{3-}	pH
0	0.0030 mol	0	0	0	2.06
5	0.0025	0.0005	0	0	
10	0.0020	0.0010	0	0	
15	0.0015	0.0015	0	0	
20	0.0010	0.0020	0	0	
25	0.0005	0.0025	0	0	
30	0	0.0030	0	0	
35	0	0.0025	0.0005	0	
40	0	0.0020	0.0010	0	
45	0	0.0015	0.0015	0	
50	0	0.0010	0.0020	0	
55	0	0.0005	0.0025	0	
60	0	0	0.0030	0	
65	0	0	0.0025	0.0005	
70	0	0	0.0020	0.0010	
75	0	0	0.0015	0.0015	
80	0	0	0.0010	0.0020	
85	0	0	0.0005	0.0025	
90	0	0	0	0.0030	
95	0	0	0	0.0030	
100	0	0	0	0.0030	

If we examine the increments from 5 ml to 25 ml, we see that we have appreciable quantities of H_3cit and H_2cit^-, which are both members of a conjugate pair. This region is a buffer solution and the pH can be determined using K_{a1}.

5 ml: $$pH = pK_{a1} + \log\left(\frac{[H_2cit^-]}{[H_3cit]}\right) = 3.128 + \log\left(\frac{0.0005\text{ mol}}{0.0025\text{ mol}}\right) = 2.43$$

10 ml: $$pH = pK_{a1} + \log\left(\frac{[H_2cit^-]}{[H_3cit]}\right) = 3.128 + \log\left(\frac{0.0010\text{ mol}}{0.0020\text{ mol}}\right) = 2.83$$

15 ml: $$pH = pK_{a1} + \log\left(\frac{[H_2cit^-]}{[H_3cit]}\right) = 3.128 + \log\left(\frac{0.0015\text{ mol}}{0.0015\text{ mol}}\right) = 3.128$$

Note that the pH at this increment is pK_{a1}.

20 ml: $$pH = pK_{a1} + \log\left(\frac{[H_2cit^-]}{[H_3cit]}\right) = 3.128 + \log\left(\frac{0.0020\text{ mol}}{0.0010\text{ mol}}\right) = 3.43$$

25 ml: $$pH = pK_{a1} + \log\left(\frac{[H_2cit^-]}{[H_3cit]}\right) = 3.128 + \log\left(\frac{0.0025\text{ mol}}{0.0005\text{ mol}}\right) = 3.83$$

30 ml: This is the first equivalence point, since we have converted all of the H_3cit to H_2cit^-. At this point we have “all” of the first intermediate (H_2cit^-) and can calculate the pH using the expression ($pK_1 + pK_2$)/2

$$\mathrm{pH} = \frac{\mathrm{pK_{a1}} + \mathrm{pK_{a2}}}{2} = \frac{3.128 + 4.761}{2} = 3.94$$

If we examine the region from 35 to 55 ml, we have appreciable quantities of H_2cit^- and $Hcit^{2-}$, a buffer solution based on K_{a2}.

35 ml: $$\mathrm{pH} = \mathrm{pK_{a2}} + \log\left(\frac{[\mathrm{Hcit^{2-}}]}{[\mathrm{H_2cit^-}]}\right) = 4.761 + \log\left(\frac{0.0005\ \mathrm{mol}}{0.0025\ \mathrm{mol}}\right) = 4.06$$

40 ml: $$\mathrm{pH} = \mathrm{pK_{a2}} + \log\left(\frac{[\mathrm{Hcit^{2-}}]}{[\mathrm{H_2cit^-}]}\right) = 4.761 + \log\left(\frac{0.0010\ \mathrm{mol}}{0.0020\ \mathrm{mol}}\right) = 4.46$$

45 ml: $$\mathrm{pH} = \mathrm{pK_{a2}} + \log\left(\frac{[\mathrm{Hcit^{2-}}]}{[\mathrm{H_2cit^-}]}\right) = 4.761 + \log\left(\frac{0.0015\ \mathrm{mol}}{0.0015\ \mathrm{mol}}\right) = 4.761$$

Note that at this point, the pH is equal to pK_{a2}.

50 ml: $$\mathrm{pH} = \mathrm{pK_{a2}} + \log\left(\frac{[\mathrm{Hcit^{2-}}]}{[\mathrm{H_2cit^-}]}\right) = 4.761 + \log\left(\frac{0.0020\ \mathrm{mol}}{0.0010\ \mathrm{mol}}\right) = 5.06$$

55 ml: $$\mathrm{pH} = \mathrm{pK_{a2}} + \log\left(\frac{[\mathrm{Hcit^{2-}}]}{[\mathrm{H_2cit^-}]}\right) = 4.761 + \log\left(\frac{0.0025\ \mathrm{mol}}{0.0005\ \mathrm{mol}}\right) = 5.46$$

60 ml: This is the second equivalence point, since we have converted all of the H_2cit^- to $Hcit^{2-}$. At this point we have “all” of the second intermediate ($Hcit^{2-}$) and can calculate the pH using the expression ($pK_2 + pK_3$)/2

$$\mathrm{pH} = \frac{\mathrm{pK_{a2}} + \mathrm{pK_{a3}}}{2} = \frac{4.761 + 6.396}{2} = 5.58$$

If we examine the region from 65 to 85 ml, we have appreciable quantities of $Hcit^{2-}$ and cit^{3-}, a buffer solution based on K_{a3}.

65 ml: $$\mathrm{pH} = \mathrm{pK_{a3}} + \log\left(\frac{[\mathrm{cit^{3-}}]}{[\mathrm{Hcit^{2-}}]}\right) = 6.396 + \log\left(\frac{0.0005\ \mathrm{mol}}{0.0025\ \mathrm{mol}}\right) = 5.70$$

70 ml: $$\mathrm{pH} = \mathrm{pK_{a3}} + \log\left(\frac{[\mathrm{cit^{3-}}]}{[\mathrm{Hcit^{2-}}]}\right) = 6.396 + \log\left(\frac{0.0010\ \mathrm{mol}}{0.0020\ \mathrm{mol}}\right) = 6.09$$

75 ml: $$pH = pK_{a3} + \log\left(\frac{[cit^{3-}]}{[Hcit^{2-}]}\right) = 6.396 + \log\left(\frac{0.0015\ mol}{0.0015\ mol}\right) = 6.396$$

Note that at this point, the pH is equal to pK_{a3}.

80 ml: $$pH = pK_{a3} + \log\left(\frac{[cit^{3-}]}{[Hcit^{2-}]}\right) = 6.396 + \log\left(\frac{0.0020\ mol}{0.0010\ mol}\right) = 6.70$$

85 ml: $$pH = pK_{a3} + \log\left(\frac{[cit^{3-}]}{[Hcit^{2-}]}\right) = 6.396 + \log\left(\frac{0.0025\ mol}{0.0005\ mol}\right) = 7.09$$

90 ml: This is the third equivalence point, since we have converted all of the $Hcit^{2-}$ to cit^{3-}. To a first approximation we only have cit^{3-} in solution. This is a polybasic base, but as we have done before, we only need to consider the first reaction in the series to calculate the pH. The relevant reaction, which is the K_b value of K_{a3}, is shown below.

$$cit^{3-} + H_2O = Hcit^{2-} + OH^- \qquad K_b \text{ of } K_{a3} = 2.5\times10^{-8}$$

We need to calculate the concentration of cit^{3-} that is present in solution, recognizing that the titrant caused a dilution of the initial concentration of citric acid (30 ml of initial solution and 90 ml of additional titrant).

Molarity of citrate = (0.0030 mol/0.120 L) = 0.025 M

	cit^{3-}	+	H_2O	⇔	$Hcit^{2-}$	+	OH^-
Initial	0.025				0		0
Equilibrium	0.025 – x				x		x
Approximation	0.025				x		x

$$K_{b3} = \frac{[Hcit^{2-}][OH^-]}{[cit^{3-}]} = \frac{(x)(x)}{0.025} = 2.5\times10^{-8}$$

$$x = [OH^-] = 2.5\times10^{-5}$$

$$pOH = 4.6 \qquad pH = 9.4$$

Checking the approximation shows that it was valid in this case. Note that the pH at this equivalence point is basic, which is not surprising since cit^{3-} is a base.

$$\frac{2.5\times10^{-5}}{0.025}\times 100 = 0.1\%$$

95 ml: In this case we have a mixture of a strong base (NaOH) with a weaker base (citrate). The extra amount of strong base (5 ml or 0.0005 moles) will determine the pH.

$$[OH^-] = \frac{0.0005\text{ mol}}{0.125\text{ L}} = 4.0\times10^{-3}$$

$$pOH = 2.4 \qquad pH = 11.6$$

100 ml: Once again, the pH is determined by the amount of extra strong base present in the solution (10 ml or 0.0010 moles).

$$[OH^-] = \frac{0.0010\text{ mol}}{0.130\text{ L}} = 7.7\times10^{-3}$$

$$pOH = 2.1 \qquad pH = 11.9$$

We can now compile an entire chart (Table 4) of the changes that occur over this titration:

Table 4. Calculated pH values for the titration of citric acid (0.1 M, 30 mL) with NaOH (0.1 M).

ml NaOH	H_3cit	H_2cit$^-$	Hcit^{2-}	cit^{3-}	pH	
0	0.0030 m	0	0	0	2.06	
5	0.0025	0.0005	0	0	2.43	
10	0.0020	0.0010	0	0	2.83	
15	0.0015	0.0015	0	0	3.128	(pK_{a1})
20	0.0010	0.0020	0	0	3.43	
25	0.0005	0.0025	0	0	3.83	
30	0	0.0030	0	0	3.94	($pK_{a1}+pK_{a2}$)/2
35	0	0.0025	0.0005	0	4.06	
40	0	0.0020	0.0010	0	4.46	
45	0	0.0015	0.0015	0	4.761	(pK_{a2})
50	0	0.0010	0.0020	0	5.06	
55	0	0.0005	0.0025	0	5.46	
60	0	0	0.0030	0	5.58	($pK_{a2}+pK_{a3}$)/2
65	0	0	0.0025	0.0005	5.70	
70	0	0	0.0020	0.0010	6.09	
75	0	0	0.0015	0.0015	6.396	(pK_{a3})
80	0	0	0.0010	0.0020	6.70	
85	0	0	0.0005	0.0025	7.09	
90	0	0	0	0.0030	9.40	
95	0	0	0	0.0030	11.60	
100	0	0	0	0.0030	11.90	

It is especially helpful to plot these values versus the ml of titrant as shown in Figure 3.

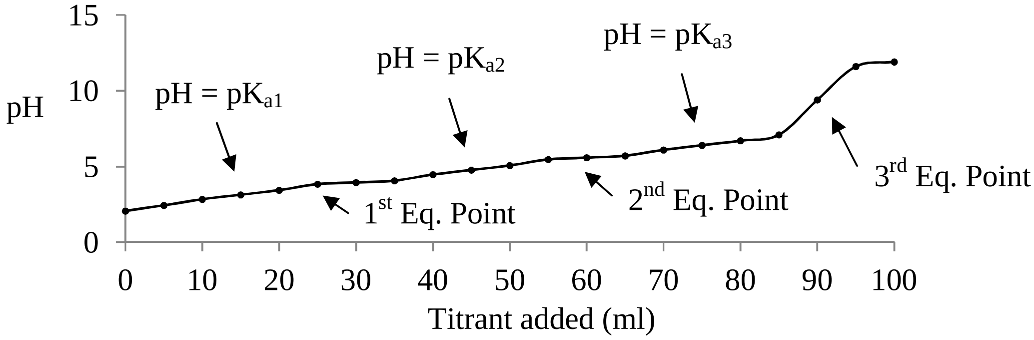


Figure 3. pH versus ml titrant for the titration of citric acid (0.1 M, 30 mL) with NaOH (0.1 M).

There are several things worth noting in this plot. One is the way that the first two equivalence points blend together and there are no clear breaks in the plot. The only equivalence point in this titration that is readily observable is the third. The other is to note that citric acid has a significant buffer region that stretches from a pH of about 2.5 to 5.5. Citric acid is commonly used as a buffer for this pH region.

It is also worth examining what would be observed for a similar plot of a different triprotic acid. The data in Table 5 is for an identical titration of phosphoric acid.

Table 5. pH values for the titration of phosphoric acid (0.1 M, 30 ml) with NaOH (0.1 M).

ml NaOH	H_3PO_4				pH	
0	0.0030 mol	0	0	0	-	
5	0.0025	0.0005	0	0	1.45	
10	0.0020	0.0010	0	0	1.85	
15	0.0015	0.0015	0	0	2.148	(pK_{a1})
20	0.0010	0.0020	0	0	2.45	
25	0.0005	0.0025	0	0	2.85	
30	0	0.0030	0	0	4.673	($pK_{a1}+pK_{a2}$)/2
35	0	0.0025	0.0005	0	6.50	
40	0	0.0020	0.0010	0	6.90	
45	0	0.0015	0.0015	0	7.198	(pK_{a2})
50	0	0.0010	0.0020	0	7.50	
55	0	0.0005	0.0025	0	7.90	
60	0	0	0.0030	0	9.789	($pK_{a2}+pK_{a3}$)/2
65	0	0	0.0025	0.0005	11.68	
70	0	0	0.0020	0.0010	12.08	
75	0	0	0.0015	0.0015	12.38	(pK_{a3})
80	0	0	0.0010	0.0020	12.68	
85	0	0	0.0005	0.0025	-	
90	0	0	0	0.0030	-	
95	0	0	0	0.0030	11.60	
100	0	0	0	0.0030	11.90	

It is worth realizing that a few data points have been omitted since there is a problem at the beginning and again at about 75 ml of titrant. In the early part, the acid is strong enough that a fairly significant proportion dissociates. At the latter part of the titration, the base is so strong that we really do not convert all of the HPO_4^{2-} to PO_4^{3-} as implied. Even with this problem, we can examine a generalized plot for the titration of phosphoric acid with sodium hydroxide (Figure 4).

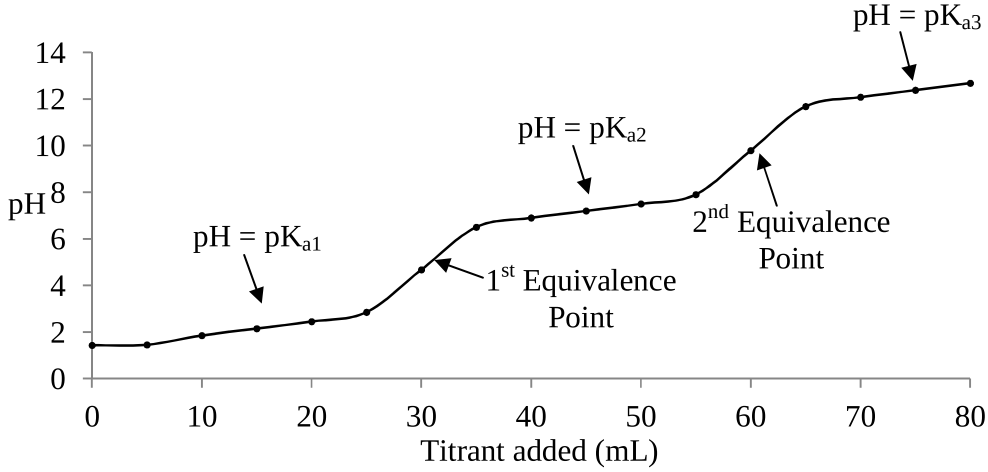


Figure 4. pH versus ml titrant for the titration of phosphoric acid (0.1 M, 30 mL) with NaOH (0.1 M).

Note here that the first two equivalence points are obvious, whereas the third equivalence point will not be distinguishable because of the very high pK_{a3} value. The concentration of citric or phosphoric acid can be determined through a titration with sodium hydroxide, provided you realize which equivalence points can be successfully monitored during the titration.

Now we can examine the last two parts of the homework problem. The first is whether 99.9% of the species is in the form cit^{3-} at the third equivalence point. Going back to the calculation at 90 ml of titrant, we determined that $[cit^{3-}]$ was 0.025 M and $[Hcit^{2-}]$ was 2.5 10^{-5} M.

$$\frac{2.5 \times 10^{-5}}{0.025} \times 100 = 0.1\%$$

If 0.1% is in the form $Hcit^{2-}$, then 99.9% is in the form cit^{3-} and it just makes it.

The other part of the problem was to calculate the concentration of all species in solution at the second equivalence point. The first thing we ought to do is compile a list of what all the species are so we know what we have to calculate. In doing this, we can ignore any spectator ions such as sodium. That means there are six species whose concentration we need to calculate.

H_3cit $\quad$ H_2cit^- $\quad$ $Hcit^{2-}$ $\quad$ cit^{3-} $\quad$ H_3O^+

Since we already calculated the pH of this solution (5.58), we can readily calculate the concentration of H_3O^+ and OH^-.

$$[H_3O^+] = 2.63\times10^{-6}$$

$$[OH^-] = 3.80\times10^{-9}$$

We also said that to a first approximation it was “all” $Hcit^{2-}$ (0.0030 mol). With 30 ml of initial solution and 60 ml of titrant, we have a total volume of 90 ml.

$$[Hcit^{2-}] = 0.0030 \text{ mol}/0.090 \text{ L} = 0.033 \text{ M}$$

Since we now have $[H_3O^+]$ and $[Hcit^{2-}]$, we can use the appropriate K_a expressions to calculate the three other citrate species.

Use the K_{a3} expression to calculate $[cit^{3-}]$:

$$K_{a3} = \frac{[cit^{3-}][H_3O^+]}{[Hcit^{2-}]} = \frac{[cit^{3-}](2.63\times10^{-6})}{0.033} = 4.02\times10^{-7}$$

$$[cit^{3-}] = 0.005 \text{ M}$$

Use the K_{a2} expression to calculate $[H_2cit^-]$:

$$K_{a2} = \frac{[Hcit^{2-}][H_3O^+]}{[H_2cit^{2-}]} = \frac{(0.033)(2.63\times10^{-6})}{[Hcit^{2-}]} = 1.733\times10^{-5}$$

$$[H_2cit^-] = 0.005 \text{ M}$$

Using the value of H_2cit^- that was just calculated, we can substitute this into the K_{a1} expression and calculate the concentration of H_3cit.

$$K_{a1} = \frac{[H_2cit^{2-}][H_3O^+]}{[H_3cit]} = \frac{(0.005)(2.63\times10^{-6})}{[H_3cit]} = 7.45\times10^{-4}$$

$$[H_3cit] = 1.77 \text{ x } 10^{-5}$$

One last set of things to examine are the calculated values for $[H_2cit^-]$, $[Hcit^{2-}]$ and $[cit^{3-}]$.

$$[Hcit^{2-}] = 0.033 \text{ M}$$

$$[H_2cit^-] = 0.005 \text{ M}$$

$$[cit^{3-}] = 0.005 \text{ M}$$

What we need to appreciate is that there is a problem with these numbers. We started this calculation by claiming that "all" of the material was in the form of $Hcit^{2-}$. What these calculations show is that there are appreciable amounts of H_2cit^- and cit^{3-} in solution. If these two values were accurate, it would mean that the concentration of $Hcit^{2-}$ could only be 0.023 M.

Why does this happen? It has to do with how close the pK_a values are for citric acid. The approximation that we could examine this as a stepwise manner, where we proceeded from one reaction to the other and that intermediates were overwhelmingly the predominant form at the equivalence points, breaks down in this case because of how close the pK_a values are. The interesting part of this is that the pH of the solution would be 5.58, and that we will get exactly equivalent concentrations of H_2cit^- and cit^{3-}, although they will not be exactly 0.005 M. In reality, I do not think we would ever try to calculate the exact amount of each of these species at a pH like this, although later in the course we are going to come back to the citric acid situation and see a way to calculate the exact concentration of species present provided we know the pH.

One thing to keep in mind is that often times we do not use equilibrium calculations to arrive at exact values of substances. For one thing, concentrations are an approximation of activities and this may not always be a good one. For another, we often use equilibrium calculations to provide ballpark values to let us know whether a particular process we may be considering is even feasible. In this case, for example, these values show that we could never use the second equivalence point in a citric acid titration for measurement purposes. This does not mean that citric acid cannot be used as a buffer, because it frequently is. However, if we prepare a citric acid buffer (or any buffer), we do not rely on calculated amounts to ensure that the pH is where we want it, we use a pH meter to monitor the buffer and use small amounts of a strong acid or strong base to adjust the pH to the value we want.

IN-CLASS PROBLEM SET #4

1. Calculate the concentration of free calcium(II) ions in a solution prepared with initial concentrations of calcium of 0.020 M and EDTA^{4-} of 0.10 M.

This is our first example involving a water-soluble metal complex. The general form of these equations is that a metal ion (M) reacts with a ligand (L) to form a water-soluble complex.

$$M(aq) + L(aq) \leftrightarrow ML(aq) \qquad K_f$$

Usually we appreciate that these are all water-soluble species and omit the (aq) notation from the equations. The general form of the equation is referred to as a formation constant, hence the notation K_f for the equilibrium constant. If you examine the values of K_f in the table, you will see that many of these are reasonably large values. In fact, because they are large, it is common for tables to report the $\log K_f$ value rather than the K_f value. It makes sense that many of these in the table would have large values because people would be interested in metal complexes that had relatively high formation constants if they wanted to use them for analytical purposes. Another thing to realize is that many ligands can form a series of stepwise complexes with a metal, as illustrated below.

$$M + L \leftrightarrow ML \qquad K_{f1}$$

$$ML + L \leftrightarrow ML_2 \qquad K_{f2}$$

$$ML_2 + L \leftrightarrow ML_3 \qquad K_{f3}$$

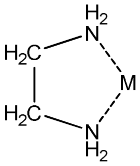
$$ML_3 + L \leftrightarrow ML_4 \qquad K_{f4}$$

It is also worth examining what types of species function as ligands. First, it’s worth realizing that the metal in these reactions is almost always a cation. Therefore, anions are one group of compounds that have to be examined as possible ligands. The way to see if complexation occurs is to determine all of the anions and metal ions that exist in a particular solution, and then see if any possible combination of a metal ion with an anion has a value or values in the table of formation constants. If any do, then that process needs to be incorporated into any calculations of equilibrium concentrations. One thing to note is that every aqueous solution has some amount of hydroxide ion, and many metal ions form water-soluble complexes with hydroxide. The presence of hydroxide ion therefore provides an additional complication when assessing the distribution of most metal species in solution.

Another thing to realize is that anions are always the conjugate bases of acids. In other words, any anion has the potential to be protonated with a hydrogen ion. If the anion is the conjugate base of a strong acid (halide, nitrate, perchlorate), then its concentration will not vary as a function of pH because it will not be protonated in water. If the anion is the conjugate base of a weak acid, which is actually far more common, then the concentration of the anion in water is a function of the pH. This means that the complexation of the metal by the anion will depend on the pH as well. What you might begin to realize now is that metal complexation in water is a complicated process that is influenced by the pH and the availability of different ligands. We will see that there are a series of systematic ways to address metal complexation and handle all of the simultaneous equilibria that occur.

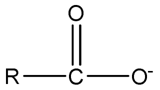
The other large group of ligands are the nitrogen bases. These are neutral ligands that have the ability to form donor-acceptor complexes with the metal ion. The ligand acts as an electron-pair donor, something we refer to as a Lewis base. The positive metal ion acts as an electron-pair acceptor, something we refer to as a Lewis acid. (Actually, the Lewis acid-Lewis base interaction also occurs for anions when they bond to metals). For example, ammonia is a ligand that forms water-soluble complexes with many metal ions. Ethylenediamine is another important nitrogen-containing ligand that forms water-soluble complexes with many metal ions. In this case, what is particularly interesting is that both nitrogen atoms bond to the metal ion at the same time, forming what is called a chelate complex.

$H_2NCH_2CH_2NH_2$

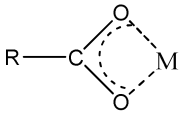


Ethylenediamine Chelate Bonding

Anions can bond to metal ions in a chelate manner as well. For example, the carboxylate ion actually bonds to metal ions through a chelate arrangement of the two oxygen atoms.

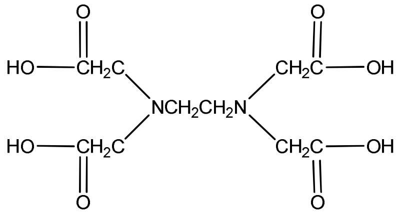


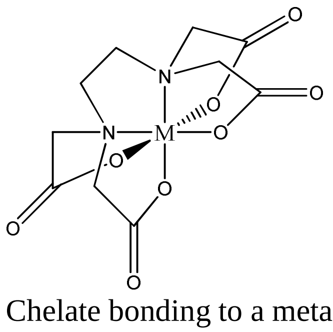
$R-C(=O)-O^-$



Carboxylate ion Chelate Bonding

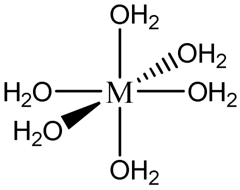
Another very important ligand is the species ethylenediaminetetraacetic acid (H_4EDTA or H_4E). EDTA is a tetraprotic acid that can act as a ligand and form very stable chelate complexes with metal ions. We have a table of K_f values for different EDTA complexes and note that these are very large numbers. An interesting thing to realize is that we always think of the fully deprotonated ligand (E^{4-}) as the species that actually forms the complex. The other forms (H_4E, H_3E^-, H_2E^{2-}, HE^{3-}) are not involved in the complexation. Note that this is a general observation. For example, in the phosphoric acid system, the species PO_4^{3-} would be the ligand, not the partially protonated HPO_4^{2-} and $H_2PO_4^{2-}$ species.





H_4EDTA Chelate bonding to a metal

Note that one E^{4-} ligand has the ability to completely surround a metal ion and fill all of the coordination sites simultaneously. It might be tempting to think that this ability to fill all the sites at one time accounts for the exceptionally large formation constants. In actuality, the large formation constants are driven more by entropy changes. If we think about the nature of a metal cation in water, we realize that the positive metal ion is surrounded by negative ends of water molecules as shown below. In this picture, the oxygen atoms of the water molecules are said to be in the first coordination sphere of the metal ion. This is typically what occurs with many metal salts in water. The cation and anion separate from each other and are solvated by water.

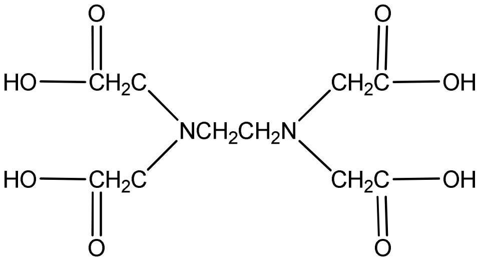


The reaction that we can now write to represent the bonding of E^{4-} to a metal ion (M^+) is shown below:

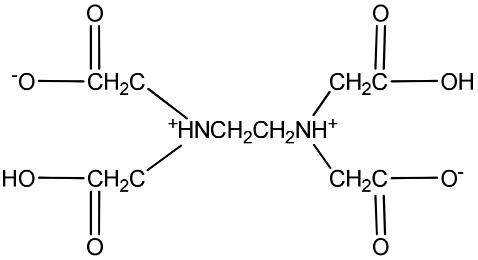
$$M(H_2O)_6^+ \ + \ E^{4-} \ \Leftrightarrow \ ME^{3-} \ + \ 6\,H_2O$$

Note that the reaction side of the equation has two species, the product side has seven species. There is considerably larger entropy associated with the seven species on the product side, and this huge gain in favorable entropy is what primarily accounts for the large formation constants of metal complexes with EDTA. We will rarely write the metal ion as $M(H_2O)_6^+$ and instead simplify it to M^+. But it's sometimes worth remembering that it is surrounded by some number of water molecules. Also note that the ME^{3-} species has a net charge of –3. Many of these water-soluble complexes have a net charge, which in part is responsible for their water solubility.

One last thing about EDTA. If you look in the structures shown in our table, you will see that EDTA is actually a zwitterion in solution (See below a neutral and zwitterionic form of EDTA). What's important to realize is that it really does not matter what form you write it in. Both forms below have four dissociable protons. Both forms have a net neutral charge. Both can be expressed as H_4EDTA.

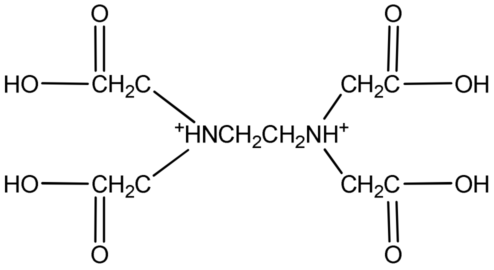


H_4EDTA
(neutral)



H_4EDTA
(zwitterion)

In theory, it might actually be possible to protonate both nitrogen atoms of EDTA, producing a species of the form H_6EDTA^{2+}.



H_6EDTA^{2+}

This species does not occur because the first two protons are so acidic that, even if we dissolved EDTA in a strong acid such as concentrated hydrochloric acid, it is doubtful that these sites would be protonated. In water, at pH values of 1 or higher, we will never be able to put more than four protons onto the EDTA.

Now we are ready to calculate the answer to the first problem.

Calculate the concentration of free calcium(II) ion in a solution prepared with initial concentrations of calcium of 0.020 M and $EDTA^{4-}$ of 0.10 M.

In solving this problem, we will start under very naïve circumstances. We will not consider any other complexation of the calcium ion (for example, by something like hydroxide), and we have been given a concentration of E^{4-} and do not need to worry about the pH of this solution, how we got a concentration of 0.10 M, or whether protonation occurs.

The first thing to do is to write the reaction and look up the relevant formation constant.

$$Ca^{2+} + E^{4-} \leftrightarrow CaE^{2-} \qquad K_f = 5.0\times10^{10}$$

What we see is that has a very large formation constant. That means that this reaction will go to completion. The approach to solving this problem is to allow it to go to completion, realizing that one of the reagents will limit the amount of product that forms. Then we need to allow a small amount of back reaction to occur. We can construct the following chart.

	Ca^{2+}	+ E^{4-}	$\leftrightarrow$ CaE^{2-}
Initial	0.020 M	0.10 M	0
Complete Reaction	0	0.08	0.02
Back Reaction	x	0.08 + x	0.02 – x
Assumption		$0.08 \gg x$	$0.02 \gg x$
Approximation	x	0.08	0.02

The approximation that $0.08 \gg x$ and $0.02 \gg x$ is reasonable since the K_f value is so large, therefore the amount of back reaction will be excessively small.

$$K_f = \frac{[CaE^{2-}]}{[Ca^{2+}][E^{4-}]} = \frac{0.02}{(x)(0.08)} = 5.0\times10^{10}$$

$$x = [Ca^{2+}] = 5\times10^{-12}$$

The amount of unreacted calcium ion is incredibly small. Obviously the approximations we made were justified and we see how far these reactions can go toward completion.

2. Calculate the concentration of free calcium(II) ions in a solution prepared with initial concentrations of calcium of 0.020 M and total EDTA of 0.10 M. The solution is buffered at a pH of 2.

Now we have added a complicating factor. We will incorporate the fact that the EDTA has several protonated forms, and that these forms depend on the pH of the solution. Since only the E^{4-} form bonds to the metal ion, protonated forms of EDTA reduce the concentration of E^{4-} available for complexation. If very little E^{4-} is available for complexation, very little of the calcium ion will be complexed.

It is also worth realizing that, in most cases, we do know the pH of a solution. One reason is because we want a particular pH so we have prepared the solution in a buffer. The other is that it is very easy to measure the pH of a solution using a pH meter, so if pH is a relevant issue, we simply measure it.

The set of reactions below show what we now know will occur in this solution (note, we are ignoring the possibility that the calcium can complex with hydroxide ion – more on that later).

$$\begin{tikzcd}
Ca^{2+} \arrow[r, phantom, "+"] & E^{4-} \arrow[r, leftrightarrow] \arrow[d, Leftrightarrow] & CaE^{2-} \\
 & HE^{3-} \arrow[d, Leftrightarrow] & \\
 & H_2E^{2-} \arrow[d, Leftrightarrow] & \\
 & H_3E^{-} \arrow[d, Leftrightarrow] & \\
 & H_4E &
\end{tikzcd}$$

The problem we face here is that the reaction we want to examine is the K_f reaction for CaE^{2-}. If we want to use our established way of doing that calculation, we need to know the initial amounts of Ca^{2+} and E^{4-} that we have in solution, but some of the E^{4-} has been protonated and we do not know how much we have. Also, we have one other problem. Suppose, in a solution with a total amount of EDTA of 0.10 M, we could calculate how much of the EDTA was in the E^{4-} form. We could conceivably allow this to complex with the Ca^{2+}, but we have an additional source of EDTA (the HE^{3-}, H_2E^{2-}, H_3E^{-}, and H_4E forms) that will redistribute to some extent and provide additional amounts of E^{4-}.

There is a very interesting observation about acid-base systems. It turns out that if we know the pH of the solution, the fraction of the total that exists in any one form is fixed. In other words, the fraction of total EDTA that exists in the H_4E, H_3E^{-}, H_2E^{2-}, HE^{3-}, and E^{4-} forms is only a function of the pH of the solution. It does not depend on the total amount of EDTA in solution. We refer to these fractions as α–values. We are usually interested in the α-value for the fully deprotonated anion, since that is the form that complexes with the metal. It's important to realize that we can calculate α-values for any of the species involved in a series of reactions for a polyprotic acid.

It is worth showing that the fraction of EDTA that exists in solution as E^{4-} is only a function of pH. This will also demonstrate the general procedure that we can use to calculate α–values.

First, write an expression for the fraction of EDTA that exists in solution as E^{4-}.

$$\alpha_{E^{4-}} = \frac{[E^{4-}]}{[H_4E] + [H_3E^-] + [H_2E^{2-}] + [HE^{3-}] + [E^{4-}]}$$

Note that this is just the concentration of E^{4-} over the total EDTA in solution. The next step is to take the reciprocal of this expression. Doing so will allow you to divide the equation into a set of separate terms.

$$\frac{1}{\alpha_{E^{4-}}} = \frac{[H_4E]}{[E^{4-}]} + \frac{[H_3E^-]}{[E^{4-}]} + \frac{[H_2E^{2-}]}{[E^{4-}]} + \frac{[HE^{3-}]}{[E^{4-}]} + \frac{[E^{4-}]}{[E^{4-}]}$$

The next step is to use the K_a values for EDTA to substitute in for each of the ratio terms. The first one to examine is the ratio of $[HE^{3-}]/[E^{4-}]$, which we can obtain using only the K_{a4} expression. Rearranging K_{a4} as shown below gives the following term to substitute in.

$$HE^{3-} + H_2O \Leftrightarrow E^{4-} + H_3O^+ \qquad K_{a4}$$

$$K_{a4} = \frac{[E^{4-}][H_3O^+]}{[HE^{3-}]} \qquad \frac{[HE^{3-}]}{[E^{4-}]} = \frac{[H_3O^+]}{K_{a4}}$$

Next we can evaluate an expression to substitute in for $[H_2E^{2-}]/[E^{4-}]$. This will involve using the K_{a3} and K_{a4} expression for EDTA. The easiest way to see this is to add up the K_{a3} and K_{a4} reactions. Remember, the equilibrium constant for the resulting reaction is the product of the equilibrium constants for those added together.

$$H_2E^{2-} + H_2O \Leftrightarrow HE^{3-} + H_3O^+ \qquad K_{a3}$$

$$HE^{3-} + H_2O \Leftrightarrow E^{4-} + H_3O^+ \qquad K_{a4}$$

$$H_2E^{2-} + 2H_2O \Leftrightarrow E^{4-} + 2H_3O^+ \qquad K = K_{a3}\,K_{a4}$$

$$K_{a3}\,K_{a4} = \frac{[E^{4-}][H_3O^+]^2}{[H_2E^{2-}]} \qquad \frac{[H_2E^{2-}]}{[E^{4-}]} = \frac{[H_3O^+]^2}{K_{a3}\,K_{a4}}$$

Perhaps by this point we see a pattern developing. Evaluating the $[H_3E^-]/[E^{4-}]$ term will require the use of K_{a2}, K_{a3}, and K_{a4} and yield the following term:

$$\frac{[H_3E^-]}{[E^{4-}]} = \frac{[H_3O^+]^3}{K_{a2}\,K_{a3}\,K_{a4}}$$

Similarly, evaluating the $[H_4E]/[E^{4-}]$ term will, which requires using K_{a1}, K_{a2}, K_{a3}, and K_{a4}, will yield the following term:

$$\frac{[H_4E]}{[E^{4-}]} = \frac{[H_3O^+]^4}{K_{a1}\,K_{a2}\,K_{a3}\,K_{a4}}$$

The final result is shown below.

$$\frac{1}{\alpha_{E^{4-}}} = \frac{[H_3O^+]^4}{K_{a1}\,K_{a2}\,K_{a3}\,K_{a4}} + \frac{[H_3O^+]^3}{K_{a2}\,K_{a3}\,K_{a4}} + \frac{[H_3O^+]^2}{K_{a3}\,K_{a4}} + \frac{[H_3O^+]}{K_{a4}} + 1$$

What we see is that the only variable in this expression is $[H_3O^+]$, so the fraction of EDTA that exists in solution as E^{4-} is only a function of the pH. There is no term for the total amount of EDTA in the equation, so that does not matter. It only depends on the pH.

Similarly, we can evaluate the fraction of the other species as a function of pH. For example, let's begin the process of evaluating the α-value of H_4E. The general procedure is the same as used for $\alpha_{E^{4-}}$. The first step is to write the relevant equation for H_4E over the total.

$$\alpha_{H_4E} = \frac{[H_4E]}{[H_4E] + [H_3E^-] + [H_2E^{2-}] + [HE^{3-}] + [E^{4-}]}$$

The next step is to take the reciprocal and divide the equation into separate terms.

$$\frac{1}{\alpha_{H_4E}} = \frac{[H_4E]}{[H_4E]} + \frac{[H_3E^-]}{[H_4E]} + \frac{[H_2E^{2-}]}{[H_4E]} + \frac{[HE^{3-}]}{[H_4E]} + \frac{[E^{4-}]}{[H_4E]}$$

The next step is to use the K_a expressions to express each ratio in terms of $[H_3O^+]$ and the K_a values. I will not show all these rearrangements here, but doing them yields the following result for $1/\alpha_{H_4E}$. You ought to try this and convince yourself that this is correct.

$$\frac{1}{\alpha_{H_4E}} = 1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}\,K_{a2}}{[H_3O^+]^2} + \frac{K_{a1}\,K_{a2}\,K_{a3}}{[H_3O^+]^3} + \frac{K_{a1}\,K_{a2}\,K_{a3}\,K_{a4}}{[H_3O^+]^4}$$

Similarly, we could write expressions, take reciprocals, and evaluate the terms for α-values for H_3E^-, H_2E^{2-}, and HE^{3-}. The full 1/α-value expressions that would result for all of the species involved in the EDTA system are shown below. Note the characteristic patterns that result.

$$\frac{1}{\alpha_{E^{4-}}} = \frac{[H_3O^+]^4}{K_{a1}\,K_{a2}\,K_{a3}\,K_{a4}} + \frac{[H_3O^+]^3}{K_{a2}\,K_{a3}\,K_{a4}} + \frac{[H_3O^+]^2}{K_{a3}\,K_{a4}} + \frac{[H_3O^+]}{K_{a4}} + 1$$

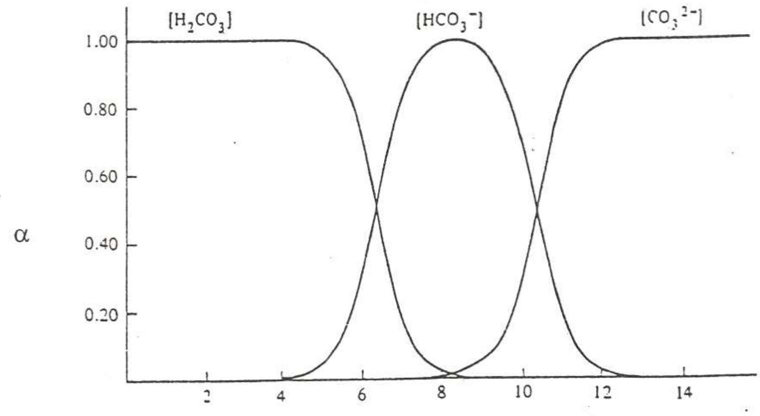
$$\frac{1}{\alpha_{HE^{3-}}} = \frac{[H_3O^+]^3}{K_{a1}\,K_{a2}\,K_{a3}} + \frac{[H_3O^+]^2}{K_{a2}\,K_{a3}} + \frac{[H_3O^+]}{K_{a3}} + 1 + \frac{K_{a4}}{[H_3O^+]}$$

$$\frac{1}{\alpha_{H_2E^{2-}}} = \frac{[H_3O^+]^2}{K_{a1}\,K_{a2}} + \frac{[H_3O^+]}{K_{a2}} + 1 + \frac{K_{a3}}{[H_3O^+]} + \frac{K_{a3}\,K_{a4}}{[H_3O^+]^2}$$

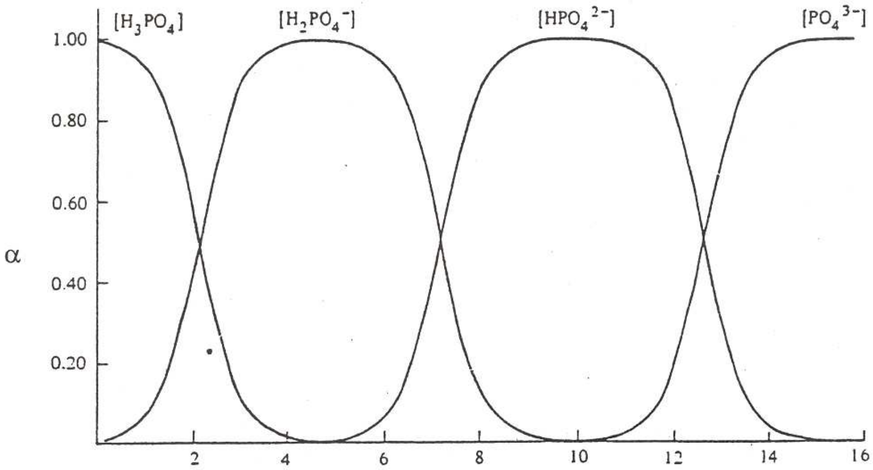
$$\frac{1}{\alpha_{H_3E^-}} = \frac{[H_3O^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H_3O^+]} + \frac{K_{a2}\,K_{a3}}{[H_3O^+]^2} + \frac{K_{a2}\,K_{a3}\,K_{a4}}{[H_3O^+]^3}$$

$$\frac{1}{\alpha_{H_4E}} = 1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}\,K_{a2}}{[H_3O^+]^2} + \frac{K_{a1}\,K_{a2}\,K_{a3}}{[H_3O^+]^3} + \frac{K_{a1}\,K_{a2}\,K_{a3}\,K_{a4}}{[H_3O^+]^4}$$

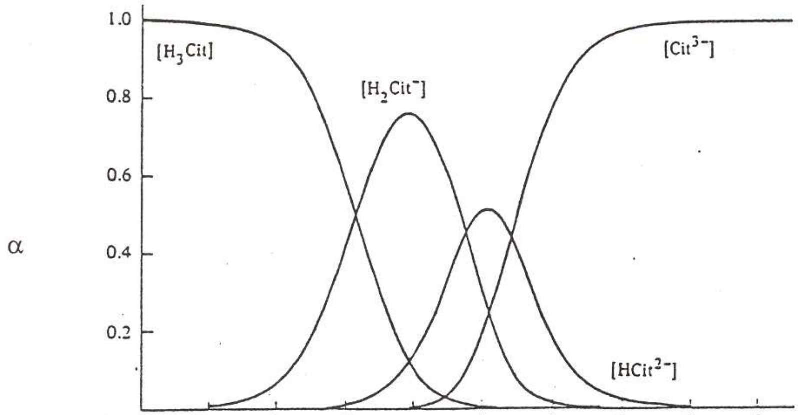
The other important thing to do with α-values is examine a plot of α-values versus pH for a series of compounds. Examples are shown in Figure 5 for carbonic acid, phosphoric acid, and citric acid.



Carbonic Acid (pK_a values of 6.4 and 10.4)



Phosphoric Acid (pK_a values of 2.12, 7.21, and 12.66)



Citric Acid (pK_a values of 3.13, 4.76, and 5.41)

Figure 5. Plots of a-values as a function of pH for carbonic, phosphoric and citric acid.

There are several important items to note about these figures on the previous page. At very low pH, meaning highly acidic conditions, the fully protonated forms predominate. At very high pH, meaning highly basic conditions, the fully deprotonated forms predominate. Since the deprotonated forms are the ones that will bond to metal ions, complexation of metal ions by ligands is favored at more basic pH values. (Note, we could do a similar plot of α-values for the different forms of ethylenediamine, H_2En^{2+}, HEn^+, and En. Remembering that the neutral form, En, is the one that complexes with metals, we would see that this form is favored at more basic pH values). At intermediate pH values, different intermediate forms increase and then diminish as the pH is raised from acidic to basic conditions. At the crossing points of two of the α-value plots, we typically have a 50:50 mixture of a conjugate pair. In other words, these crossing points are the excellent buffer regions for these reagents.

Observe that the forms of the carbonic and phosphoric acid systems are very regularized. There is some pH where only one species of the series predominates and the concentrations of all others are minimal. This is not the case with citric acid. We see a somewhat unusual situation in which at a pH of around 4 and 5, we see that the H_2cit^- and $Hcit^{2-}$ forms respectively do not reach 99%. At these points we find appreciable amounts of the neighboring species. Also note that the amounts of H_2cit^- and cit^{3-} present at the point at which $Hcit^{2-}$ is maximized are exactly equal to each other. The same thing occurs for the two neighboring species at pH 4. This is a rather rare occasion of having appreciable quantities of three species from an acid-base system present at the same time. The reason for this unusual behavior is that the pK_a values are very close to each other. (Note: pK_{a3} in this chart is reportedly 5.41, which is different than the value of 6.396 in our table of K values!) We have already examined citric acid when it was titrated with sodium hydroxide and introduced its somewhat unusual behavior. The plot of α-values really points out the effects of having close pK_a values and how this influences the concentrations of species in solution.

We are now in a position to finally see how to incorporate an α-value into the calculation involving complexation of Ca^{2+} by E^{4-} at a pH of 2. Write the formation constant expression and recognize that we can substitute in for the $[E^{4-}]$ term.

$$Ca^{2+} + E^{4-} \leftrightarrow CaE^{2-} \qquad\qquad K_f$$

$$K_f = \frac{[CaE^{2-}]}{[Ca^{2+}][E^{4-}]}$$

$$[E^{4-}] = \alpha_{E^{4-}}[E]_{TOT}$$

Substituting the $[E^{4-}]$ expression into the K_f equation gives the following:

$$K_f = \frac{[CaE^{2-}]}{[Ca^{2+}]\alpha_{E^{4-}}[E]_{TOT}}$$

The $\alpha_{E^{4-}}$ term is a constant, since the pH is known, and we can rearrange the expression into the following:

$$(K_f)(\alpha_{E^{4-}}) = \frac{[CaE^{2-}]}{[Ca^{2+}][E]_{TOT}}$$

$(K_f)(\alpha_{E^{4-}})$ is something we call a **conditional constant (K_{COND})**. Why a conditional constant? It turns out that the pH is a "condition" in this solution that influences the concentration and availability of E^{4-}. Incorporating the α-value into the conditional constant will allow us to assess whether it is likely that the Ca^{2+} will complex with the E^{4-}. The conditional constants for the complexation of Ca^{2+} with E^{4-} are shown in Table 6 as a function of pH. What we need to do is calculate the conditional constant, and then examine its magnitude. If the conditional constant is large, the reaction goes to completion. If the conditional constant is small, the reaction does not go to completion.

Table 6. Conditional constants for the complexation of Ca^{2+} with E^{4-}.

pH	$\alpha_{E^{4-}}$	$(K_f)(\alpha_{E^{4-}})$	Extent of reaction
1	3.66×10^{-18}	1.83×10^{-7}	Very small
2	2.00×10^{-14}	1.00×10^{-3}	Fairly small
3	1.61×10^{-11}	0.805	Intermediate
4	2.48×10^{-9}	1.24×10^{2}	Intermediate
5	2.47×10^{-7}	1.24×10^{4}	Close to completion
6	1.67×10^{-5}	8.35×10^{6}	Completion
7	3.89×10^{-4}	1.95×10^{7}	Completion
8	4.47×10^{-3}	2.24×10^{8}	Completion
9	4.36×10^{-2}	2.18×10^{9}	Completion
10	0.314	1.57×10^{10}	Completion
11	0.820	4.10×10^{10}	Completion
12	0.979	4.90×10^{10}	Completion
13	0.998	4.99×10^{10}	Completion

Note how the reaction, based on the magnitude of the conditional constant, goes further to completion as the pH is made more basic. At very acidic pH values, very little reaction occurs. Also note that the conditional constant is large by a pH of 6, even though the α-value for the E^{4-} is still fairly small (1.67×10^{-5}). This shows how the very large formation constant (5×10^{10}) leads to formation of the complex (as the E^{4-} is used up, we have a source of additional E^{4-} from the protonated E species HE^{3-}, H_2E^{2-}, H_3E^{-}, and H_4E). But also note, the α-values for the E species do not change as long as the pH remains fixed. If E^{4-} is removed by complexation, some new E^{4-} will form to maintain the same distribution of α-values for all of the E species.

If we have the expression:

$$(K_f)(\alpha_{E^{4-}}) = \frac{[CaE^{2-}]}{[Ca^{2+}][E]_{TOT}}$$

We could write this as belonging to the following reaction. Note that the procedure we use assumes that only a small amount of reaction occurs since the conditional constant is only 1×10^{-3}.

	Ca^{2+} +	E_{TOT} ↔	CaE^{2-}	$K_{COND} = (K_f)(\alpha_{E^{4-}}) = 1\times10^{-3}$
Initial	0.02	0.10	0	
Equilibrium	0.02 – x	0.10 – x	x	
Approximation	0.02	0.10	x	

Substitute these in to calculate the value of $[CaE^{2-}]$:

$$K_{COND} = \frac{[CaE^{2-}]}{[Ca^{2+}][E]_{TOT}} = \frac{x}{(0.02)(0.1)} = 1\times10^{-3}$$

$$x = [CaE^{2-}] = 2\times10^{-6}$$

Checking the approximation shows that it was valid to assume that very little of the Ca^{2+} and E^{4-} complexes.

$$\frac{2\times10^{-6}}{0.02}\times 100 = 0.01\%$$

Let’s also consider how we would handle this if we had a pH with a large conditional constant. For example, consider the situation at pH 6. In this case, we treat it assuming that the reaction goes to completion and that some back reaction then occurs.

	Ca^{2+} +	E_{TOT} ↔	CaE^{2-}	$K_{COND} = 8.35\times10^{6}$
Initial	0.02	0.10	0	
Completion	0	0.08	0.02	
Back reaction	x	0.08 + x	0.02 – x	
Approximation	x	0.08	0.02	

Substituting this in gives the following concentration of free calcium ion. This concentration is very low such that we know the approximations were valid.

$$K_{COND} = \frac{[CaE^{2-}]}{[Ca^{2+}][E]_{TOT}} = \frac{0.02}{(x)(0.08)} = 8.35\times10^{6}$$

$$x = [Ca^{2+}] = 2.99\times10^{-8}$$

An important thing to notice is that the total concentration of EDTA drops in this process because some of it reacts with the Ca^{2+} to form the complex. Remember that $[E]_{TOT}$ refers only to those forms of EDTA that are not complexed with Ca^{2+} and does not include the complexed form (CaE^{2-}).

There is one other aspect to this problem we have not yet considered. That is whether calcium can complex with the hydroxide ion and whether this complexation is significant enough to alter any of the results we have seen before regarding complexation of Ca^{2+} by E^{4-}. Looking in the table of formation constants indicates that calcium ions can complex with hydroxide according to the following equation. Since only one K_f value is listed, it is only a one-step process. We might also notice that it's a fairly small association constant, so that we might anticipate that this reaction would never represent that much of an interference in the complexation of Ca^{2+} with E^{4-}.

$$Ca^{2+} + OH^{-} \leftrightarrow Ca(OH)^{+} \qquad K_f = 1.99\times10$$

We can couple this process into the overall scheme as shown below:

$$\begin{tikzcd}
Ca^{2+} \arrow[d, leftrightarrow, "OH^{-}"'] & + & E^{4-} \arrow[d, leftrightarrow] \arrow[r, leftrightarrow] & CaE^{2-} \\
Ca(OH)^{+} & & HE^{3-} \arrow[d, leftrightarrow] & \\
& & H_2E^{2-} \arrow[d, leftrightarrow] & \\
& & H_3E^{-} \arrow[d, leftrightarrow] & \\
& & H_4E &
\end{tikzcd}$$

The approach we will use is analogous to that employed with the protonation of E^{4-}. If we know the concentration of ligand, it is possible to calculate α–values for the uncomplexed metal ion and the metal-ligand species. In this case of hydroxide ion, the concentration is known and fixed provided the pH is known and fixed. With other ligands, we may need to assess whether the initial ligand concentration we are provided remains fixed. In some cases, the ligand will complex with the metal and this causes the concentration to drop from its initial value, changing the α-values that were calculated.

For the situation in this problem, we need to calculate $\alpha_{Ca^{2+}}$. We do this by setting up a ratio of Ca^{2+} to the total of other calcium species. There is one important thing to realize in setting up this ratio. We only want to look at the distribution of calcium species in the set of reactions involving complexation with hydroxide ion. We therefore do not include CaE^{2-} as a term in the ratio.

$$\alpha_{Ca^{2+}} = \frac{[Ca^{2+}]}{[Ca(OH)^{+}] + [Ca^{2+}]}$$

The next step is to take the reciprocal, and divide the equation into a series of separate terms.

$$\frac{1}{\alpha_{Ca^{2+}}} = \frac{[Ca(OH)^{+}]}{[Ca^{2+}]} + \frac{[Ca^{2+}]}{[Ca^{2+}]}$$

We can now use the K_f expression to substitute in for the first term in this equation. Using K_f for complexation of Ca^{2+} with hydroxide, we get as follows:

$$Ca^{2+} + OH^{-} \leftrightarrow Ca(OH)^{+} \qquad K_f = 1.99\times10$$

$$K_f = \frac{[Ca(OH)^{+}]}{[Ca^{2+}][OH^{-}]}$$

Rearrange the K_f expression as follows:

$$\frac{[Ca(OH)^{+}]}{[Ca^{2+}]} = K_f[OH^{-}]$$

Substitute this into the $1/\alpha_{Ca^{2+}}$ expression to get:

$$\frac{1}{\alpha_{Ca^{2+}}} = K_f[OH^{-}] + 1$$

What we see is that the fraction of calcium that exists as Ca^{2+} only depends on the K_f value and the concentration of ligand (hydroxide in this case). We could also write the following expression:

$$[Ca^{2+}] = \alpha_{Ca^{2+}}[Ca]_{TOT}$$

Remember, $[Ca]_{TOT} = [Ca^{2+}] + [Ca(OH)^{+}]$ in this expression.

We can substitute this into our original K_f expression for the complexation of Ca^{2+} with E^{4-}, just as we did previously to account for the protonation of EDTA as a function of pH.

$$Ca^{2+} + E^{4-} \leftrightarrow CaE^{2-}$$

$$K_f = \frac{[CaE^{2-}]}{[Ca^{2+}][E^{4-}]}$$

$$K_f = \frac{[\mathrm{CaE^{2-}}]}{(\alpha_{\mathrm{Ca^{2+}}}[\mathrm{Ca}]_{\mathrm{TOT}})(\alpha_{\mathrm{E^{4-}}}[\mathrm{E}]_{\mathrm{TOT}})}$$

$$(K_f)(\alpha_{\mathrm{Ca^{2+}}})(\alpha_{\mathrm{E^{4-}}}) = \frac{[\mathrm{CaE^{2-}}]}{[\mathrm{Ca}]_{\mathrm{TOT}}[\mathrm{E}]_{\mathrm{TOT}}}$$

This provides a conditional constant $(K_f)(\alpha_{\mathrm{Ca^{2+}}})(\alpha_{\mathrm{E^{4-}}})$ that incorporates both conditions that are present: protonation of the E^{4-} and complexation of Ca^{2+} by hydroxide ion. This conditional constant is essentially the equilibrium constant for the following reaction:

$$[\mathrm{Ca}]_{\mathrm{TOT}} + [\mathrm{E}]_{\mathrm{TOT}} \leftrightarrow \mathrm{CaE^{2-}}$$

What we then need to do is examine the magnitude of this conditional constant to assess whether the complexation of calcium with EDTA will occur.

Table 7 is a compilation of $\alpha_{\mathrm{E^{4-}}}$, $\alpha_{\mathrm{Ca^{2+}}}$, conditional constants, and extent of reaction for this entire process as a function of pH.

Table 7. Conditional constants for the complexation of Ca^{2+} with E^{4-}.

pH	$\alpha_{\mathrm{E^{4-}}}$	$\alpha_{\mathrm{Ca^{2+}}}$	$(K_f)(\alpha_{\mathrm{E^{4-}}})(\alpha_{\mathrm{Ca^{2+}}})$	Extent of reaction
1	3.66×10^{-18}	1	1.83×10^{-7}	Very small
2	2.00×10^{-14}	1	1.00×10^{-3}	Fairly small
3	1.61×10^{-11}	1	0.805	Intermediate
4	2.48×10^{-9}	1	1.24×10^{2}	Intermediate
5	2.47×10^{-7}	1	1.24×10^{4}	Close to completion
6	1.67×10^{-5}	1	8.35×10^{6}	Completion
7	3.89×10^{-4}	1	1.95×10^{7}	Completion
8	4.47×10^{-3}	1	2.24×10^{8}	Completion
9	4.36×10^{-2}	1	2.18×10^{9}	Completion
10	0.314	0.998	1.57×10^{10}	Completion
11	0.820	0.980	4.02×10^{10}	Completion
12	0.979	0.834	4.09×10^{10}	Completion
13	0.998	0.334	1.67×10^{10}	Completion

First, let's consider the situation at pH 2. The $\alpha_{\mathrm{Ca^{2+}}}$ value is 1, which means that essentially none of the Ca^{2+} is complexed with the hydroxide ion. This makes sense since there is a very low level of hydroxide ion at pH 2 ($[OH^-] = 10^{-12}$) and because the K_f value for calcium complexation with hydroxide is not that large. The complexation of calcium by hydroxide has no significant effect on the system at this pH. As the pH becomes more basic, notice how $\alpha_{\mathrm{Ca^{2+}}}$ eventually falls below 1. This means that some of the calcium ion will complex with hydroxide. But if we examine the overall conditional constant, we also see that there is so much E^{4-} available at the more basic pH values, that complexation with hydroxide is never sufficient enough to overcome the complexation of Ca^{2+} with the E^{4-}. It would take a much larger K_f value for complexation of Ca^{2+} with hydroxide for this reaction to compete with the reaction with E^{4-}.

Calcium ion in tap water forms an insoluble precipitate with soap molecules and prevents the formation of lots of suds. Because it's hard to get suds when a high concentration of calcium ion is present, the water is referred to as "hard water". The classic procedure for analyzing the calcium concentration in hard water is to perform a titration with EDTA. The solution is buffered at a pH of 10 to ensure that there is complete complexation of the calcium with the EDTA. The conditional constants in the table above show the reason why a pH of 10 is used.

One last thing we need to consider is how we would handle a metal complex in which there were multiple formation constants. For example, if we look up the complexation of Cd^{2+} with hydroxide, we see that there are four steps in the process and that the K_f values are larger than the one with Ca^{2+}. If we had substituted Cd^{2+} for Ca^{2+} in the problem above, the competing complexation of Cd^{2+} with hydroxide might have had more of an influence on the complexation of Cd^{2+} with E^{4-}. Of course, we also need to examine the complexation of Cd^{2+} with E^{4-}, which has a K_f value of 3.16×10^{16} from the table.

The relevant equilibria for Cd^{2+} in this case are as follows:

$$Cd^{2+} + OH^- \leftrightarrow Cd(OH)^+ \qquad K_{f1}$$

$$Cd(OH)^+ + OH^- \leftrightarrow Cd(OH)_2 \qquad K_{f2}$$

$$Cd(OH)_2 + OH^- \leftrightarrow Cd(OH)_3^- \qquad K_{f3}$$

$$Cd(OH)_3^- + OH^- \leftrightarrow Cd(OH)_4^{2-} \qquad K_{f4}$$

The evaluation of $\alpha_{Cd^{2+}}$ would involve the initial equation shown below:

$$\alpha_{Cd^{2+}} = \frac{[Cd^{2+}]}{[Cd(OH)_4^{2-}] + [Cd(OH)_3^-] + [Cd(OH)_2] + [Cd(OH)^+] + [Cd^{2+}]}$$

Taking the reciprocal leads to the following terms:

$$\frac{1}{\alpha_{Cd^{2+}}} = \frac{[Cd(OH)_4^{2-}]}{[Cd^{2+}]} + \frac{[Cd(OH)_3^-]}{[Cd^{2+}]} + \frac{[Cd(OH)_2]}{[Cd^{2+}]} + \frac{[Cd(OH)^+]}{[Cd^{2+}]} + \frac{[Cd^{2+}]}{[Cd^{2+}]}$$

Using the K_f expressions for the complexation of Cd^{2+} with hydroxide, each ratio can be evaluated in terms of K_f values and $[OH^-]$, leading to the following equation.

$$\frac{1}{\alpha_{Cd^{2+}}} = K_{f1}\,K_{f2}\,K_{f3}\,K_{f4}[OH^-]^4 + K_{f1}\,K_{f2}\,K_{f3}[OH^-]^3 + K_{f1}\,K_{f2}[OH^-]^2 + K_{f1}[OH^-] + 1$$

$$(K_f)(\alpha_{Cd^{2+}})(\alpha_{E^{4-}}) = \frac{[CdE^{2-}]}{[Cd]_{TOT}[E]_{TOT}}$$

Evaluation of a similar set of conditional constants over the entire pH range for the complexation of Cd^{2+} with E^{4-} leads to the set of data in Table 8.

Table 8. Conditional constants for the complexation of Cd^{2+} with E^{4-}.

pH	$\alpha_{E^{4-}}$	$\alpha_{Cd^{2+}}$	$(K_f)(\alpha_{Cd^{2+}})(\alpha_{E^{4-}})$	Extent of reaction
1	3.66×10^{-18}	1	1.20×10^{-1}	Intermediate
2	2.00×10^{-14}	1	6.32×10^{2}	Intermediate
3	1.61×10^{-11}	1	5.09×10^{5}	Close to completion
4	2.48×10^{-9}	1	7.84×10^{7}	Completion
5	2.47×10^{-7}	1	7.81×10^{9}	Completion
6	1.67×10^{-5}	1	5.28×10^{11}	Completion
7	3.89×10^{-4}	0.998	1.23×10^{13}	Completion
8	4.47×10^{-3}	0.980	1.38×10^{14}	Completion
9	4.36×10^{-2}	0.830	1.14×10^{15}	Completion
10	0.314	0.284	2.81×10^{15}	Completion
11	0.820	1.09×10^{-2}	2.82×10^{14}	Completion
12	0.979	2.84×10^{-5}	8.79×10^{11}	Completion
13	0.998	8.30×10^{-9}	2.62×10^{8}	Completion

If we compare this data to that for Ca^{2+}, we see that a much higher proportion of the Cd^{2+} is complexed with hydroxide ion at the more basic pH values. The complexation with hydroxide is sufficient enough at pH 12 and 13 to significantly lower the conditional constant compared to the maximum at pH 10. Nevertheless, the complexation of Cd^{2+} by the EDTA is still complete at pH 12 and 13 because of such a high formation constant.

What we see for a species like Cd^{2+} is some optimum pH for complexation with EDTA. At low pH, protonation of the EDTA reduces the extent of complexation. At high pH, complexation of the Cd^{2+} with hydroxide competes with the EDTA to some extent. If we wanted to perform an analysis of Cd^{2+} using EDTA, we would buffer the solution at the pH that produces the maximum conditional constant, which is at a pH of 10.

MASS AND CHARGE BALANCES

Sometimes when performing a calculation concerning a process at chemical equilibrium there are no simplifying assumptions that can be made. If the system is a relatively simple one, like the dissolution of a weak acid or base in water, the problem can be answered by solving a quadratic formula. At other times, the problem can be considerably more complex with many more species found in the solution. In such an instance the problem usually must be answered by writing and solving a set of simultaneous equations. To determine the number of equations needed, one must first determine the number of unknowns in the solution. As an example, consider the first problem that we solved in this course, a solution of ammonia in water. It turns out that in this case, there are four unknowns in the solution.

Ammonia	NH_3
Ammonium ion	NH_4^+
Hydronium ion	H_3O^+
Hydroxide ion	OH^-

Did we use four equations to solve this? We used the K_b for ammonia and the K_w for water (remember, using the K_b, we ended up calculating the pOH, which we then converted to pH using K_w). A third equation we used (probably without you realizing it) is what is known as a **mass balance**. In this case, if we were told that the initial concentration of ammonia was 0.10 M, we wrote an expression for the final concentration as (0.10 – x). Another way of saying this is:

$$[NH_3]_{Final} + [NH_4^+]_{Final} = [NH_3]_{Initial} = 0.10 \text{ M.}$$

Before going on, convince yourself that the equation above is correct.

The fourth equation we used to solve the problem was to say that the concentration of ammonium ion in the final solution equaled the concentration of hydroxide ion (remember, we assumed that the initial amount of hydroxide ion was small compared to what was produced by the reaction of the ammonia).

$$[NH_4^+]_{Final} = [OH^-]_{Final}$$

This equation is known as a **charge balance**. It is important to realize that all solutions must be electrically neutral; that is, for every substance of positive charge there must be an equivalent amount of negative charge to balance it out. If something dissolves in water and produces positive ions, then there must be negative ions around to balance them out.

It is also worth pointing out that the equation shown above is not really the entire charge balance for that solution, (we ignored some original hydroxide and hydronium ion in solution). The exact form would actually be:

$$[NH_4^+]_{Final} + [H_3O^+]_{Final} = [OH^-]_{Final}$$

When faced with a problem requiring a set of simultaneous equations, in addition to all of the relevant equilibrium constant expressions, the mass and charge balances are usually needed to come up with as many equations as there are unknowns.

Consider another example, that of dissolving sodium acetate in water to make up a 0.10 M solution. We can write two mass balance expressions.

$$[Na^+] = 0.10\ M$$

Remember that the sodium acetate will dissociate into its component ions. The sodium ion does not undergo any reaction with water, but acetate does to produce acetic acid. The concentration of acetic acid in the final solution will drop below 0.10 M, but the total of the two species must equal 0.10 M, the initial amount that was put into solution.

$$[\text{Acetic acid}] + [\text{acetate}] = 0.10\ M$$

The charge balance must account for all positively charged (sodium and hydronium ions) and negatively charged (acetate and hydroxide ions) species in solution. We can only write one complete charge balance for a solution.

$$[Na^+] + [H_3O^+] = [\text{acetate}] + [OH^-]$$

Charge balances get interesting when one of the ions has a charge greater than one. If you consider calcium(II)chloride ($CaCl_2$), note that two chloride ions result for each calcium ion.

$$CaCl_2 = Ca^{2+} + 2Cl^-$$

The charge balance for a solution of calcium chloride in water is written as follows (assuming that neither calcium nor chloride ions undergo any reactions with water, hydronium, or hydroxide).

$$2[Ca^{2+}] + [H_3O^+] = [Cl^-] + [OH^-]$$

You must convince yourself that the above equation is correct, especially that the concentration of calcium ion should be multiplied by two. Many people are initially troubled that the (2+) ion gets multiplied by two, since that seems counter-intuitive. What you must realize is that the equation actually equates concentrations of species in solution. Leave out the hydronium and hydroxide ions from the equation, and notice again in the reaction written above, that for every one calcium ion there are two chloride ions produced. If you plug in a 1 for calcium in the charge balance equation, you will see that the concentration of chloride calculates to be 2. Once you appreciate that the coefficient is in the right place, you may also appreciate that this can be generalized. The concentration of an ion with a charge of (3–) will be multiplied by 3, the concentration of an ion with a charge of (4+) will be multiplied by 4, etc. Knowing how to write mass and charge balances correctly is a critical skill to have when solving equilibrium problems.

IN-CLASS PROBLEM SET #5

Calculate the solubility of lead(II)phosphate under the following constraints.

SOLUBILITY: For our purposes, the solubility of a substance is defined as the moles of the solid that will dissolve in one liter of solution.

a) No other simultaneous equilibria occur.

The first step in a problem like this is to write the relevant reaction that describes the process. This involves the solubility of a sparingly soluble substance. Reactions of sparingly soluble substances are always written with the solid on the reactant side and the dissolved ions on the product side.

$$Pb_3(PO_4)_2(s) \leftrightarrow 3Pb^{2+}(aq) + 2PO_4^{3-}(aq) \qquad K_{sp} = 8.1\times10^{-47}$$

The equilibrium expression for this reaction is written as follows:

$$K_{sp} = [Pb^{2+}]^3[PO_4^{3-}]^2$$

and is known as the solubility product. Note that the solid does not appear in the equilibrium constant expression.

The way to solve this problem is to write two expressions for the solubility (S), one in terms of lead ion, the other in terms of phosphate ion. What we need to consider is that the only way we get lead or phosphate ions in solution is to have some of the lead phosphate dissolve. Remember, solubility refers to the moles of solid that dissolve in a liter of solution.

If we consider the equation, one thing we would see is that for every one molecule of solid lead phosphate that dissolves, we get three lead ions. This leads to the following expression for solubility:

$$S = \frac{[Pb^{2+}]}{3} \qquad \text{or} \qquad [Pb^{2+}] = 3S$$

Before we continue, we need to make sure that this makes sense. Remember, S is a measure of the number of lead phosphate molecules that dissolve, and if we have three lead ions, only one lead phosphate has dissolved. If $[Pb^{2+}] = 3$, $S = 1$ in the above equation.

We can write a similar equation for phosphate ion, keeping in mind that for every one molecule of solid lead phosphate that dissolves, we get two phosphate ions.

$$S = \frac{[PO_4^{3-}]}{2} \qquad \text{or} \qquad [PO_4^{3-}] = 2S$$

We can now substitute these two solubility expressions into the K_{sp} expression:

$$K_{sp} = [Pb^{2+}]^3[PO_4^{3-}]^2 = (3S)^3(2S)^2 = 108S^5$$

$$S = 2.37\times10^{-10}$$

So this is a sparingly soluble material and we have an exceptionally low solubility.

b) Calculate the solubility at pH 3.

Now you need to consider the protonation of phosphate that can occur. If we look back at the K_{sp} expression, we notice that it only contains lead ion and phosphate ion. Protonation of the phosphate will reduce the concentration of phosphate in solution, thereby causing more of the lead phosphate to dissolve based on Le Châtelier’s principle.

$$\begin{array}{lcl} Pb_3(PO_4)_2 \Leftrightarrow 3Pb^{2+} & + & 2PO_4^{3-} \\ & & \Updownarrow \\ & & HPO_4^{2-} \\ & & \Updownarrow \\ & & H_2PO_4^{-} \\ & & \Updownarrow \\ & & H_3PO_4 \end{array}$$

The problem with trying to solve this is that we do not know the concentration of phosphate (PO_4^{3-}) because it no longer relates directly to the amount of lead in solution. Once again, the way to approach solving this is to write two expressions for the solubility, one in terms of lead ion, the other in terms of phosphate species.

The situation for lead has not changed from part (a) of this problem, so we have the same expression for solubility for lead.

$$S = \frac{[Pb^{2+}]}{3} \qquad \text{or} \qquad [Pb^{2+}] = 3S$$

For phosphate, we know that the only source of phosphate is by dissolution of lead phosphate. If there was a way for us to find the total amount of all phosphate species in solution, we could relate that back to the amount of lead phosphate that had to dissolve. This leads to the following expression relating the concentrations of phosphate species to solubility:

$$S = \frac{[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]}{2} = \frac{[PO_4]_{TOT}}{2}$$

$$[PO_4]_{TOT} = 2S$$

But we also know the following:

$$[PO_4^{3-}] = \alpha_{PO_4^{3-}}[PO_4]_{TOT}$$

Since we were told the pH of this solution, we realize that we can evaluate the α-value and it's a fixed number. We can then substitute in from the solubility expression above to get:

$$[PO_4^{3-}] = \alpha_{PO_4^{3-}}(2S)$$

If we now substitute the terms for $[Pb^{2+}]$ and $[PO_4^{3-}]$ back into the K_{sp} expression, we get the following equation:

$$K_{sp} = [Pb^{2+}]^3[PO_4^{3-}]^2 = (3S)^3[\alpha_{PO_4^{3-}}(2S)]^2$$

$$K_{sp} = 108S^5(\alpha_{PO_4^{3-}})^2 = 8.1\times10^{-47}$$

We now need to evaluate $\alpha_{PO_4^{3-}}$ at a pH of 3. The form of the 1/α-value expression is as follows:

$$\frac{1}{\alpha_{PO_4^{3-}}} = \frac{[H_3O^+]^3}{K_{a1}\,K_{a2}\,K_{a3}} + \frac{[H_3O^+]^2}{K_{a2}\,K_{a3}} + \frac{[H_3O^+]}{K_{a3}} + 1$$

Substituting in for $[H_3O^+]$ and the K_a values gives an α-value of 2.315×10^{-14} at a pH of 3. Putting this value into the K_{sp} expression above gives a final solubility of:

$$S = 6.75\times10^{-5}$$

At this point, it would be worthwhile comparing the solubility in part (a) (no competing equilibria) to the solubility at pH 3.

(a) $S = 2.37\times10^{-10}$

(b) $S = 6.75\times10^{-5}$

Notice how the solubility is much higher at pH 3. This is reasonable since protonation of the phosphate ion was expected to increase the solubility. This trend points out an important aspect of the solubility of metal ions. Assuming that the anion of the solid is the anion of a weak acid, lowering the pH of the solution will cause a higher extent of protonation of the anion and increase the solubility of the solid.

In general, the solubility of sparingly soluble substances increases with the acidity of the water. It turns out that this is one of the principle concerns of acid rain. Acid rain into unbuffered natural waters raises the acidity (lowers the pH) of the water. The higher acidity causes solid metal salts and minerals in the lake or river bed to dissolve at higher levels. For example, there are lakes with poor buffering in which the impact of acid rain has increased the levels of dissolved aluminum ion (Al^{3+}). Aluminum ion is known to form a highly insoluble complex with hydroxide ion [$Al(OH)_3$, $K_{sp} = 2.20\times10^{-32}$]. Obviously the solubility of this complex is critically dependent on pH. At acidic pH values, it will dissolve because hydroxide is low. At neutral to basic pH, it will precipitate because the hydroxide level becomes high enough. Aluminum hydroxide is a very gelatinous solid that is sometimes used as a sticky flocculent in water treatment processes (undesirable impurities essentially stick to this material and slowly settle out with it). When the fish take the water through their gills (which are at a pH of 7.4) to remove the dissolved oxygen, the pH of the water increases and the aluminum ion now precipitates out as aluminum hydroxide. The gelatinous precipitate clogs up the gills of the fish and actually causes the fish to die of suffocation. The fish deaths that have occurred in some lakes heavily impacted by acid rain are attributable to this phenomenon.

c) Now you realize for the solution in part (b) that lead can form soluble hydroxide complexes. Incorporate these into the expression.

The scheme below shows the total set of reactions that occur in this solution.

$$\begin{tikzcd}
Pb_3(PO_4)_2 \arrow[r, leftrightarrow] & 3Pb^{2+} \arrow[d, Leftrightarrow] & + & 2PO_4^{3-} \arrow[d, Leftrightarrow] \\
& Pb(OH)^{+} \arrow[d, Leftrightarrow] & & HPO_4^{2-} \arrow[d, Leftrightarrow] \\
& Pb(OH)_2 \arrow[d, Leftrightarrow] & & H_2PO_4^{-} \arrow[d, Leftrightarrow] \\
& Pb(OH)_3^{-} & & H_3PO_4
\end{tikzcd}$$

The approach in this case is going to be analogous to what we just did for the protonation of the phosphate ion. We know the concentration of hydroxide because the pH is known. This enables us to calculate an $\alpha_{Pb^{2+}}$ value and incorporate that into the K_{sp} expression.

The next step is to write two expressions for the solubility, one in terms of lead species, the other in terms of phosphate species.

The equation in terms of phosphate is identical to what was just done in part (b).

$$S = \frac{[PO_4]_{TOT}}{2} \qquad\qquad [PO_4]_{TOT} = 2S$$

$$[PO_4^{3-}] = \alpha_{PO_4^{3-}}[PO_4]_{TOT} = \alpha_{PO_4^{3-}}(2S)$$

The equation for lead is as follows:

$$S = \frac{[Pb^{2+}] + [Pb(OH)^{+}] + [Pb(OH)_2] + [Pb(OH)_3^{-}]}{3} = \frac{[Pb]_{TOT}}{3}$$

$$[Pb]_{TOT} = 3S$$

$$[Pb^{2+}] = \alpha_{Pb^{2+}}[Pb]_{TOT} = \alpha_{Pb^{2+}}(3S)$$

Evaluation of $\alpha_{Pb^{2+}}$ is done by writing the ratio of Pb^{2+} over the total, taking the reciprocal so that there is a set of individual terms, and then using the K_f expressions for lead complexation with hydroxide to substitute in for each of the terms. The final equation for $1/\alpha_{Pb^{2+}}$ is shown below.

$$\frac{1}{\alpha_{Pb^{2+}}} = K_{f1}\ K_{f2}\ K_{f3}[OH^{-}]^3 + K_{f1}\ K_{f2}[OH^{-}]^2 + K_{f1}[OH^{-}] + 1$$

Evaluation of $\alpha_{Pb^{2+}}$ at a pH of 3 gives a value of 0.999984. So very little of the lead actually complexes with hydroxide, which should not be that surprising given the small amount of hydroxide ion in solution at pH 3.

Above we have expressions for $[Pb^{2+}]$ and $[PO_4^{3-}]$ that are in terms of α-values and S. These can be substituted into the K_{sp} expression to give the following:

$$K_{sp} = [Pb^{2+}]^3[PO_4^{3-}]^2 = [\alpha_{Pb^{2+}}(3S)]^3[\alpha_{PO_4^{3-}}(2S)]^2 = 8.1\times10^{-47}$$

$$8.1\times10^{-47} = 108S^5(\alpha_{Pb^{2+}})^3(\alpha_{PO_4^{3-}})^2$$

$$S = 6.75\times10^{-5}$$

If we compare this to the answer in part (b), it turns out that the two are the same. This means that so little lead complexes with the hydroxide ion at pH 3 that it does not lead to any increase in the solubility. If we were to make the solution more basic, complexation of lead by hydroxide would become more important. But also note that protonation of the phosphate would become less important, so the overall solubility is a balance between two processes that influence the solubility in opposite ways as a function of pH. What we might well observe for lead phosphate is that its solubility is smallest at some intermediate pH. At low pH, protonation of the phosphate increases the solubility. At high pH, complexation of lead with hydroxide increases the solubility. If we wanted to use precipitation of lead phosphate as a way to analyze lead (say by collecting the precipitate by filtration and weighing) or remove lead from a solution, we would need to perform a calculation over the entire pH range to find the best value for precipitation of the most amount of material.

d) Revisit problem (a). What is the actual solubility of lead phosphate in unbuffered water given that other equilibria will simultaneously occur?

This is a difficult situation because we know that hydroxide complexes of lead can form and that protonation of phosphate can occur, but it does not seem like we can use α-values because we really do not know the pH. The best approach might be to try some simplifying treatments to see if anything will work.

One thing we could do is assume that the pH of the water is 7, and that dissolving of the lead phosphate does not change it. If that were the case, we should evaluate $\alpha_{PO_4^{3-}}$ at pH 7 to see what fraction of the phosphate stays in this form. Evaluation of $\alpha_{PO_4^{3-}}$ at pH 7 gives a value of 1.62×10^{-6}. This means that only a small fraction of the phosphate species will exist as PO_4^{3-} and more of it will be protonated. The protonation has the possibility of changing the pH enough from 7 to make a difference. Similarly, if we evaluate $\alpha_{Pb^{2+}}$ at a pH of 7 we get a value of 0.864, so some lead complexes as well. If we go ahead and plug in these values into the K_{sp} expression:

$$K_{sp} = [Pb^{2+}]^3[PO_4^{3-}]^2 = [\alpha_{Pb^{2+}}(3S)]^3[\alpha_{PO_4^{3-}}(2S)]^2 = 8.1\times10^{-47}$$

$$S = 7.49\times10^{-6}$$

This is a small number, but the problem is that it's an appreciable number compared to the concentration of H_3O^+ at a pH of 7. This means that the pH will probably change enough from 7 to make a difference in the solubility.

It turns out that we cannot make any simplifying assumptions in this case. In this event, we need to solve a series of simultaneous equations. If we write all the unknown species, you find that there are a total of ten for this solution.

$[H_3O^+]$
$[OH^-]$

$[Pb^{2+}]$
$[Pb(OH)^+]$
$[Pb(OH)_2]$
$[Pb(OH)_3^-]$

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

We may be able to eliminate some of these as insignificant, since it might be unlikely that we would get any significant levels of hydroxide complexes or protonation of phosphate besides the first species ($Pb(OH)^+$ and HPO_4^{2-}) . Even if that is the case, we would still need to solve a set of simultaneous equations.

What would be the ten equations? Eight of them are equilibrium constant expressions needed to describe the reactions taking place.

K_{sp} K_{a1} K_{a2} K_{a3} K_{f1} K_{f2} K_{f3} K_w

One is the mass balance, which involves the relationship between the two solubility expressions we can write for this solution.

$$S = \frac{[\mathrm{Pb}]_{\mathrm{TOT}}}{3} \qquad\qquad S = \frac{[\mathrm{PO_4}]_{\mathrm{TOT}}}{2}$$

$$\frac{[\mathrm{Pb}]_{\mathrm{TOT}}}{3} = \frac{[\mathrm{PO_4}]_{\mathrm{TOT}}}{2}$$

The final equation is the charge balance:

$$[\mathrm{H_3O^+}] + 2[\mathrm{Pb^{2+}}] + [\mathrm{Pb(OH)^+}] = [\mathrm{OH^-}] + [\mathrm{Pb(OH)_3^-}] + [\mathrm{H_2PO_4^-}] + 2[\mathrm{HPO_4^{2-}}] + 3[\mathrm{PO_4^{3-}}]$$

Next step? HAVE FUN!

Suppose you are given a question that asks whether a precipitate of a particular compound will form?

This is actually a common question to ask. Many solutions have a complex mix of metal cations and anions. It is quite likely that some of these combinations have small K_{sp} values, and so are sparingly soluble. In this case, we might be interested to understand ahead of time whether it is likely that a precipitate will form in the solution. Another common example is that many metals form insoluble hydroxide complexes. We therefore may want to know whether a change in pH is going to cause a dissolved metal ion to precipitate out of solution.

The thing to keep in mind is that the solubility product can never exceed the value of K_{sp}. For example, suppose you were to consider the species silver carbonate (Ag_2CO_3). The solubility reaction and K_{sp} expression is shown below.

$$Ag_2CO_3 \Leftrightarrow 2Ag^+ + CO_3^{2-}$$

$$K_{sp} = [Ag^+]^2[CO_3^{2-}] = 7.7\times10^{-12}$$

Suppose we had a process that would lead to a solution with silver and carbonate ions in it. Suppose that we were also able to calculate the starting value of each ion that we expected in the solution.

If we expected a concentration of silver of 5×10^{-4} M and a concentration of carbonate of 1×10^{-3} M, would a precipitate form? What we need to do is take these values and put them into the form of the K_{sp} expression. Since these are not likely to be equilibrium concentrations, instead of calling this expression K, we use the notation Q.

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

$$Q = [5\times10^{-4}]^2[1\times10^{-3}] = 2.5\times10^{-10}$$

What we now need to do is compare the magnitude of Q (2.5×10^{-10}) to the magnitude of K_{sp} (7.7×10^{-12}). If Q is greater than K_{sp}, a precipitate will form since the solubility product term can never exceed K_{sp}. If Q is less than K_{sp}, no precipitate will form (this is not yet a saturated solution).

Since $2.5\times10^{-10} > 7.7\times10^{-12}$, a precipitate will form in this case. Not all of the silver and carbonate will precipitate out of solution. Instead, the concentrations will be lowered so that the concentrations exactly satisfy the K_{sp} expression.

Another common question is whether it is possible to quantitatively precipitate (99.9%) of one metal cation in the presence of another.

If we assume that the concentrations of the metal ions in the solution are known, we can calculate the concentration of the precipitating anion that is the highest possible value that will not cause any precipitation. We can also calculate the concentration of the precipitating anion that is needed to precipitate 99.9% of the metal ion.

For example, suppose we had a solution that was 1×10^{-3} M in Pb^{2+}, and we wanted to try to precipitate 99.9% of the lead as its bromide salt. The relevant reaction and equilibrium expression is shown below.

$$PbBr_2 \Leftrightarrow Pb^{2+} + 2Br^-$$

$$K_{sp} = [Pb^{2+}][Br^-]^2 = 6.2\times10^{-6}$$

We could calculate the concentration of bromide ion that is the highest one at which none of the lead ion will precipitate. This will be the value where the solubility product exactly equals the value of K_{sp}.

$$K_{sp} = [Pb^{2+}][Br^-]^2 = 6.2\times10^{-6} = (1\times10^{-3})[Br^-]^2$$

$$[Br^-]^2 = 6.2\times10^{-3} \qquad [Br^-] = 7.87\times10^{-2}$$

Any concentration of bromide higher than 7.87×10^{-2} M will cause some of the lead to precipitate as lead bromide. Suppose we had another metal ion in solution besides lead, and this other ion formed a bromide complex that was much less soluble than lead bromide. We could calculate the concentration of bromide needed to precipitate 99.9% of this other ion, and then compare that value to 7.87×10^{-2} M. If the value was less than 7.87×10^{-2} M, it is theoretically possible to precipitate this other ion in the presence of lead. If the value is greater than 7.87×10^{-2} M, lead bromide will start to precipitate and interfere with the separation.

If we want to precipitate 99.9% of the lead, that means that 0.1% remains. Since the lead concentration was initially 1×10^{-3} M, the final concentration of Pb^{2+}after 99.9% precipitates will be 1×10^{-6} M. We can plug this into the K_{sp} expression to solve for the concentration of bromide that is needed to precipitate 99.9% of the lead.

$$K_{sp} = [Pb^{2+}][Br^-]^2 = 6.2\times10^{-6} = (1\times10^{-6})[Br^-]^2$$

$$[Br^-]^2 = 6.2 \qquad [Br^-] = 2.49$$

So a bromide concentration of 2.49 M would be needed to precipitate 99.9% of the lead ion as lead bromide in this solution. This is a reasonably high concentration of bromide ion. We could presumably get that high a level with a solution of hydrobromic acid. The solubility of sodium bromide might be as high as this, but it is getting to be a bit of a high concentration of bromide to precipitate out the lead.