# INSTRUCTOR'S MANUAL – SEPARATION SCIENCE
## EQUILIBRIUM UNIT

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The problem sets on chemical equilibrium can be used in at least two different manners. The primary intent is to use these as a set of in-class, collaborative learning exercises. Groups of 3-4 students work together in discussing and working through the problems. When using the problem sets in this manner, the instructor must actively facilitate and guide students through the material. This manual will guide instructors through each of the problem sets, identifying possible student responses to the questions and the response and activities of the instructor during the progression of the problem.

An alternative to the use of the problems in class is to assign them as out-of-class activities, preferably done as a group activity among students or as a peer-led learning activity (REF). The accompanying text that goes with each problem provides a detailed discussion of each step of the thought process of solving it, such that students could work back and forth between the problem and text on an iterative basis to gain an understanding of the material.

There is no perfect way to assemble groups for such collaborative learning activities. I gather information on the first day of class (year in college, major, prior chemistry courses) and then use this to set groups of 3-4 students that start on the second day of class. I try to make the groups as heterogeneous as possible and they work together for the entire semester. Another strategy is to assign groups for a shorter period of time that might encompass completion of a specific topic or unit, and to then create new groups for the next unit. One other possibility is to have different groups every day of class. Since it is important for groups to work well together, having new groups every day may be less successful than allowing groups to work together for more extended periods of time. I would recommend that the instructor assign groups rather than allowing the students to pick their own. This avoids the potential problem of friends who want to be in the same group but who then do not work well together or stay focused on the assigned task. It also avoids the problem of the student who is left without a group at the end of the selection process, something that can be especially problematic if it is a member of a minority group. When using collaborative groups, it is also important for the instructor to monitor the functioning of the groups and to step in to address either dysfunctional groups or the recalcitrant individual within a group. (Ref articles on group learning). Peer-evaluation processes are often used by instructors who employ group activities as a way of assessing how well groups are working (REF).

I also expect the groups to meet outside of class for any homework assignments, something that is aided because I am at a residential college. An alternative to this is to schedule a room on the evening before a homework assignment is due and encourage them to come to this place and work in any arrangement they wish on the homework. I have run such sessions for several years now and attend them as a facilitator (one result is that it has cut down considerably the individual traffic to my office seeking help on the homework problems) and it has been an excellent way to promote collaboration among the students.

The instructor has an especially important role to fulfill during such group activities. I have observed that the more engaged that I am in the process in helping to guide the students through the material, the more effective the learning that occurs. In most instances, it seems that the students are initially stumped by the question, that they begin to explore things that they do know that might apply to answering the question, and that help from the instructor either by letting them know that they are on the right track or by suggesting another direction in which to take their thinking is necessary. As they begin a question, I roam around the room listening in on conversations and looking over their shoulders at what might be written in their notebook. If I hear something interesting, I indicate that to the group. If I see that someone has written something interesting and relevant in their notebook, I tell other group members that they ought to talk with this individual about what they have written, and that the individual should explain to the other group members why they wrote that down. If I hear a group going entirely in the wrong direction, I probe them on why they are heading in that way and then offer suggestions about things to consider that will set them off in the right direction. When all groups have realized an important point, I call time out and summarize the concept at the board. Then I send them back to continue with the next part of the problem. Most of the problems are handled in such an iterative manner where the students work through some important part of the problem, I summarize it at the board when they have developed the concept, and then they return to the next part of the problem. Occasionally a group will just not see something, whereas every other group has gotten the point, and it may require a direct intervention from the instructor with that group to explain the concept. Similarly, there are times when I call their attention to the board to summarize a point when one of the groups still has not gotten the concept but waiting would slow down the remainder of the class to an unacceptable level.

When using these materials, I want the students to discuss and discover the concepts inherent in the problems, so they do not have the text when working on the problems. After they have completed a particular problem, I then give them a copy of that portion of the text (everyone is instructed to have a three-ring loose-leaf binder of a certain minimum thickness that will accommodate the entire text that will be passed out in increments as the semester develops). The text thoroughly goes through the thought process for solving each problem and I encourage the students to read it over that evening to reinforce the concepts developed in class that day. I also give homework problems designed to reinforce the concepts developed in class.

## Overview: Significance of chemical equilibrium

**You are a chemist involved in developing a new product for a textile company. As part of the new process, a suspension of the compound lead phosphate will be used to treat the surface of the textile. The lead phosphate will end up in the waste effluent from your plant. This effluent will be discharged to the local municipal waste water treatment plant. Unfortunately, from your standpoint (fortunately, from the standpoint of an environmentalist) the waste water treatment plant faces strict requirements on the amount of lead that is permitted in their end products. (A waste water 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 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?**

I use this problem on the first day of class to show the types of problems we will be addressing by the end of the equilibrium unit and to set the stage for the different processes (acid-base reactions, formation of water-soluble metal complexes, solubility of a sparingly soluble salt) that we will be using over the term. It allows me to introduce the different tables of equilibrium constants that we will use over the term and to show how these different processes usually occur simultaneously in real systems (e.g., environment, living organisms) and that we need to develop the expertise to handle these real systems.

The in-class problems on chemical equilibrium are intended for a student who has taken general chemistry and had a previous introduction to the topics of chemical equilibrium, acid-base chemistry, solubility equilibria, and complex-formation equilibria. I usually find that, while students have been introduced to these topics, their understanding is still marginal and they need a refresher on the concepts that we had hoped they would learn in the general chemistry course.

Before passing out the first problem set to the class, I spend a relatively brief period of time discussing with them some background information on chemical equilibrium. Using the generalized equation shown below, I ask them what things we might say about the equilibrium state of this reaction.

$$aA + bB = cC + dD$$

Usually it does not take too long before students in the class indicate that one characteristic of the equilibrium state is that the concentrations of the chemicals remain fixed. I point out that viewing the system at the macroscopic level (i.e., concentration), we would define equilibrium as a static state. Students also offer up that another thing that characterizes the equilibrium state is that the rate of the forward reaction is equal to the rate of the reverse reaction. Therefore, at the microscopic level of individual species, we find that the system is dynamic and species are actually changing their identities.

I then ask if someone would provide me with the equilibrium constant expression, and many of the students can usually give the answer I am looking for.

Equilibrium constant expression

I then ask the person who provided the answer (and also throw this out more generally to the class) whether they are so certain that this is the correct expression that they would be willing to stake their entire grade in the course on it – if it's correct, they receive an A for the course and do not have to attend; if it's incorrect, they receive an F for the course and also do not have to attend (one bright side (?) to taking the offer no matter whether the answer is correct or not is that they don't need to attend the class). The students immediately sense that the answer is likely not correct (why the offer if it is correct?), but rarely do they come up with why (we either do not cover the concept of activity in general chemistry or if we do, since we then do all the calculations using terms for concentration, they forget this).

This allows me to introduce the concept of activity, and how equilibrium constant expressions are correctly written in terms of activity and not in terms of concentration. I write something to the effect of the following on the board, and ask them if they could identify an A species in the picture that might be regarded as "inactive". They readily identify the one shown in bold as an "inactive" form of A.

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

I then ask them why they think equilibrium constant expressions and calculations in general chemistry were always done using concentrations rather than activities. They are usually stumped by this and I do not let them spend too long thinking about it. I point out that chemists rarely shy away from difficult calculations, so it is likely something different than that, and indicate that in many instances we simply do not know how to accurately express the activity of a chemical, so that using concentration as a approximation for activity is the best we can do. I also point out that since any equilibrium calculation that uses concentrations is at best an approximation of the system, that it will reasonably allow us to make other approximations when doing equilibrium calculations that will not compromise the outcomes. Furthermore, I point that from the perspective of an analytical chemist, what we usually care about is whether a reaction goes to completion or not (how large is K) or whether a reaction hardly occurs at all (how small is K), and that many analytical procedures are predicated on using systems that have either exceptionally large or exceptionally small values of K so that we can be assured that we are measuring all of what we desire or that no other substance is interfering in the measurement.

Realizing that we will use concentration as an approximation of concentration, I then ask them to consider whether this approximation is more valid at high or low concentration. I encourage them to talk to their neighbors (they are not yet in assigned groups) and then take a poll of the class. Usually it seems that most students think the approximation will be better at high concentration. I go back to my example of As and Bs that is still on the board and ask them to put in more A species and tell me whether it will lead to more or fewer inactive forms. The students then realize that the concentration is a better approximation of activity at lower values. I also point that those methods we do have for rigorously determining activity also break down at higher concentrations, so that they rarely help us in the cases where we would most benefit by using activity instead of concentration. I also point out that while we could get more accurate answers for systems at low concentrations, the use of concentrations is valid enough that all the extra work to use activities is often not warranted.

With this background, I indicate that throughout the remainder of the course we will always use concentration as an approximation of activity, that with our use of concentration we must always keep in mind that we are obtaining "ballpark" figures for the amounts of species in a solution that is at equilibrium, and that because we are only obtaining ballpark values, it will allow us to use other approximations to simplify many of the calculations.

Occasionally throughout the unit I like to ask them to just generally assess the extent to which the utilization of concentrations as an approximation of activities is valid for the system described in a particular problem.

With this background the students are ready to divide into their groups and start on the first problem on the in-class set. When I have passed out the first set, and asked them to read the first question, I point out that the concentration provided in this (0.155 M) and all subsequent problems refers to the initial concentration of species in solution (rigorously referred to as the Formality of the chemical) rather than the equilibrium concentration – that the is prepared with a certain concentration but then proceeds to equilibrium such that the final concentration will be different than the initial concentration.

***In-class Problem Set #1***

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

As students begin to ponder this question, and as the instructor begins to circulate among the groups, some things to ask are:

*What is ammonia? Is it an acid or a base? Is it strong or weak?*

After about five minutes, everyone should have identified ammonia as a weak base and have the correct chemical formula. I write the correct chemical formula on the board and that it is a weak base. With this information, they can next be asked:

*What does ammonia react with? Can you write the correct chemical equation representing this reaction?*

Students may not recall that the solution contains water and that the water is necessary in the proper reaction. Once groups have written the correct reaction, I call timeout, write it on the board, and indicate how we can use this to describe the general reaction of a base – a base reacts with water to produce its protonated form and hydroxide ion. I then ask the following question:

*What is the K expression for this equation?*

Which invariably leads to the question:

*Should [$H_2O$] appear in this expression?*

Using a timeout, we spend about five minutes as a class discussing what [$H_2O$] is and why it shouldn't appear in the equation. It may be worth mentioning other species that do not appear in the *K* expression such as other solvents and solids.

*What subscript do we attach to this K?*

Students usually realize that it is $K_b$. The equilibrium constant tables that we use in the course only have $pK_a$ values so there is only a value for the ammonium ion. This leads to the following questions:

*What is the relationship between $K_a$, $K_b$, $pK_a$, and $pK_b$? What reaction is the $K_a$ expression describing? What is the relationship between Kb, $K_w$ and this reaction?*

Allow the students several minutes to discuss this and to try to figure out the relationships. At some point in the discussion the concept of a conjugate pair will come up and this should be summarized by the instructor at the board. Also, the relationship between pK and K will come up in the discussion. Some students will remember that Ka times Kb for a conjugate pair equals Kw (or at least remember that there is some connection between these three equilibrium constants even if they do not remember the exact relationship). When groups get to the correct expression, I ask them to:

*Prove that Ka times Kb for a conjugate pair equals Kw.*

Some groups immediately write the two K expressions and multiply them together. Others need prompting to do this. It is then worth summarizing at the board the proof that Ka times Kb for a conjugate pair equals Kw. Students can then be asked:

*What is the value of $K_b$ for ammonia? What does the magnitude of $K_b$ tell you about the strength of ammonia as a base?*

It may take the groups a few minutes arrive at a $K_b$ value that they all agree on. They should be able to recognize that a small $K_b$ value implies that the base is weak and therefore not very reactive. This is a good time to talk about what the magnitude of any *K* value tells you about the reaction. At this point, students can now perform the actual calculation.

*Instruct students to create a table of concentrations below each species in the reaction where the first row is the starting concentration and the second row is the concentration at equilibrium. Ask them just to fill in the first row.*

> Groups usually correctly write the concentrations of ammonia and ammonium, but will probably have a “0” as the initial concentration of $OH^-$.

*Is the initial concentration of $OH^-$ really 0?*

> Students will remember that water dissociates and it is worth spending a brief amount of time discussing the auto-protolysis of water and how the initial concentrations of both $OH^-$ and $H_3O^+$ must be $10^{-7}$ in order for $K_w$ to have a value of $10^{-14}$.

*Instruct them to fill in the next row on the table.*

> Students should very quickly identify that the concentration of $NH_3$ will decrease by $x$ while the concentration of $NH_4^+$ and $OH^-$ will increase by $x$.

*What happens if these values were substituted directly into the $K_b$ expression*?

> They will probably recognize that this would result in having to solve a quadratic.

*Ask the students to think about the magnitude of x as it might compare to the initial concentration of ammonia and the initial concentration of hydroxide.?*

> Most realize it will be small compared to the initial amount of ammonia and large compared to the initial amount of hydroxide. It is helpful to then briefly explain why these two conclusions are valid.

*If x is small relative to the initial concentration of ammonia and large relative to the initial concentration of hydroxide, are there any approximations that can be made?*

> Groups will usually realize right away that the value of x can be ignored relative to the amount of initial ammonia and that the initial amount of hydroxide can be ignored relative to x. It is then worth summarizing these conclusions and explaining that we will use a 5% or less criteria throughout the semester to determining whether simplifying approximations are valid. I usually remind them of our overall approximation in which we are using concentration instead of activity and ask them to consider whether the use of concentration is truly warranted for an initial ammonia concentration of 0.155 M.

*What is the final concentration of $OH^-$?*

*Are the two approximations valid?*

> Some groups may need to be reminded how to calculate a percent.

*What is the relationship between $OH^-$ and pH?*

*What is the pH of the solution at equilibrium? Is it basic and does the value seem about right given the magnitude of the Kb value? What would we expect for a pH if the Kb was smaller and what would we expect if the Kb was larger?*

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

Before beginning this problem, spend a few minutes talking about nomenclature of acids, bases, cations and anions, including the suffixes that are used to denote negatively ("ate", "ide", "ite") and positively ("ium") charged species.

*Write the correct chemical equation that represents this solution at equilibrium.*

Allow the students about ten minutes to get started on this problem. Many students may be tempted to have both pyridine and pyridinium appear as reactants in the same chemical equation. Talk about the possibility of having two expressions representing this system. Groups are then usually able to write both the Ka and Kb expressions that could be used to describe the system. Sometime during this discussion the students need to think about the following two questions:

*What happens to the pyridinium chloride when dissolved in water? What is the role of* $Cl^-$ *in the solution?*

Talk for about five minutes about spectator ions and their role in the system.

*Instruct the students to pick one equation (either Ka or Kb) and use it to find the pH of the solution using the system established in problem 1.*

It may take them a while to arrive at a pH that they are satisfied with. Some may need a reminder that there are initial amounts of both pyridine and pyridinium. If some groups finish before others instruct them to try finding the pH using the other equation.

*Are they two pH values the same? Is this a surprise?*

*How does the magnitude of* $K_a$ *compare to the magnitude of* $K_b$*? What does this tell us about which equation we should use?*

Discuss how both reactions cannot be going towards product at the same time, so there must be one expression that more accurately represents this system.

*What is the relationship between the two species present?*

Talk for about fifteen minutes about conjugate pairs and buffers. Talk about what sorts of factors influence the buffer capacity of a system. Introduce the Henderson-Hasselbalch expression. Discuss how by examining the form of the Henderson-Hasselbalch equation, we can explain why diluting a buffer does not lead to a change in pH (unless the solution becomes excessively dilute – which then is no longer really a buffer).

*Is the pH found using the Henderson-Hasselbalch expression the same as the one found before?*

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

*Is anilinium an acid or a base?*

After about ten minutes everyone should have the correct chemical equations representing this system. Some students may identify iodine as a spectator ion and some may write out the reaction of iodine with a proton. Some students may be tempted to say that the presence of HI will affect the acidity of anilinium.

*What is the pH of this solution?*

After about ten minutes the students should have all calculated a pH for this system. They should be able to identify this as a straightforward problem based on the procedure developed in problem 1. They may need to be reminded to use approximations.

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

*Is ethylamine an acid or a base? What is its chemical formula?*

After a few minutes the groups should have identified the species as an acid or base. It may be helpful at this point to introduce abbreviations for the species (e.g., Hcba = chlorobenzoic acid) present that take into account their acidic or basic properties that will simplify writing the reaction and equilibrium constant expression.

*What happens when we add an acid to a base?*

Students usually realize that neutralization occurs.

*What is the correct reaction to express the neutralization that occurs? Write the $K_n$ expression for this reaction?*

It should take the students no more than five minutes to correctly answer both of these questions.

*Do we have a table of Kn values?*

*Since we do not, is there a way we could construct the Kn reaction by adding together a series of reactions for which we do know the K values?*

*In general, if a reaction can be broken down into steps, how do we calculate the K value for a net equation based on the K values for the steps?*

Most likely a few students will recall that *K* values are multiplied together to find a *K* value for the net equation.

*Based on this relationship, write an expression for $K_n$ in terms of values we know.*

All of the groups realize that the $K_a$ and $K_b$ expressions are needed, but most ignore the H3O+, OH- and H2O in these reactions and initially believe that Kn = Ka x Kb. If so, ask them to evaluate the value for Kn using this expression. Finding that the value is small:

*What does it mean if $K_n$ is quite small and does this make sense based on your knowledge of neutralizations?*

Some students may not be bothered by the small $K_n$ because it came from the reaction of a weak acid with a weak base.

*What about the reaction involving $H_2O$ that is also occurring in the solution?*

After a few minutes students should identify the reaction as the opposite of the $K_w$ reaction. They will probably need to be reminded that when the opposite of a reaction with a known $K$ is occurring, you multiply by the inverse.

*What is the expression for Kn and what is the actual value of $K_n$ in the problem. In general, how can we predict the magnitude of $K_n$?*

Spend about ten minutes talking about $K_n$ values in general. When will $K_n$ be big? What would it take for $K_n$ to be small? Point out that Kn will always be large when either the acid or base is strong.

*Groups can then be instructed to set up a table of values under the neutralization reaction that show the initial concentrations and to construct other appropriate rows under that (e.g., equilibrium concentration, etc.)*

Most groups often subtract x from the initial amounts of both reactants. If so, it helps to ask:

*What should x be when K is large?*

Groups soon realize that x would be large and that a large K means that the reaction will go to completion. Indicate that the second line in the table should be the concentrations present in solution after the reaction has gone to zero.

*What are the concentrations of the four species once the reaction has gone to completion?*

One of the values in this line will be 0 and it is useful to ask whether this value could actually be zero. Groups will realize that it cannot and must be a finite number. The concept of a back reaction occurring for a reaction that goes to completion can be introduced.

*Is there any substantial back reaction?*

Must groups realize that the back reaction must be small for a reaction with a large K. They can now write the third line of the chart, which has terms for the concentrations of each species at equilibrium.

*Groups are now asked to calculate the pH for the solution?*

Most groups see that there is extra chlorobenzoic acid and use this extra amount with its Ka expression to calculate a pH. Rarely do the students see that appreciable amounts of chlorobenzoic acid and the chlorobenzoate anion exist such that this constitutes a buffer with appreciable quantities of a conjugate pair. At this point I usually like to go up to the board where I have written the reaction and say let's circle all those species that we have appreciable amounts of. Prompting that there are appreciable amounts of chlorobenzoic acid and its conjugate anion usually eventually triggers the realization that it is a buffer. It is worth mentioning that neutralization reactions frequently result in buffer solutions.

At this point, the groups can calculate the pH using the Henderson-Hasselbach expression for the chlorobenzoic acid. They can also calculate the pH by substituting the amounts of aniline and anilinium obtained from the neutralization reaction into its corresponding Henderson-Hasselbach expression. We then discuss why both values must be identical if we have done the problem correctly.

**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 nitrophenol (2-).**

Since this is just another neutralization reaction, the groups can usually advance through the following steps with minimal prompting.

*Which is the acid and which is the base?*

*What is the chemical equation representing this system at equilibrium?*

*What is $K_n$ for this neutralization? Does it go to completion?*

In this case, the value of Kn is small and most groups realize that they know how to do a set up a calculation for a reaction with a small K value.

*What assumptions can we make? What is the value of x for this system?*

*What do we have in the solution when it has reached equilibrium?*

*Which conjugate pair should we use to calculate the pH? Does it matter?*

It is useful to have every group or different groups calculate the pH using the two different sets of conjugate pairs to show that the pH is the same for each of the two.

*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-axis).**

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

*What is the initial pH of the solution?*

It should take the groups a few minutes to calculate the initial pH of the system. Point out after that this is a solution of a weak base so the initial pH being basic is not a surprise.

*What happens when we add 5 mL of 0.1 M HCl?*

Allow the students a few minutes to think about what will happen then spend some time discussing the neutralization and conversion of butyl amine to butyl ammonium, leading to the formation of a buffer. Talk about how the concentration of butylamine will change with each addition of HCl, but if we use moles we can ignore the change in volume (consider the form of the Henderson-Hasselbalch and how each component of the buffer is in the same volume so a mole ratio is the same as the ratio of molarities).

*Sometimes students ask about the amount of butyl amine that reacted to produce butyl ammonium in the initial solution (0.002 moles of the 0.030 moles in solution) and whether they should start with 0.030 or 0.028 moles of butyl amine. Or you may wish to raise this as a question for the class.*

Discuss the fact that 0.002 moles of hydroxide ion (a strong base) is produced in the initial solution and that this reacts first with 0.002 moles of the HCl. Once the hydroxide is used up, the butyl amine begins to react.

*What will happen after an additional 5 mL of 0.1 M HCl is added?*

Have students make a table to keep track of the moles of each species present at each step up to 30 ml of added titrant. It may take the students about fifteen minutes to correctly set up the table and decide how to fill in each column.

*What happens after the addition of 30 mL of 0.1 M HCl? How do you find the pH at that point?*

Students should recognize that once all of the butylamine has been used up there is no longer a buffer. Talk about the equivalence point and various methods of indicating the progress of a titration. Students may be tempted to calculate the pH by evaluating how much of the excess strong acid has been added, but should recognize that only butylammonium is present and so the question simply becomes a weak acid problem. It may take them about ten minutes to realize this and calculate the pH.

*What is the pH when 35 and 40 ml of titrant has been added?*

Most groups readily see that there is now extra strong acid that will be most important in determining the pH.

*What would a plot of pH vs. mL of acid added look like?*

Have the students make a plot of the titration curve and point out distinguishing features such as the equivalence point, buffer region, and the inflection point. Discuss how the plot would look if the base had a p$K_a$ of 8. How would it look if the p$K_a$ was 6?

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

Students may have some trouble recognizing that calculating the *x* value for the $K_a$ expression at the equivalence point can provide them with information regarding how much butylamine is in the system at the end of the titration.

***In-class Problem Set #3***

**1. Calculate the pH of a 0.127 M solution of ascorbic acid.**

Groups quickly see that ascorbic acid has two pKa values.

*What does it mean if something has two p$K_a$ values? What two chemical expressions represent the two equilibria that are occurring?*

Students may be tempted at first to ignore the presence of a second p$K_a$ value, but encourage them to investigate what it implies about the acid. Once they have realized that there are two dissociable protons, ask them to write the correct chemical expressions making sure to include the proper charges. This should take about ten minutes. Some groups then use Ka1 to solve for a concentration of H3O+ and Ka2 to solve for a second value of H3O+. If they do so, they realize that the second value is much smaller than the first. But they also apparently have a solution with two different concentrations of H3O+.

*What do we know about [$H_3O^+$] in the two expressions?*

Remind the students that since only one pH value can be measured, the concentration of $H_3O^+$ in the two equations must be equal.

*Write an expression for [$H_3O^+$] in terms of the ascorbic acid species.*

Students should have no trouble recognizing that for every one mole of ascorbic acid that is deprotonated, one mole of $H_3O^+$ is produced, but they may have some trouble understanding that for every one mole of the fully deprotonated ascorbate formed, two moles of $H_3O^+$ are formed.

*What is x for the $K_{a1}$ expression?*

*What is x for the* $K_{a2}$ *expression? What does this tell us about the second reaction?*

Students should realize very quickly that the second $x$ value is equal to the $K_{a2}$. With an $x$ value this small, they should recognize that the second reaction is insignificant and that solving for the pH using just the p$K_{a1}$ is sufficient. Spend several minutes talking about the general differences between p$K_a$ values and when the second one can be ignored. Make sure students are clear that this was an example that began with the fully protonated species of a polyprotic acid.

*What is the pH of the solution?*

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

Before starting this problem, talk about nomenclature for polyprotic acids. For example:

| | |
|---|---|
| $H_3PO_4$ | phosphoric acid |
| $NaH_2PO$ | sodium dihydrogen phosphate |
| $Na_2HPO_4$ | disodium hydrogen phosphate |
| $Na_3PO_4$ | sodium phosphate |

*What are the two equilibria are occurring in this solution? What are the chemical expressions representing them?*

Students may be tempted to initially say that the presence of sodium will result in the formation of sodium hydroxide which could shift the equilibrium. Remind them when ions can be assumed to be spectators. It should take the students about five minutes to write the correct expressions and recognize that they correspond to the $K_b$ expressions. Make sure that the students determine the $K_{b1}$ and $K_{b2}$ values from the correct $K_a$ values.

*Can the second expression be ignored?*

Students should recognize that a large difference in $K_b$ values implies that the second reaction is negligible. Point out that this is just the opposite of the previous scenario; in this case we started with all of a deprotonated polyprotic acid.

*What is the pH of the solution?*

**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.**

*What sort of reaction is occurring?*

After several minutes the groups should recognize that the malonate can be protonated as it is neutralized by the strong acid.

*Since a neutralization reaction is occurring, what is $K_n$?*

Students should immediately recognize that since HCl is a strong acid $K_n$ will be large and the reaction can be assumed to go to completion.

*What is in the solution after the neutralization occurs?*

After several minutes, the students should recognize that once the HCl has converted some of the malonate, a buffer is formed. Make sure that they convert the amounts into moles since dilution will occur. They may be tempted to incorporate the fully protonated malonic acid into the equilibrium but remind them that the $K_a$ values differ so much that formation of malonic acid is negligible.

*Calculate the concentration of malonic acid at equilibrium to ensure that it is negligible.*

*Which $K_a$ value should be used in the Henderson-Hasselbalch equation?*

Students should recognize that since the $K$ value that relates the two species forming the buffer is $K_{a2}$, they should use that value in the Henderson-Hasselbalch equation.

*What is the pH of the solution?*

**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.**

If groups are having trouble getting started on this problem, encourage them to write all of the reactions corresponding to the phosphate species and identify (circle) the species that are initially present. When groups have written the proper reactions, write them on the board and circle the two species that are present in the initial solution.

*What type of reaction is going to occur? What type of species is phosphoric acid? What type of species is phosphate?*

Students should recognize very quickly that phosphoric acid is an acid and phosphate is a base (but not conjugate pairs) and that these two can neutralize each other leading to the formation of intermediate species.

*Write the neutralization reaction that will occur.*

Write this reaction on the board once the groups have written it.

*What is the $K_n$ for this reaction? Does it go to completion?*

Students should not have trouble with this question at this point.

*What is present after the initial neutralization?*

Students should have no trouble calculating the concentration (or moles) of all of the phosphate species present after neutralization, and should recognize that one of the reactants is in excess. Encourage them to rewrite the equations corresponding to this system and circle all of the species present.

*What will happen next?*

Students may struggle with the next step of this problem. They may be tempted to assess the extent of back-reaction. They may need help seeing that another neutralization reaction can occur. If they are tempted to treat this system as a buffer, ask them which one they would use to calculate the pH in order to get them thinking more about species present. Spend about five to ten minutes discussing this.

*Write the neutralization reaction that will occur.*

Write this reaction on the board once the groups have written it. Remind groups to carry forward any amounts that were already produced in the first neutralization reaction as the initial concentrations for the second neutralization reaction.

*What is the $K_n$ for the neutralization reaction that will occur with the remaining species?*

Students may have trouble knowing which $K_a$ and which $K_b$ to use when calculating the $K_n$. Encourage the students to take their time with this step.

*What is present after the second neutralization reaction? Are there any further neutralization reactions that can occur with those species that are now in solution? What is the pH?*

Remind students to keep the stoichiometric coefficients in mind when carrying out these calculations. It should take students about ten minutes to complete this problem. Spend some time at the board to summarize the entire calculation and describe why it makes sense for the system to eventually get to the state where only one reaction is needed to calculate the pH. It can also be helpful to have groups use the major species and calculated pH to calculate the concentration of the other species in solution. Writing the final concentrations of everything in solution further demonstrates how the other reactions and other species are insignificant compared to the two major species.

**5. Calculate the pH of a 0.240 M solution of sodium bicarbonate.**

*Write the appropriate reactions that incorporate the bicarbonate species?*

Give the students about five minutes to begin working on this problem. They will probably identify sodium bicarbonate as both a weak acid and a weak base.

*Write an expression for $H_3O^+$ in terms of the other species?*

Groups should eventually recognize that for every one mole of $CO_3^{2-}$ formed, one mole of $H_3O^+$ was formed, and for every mole of $H_2CO_3$ formed, one mole of $H_3O^+$ was used up. They may need some prompting to think about what will occur for the H2CO3. Once the groups have the correct expression, spend time at the board going through the algebraic manipulation that incorporates this expression into the Ka expressions to arrive at the formula that can be used to calculate the pH.

At the end of this problem, it is beneficial to most students to spend several minutes generalizing the methods used in the last five problems. Address how to approach problems of each of the following starting species: a fully protonated acid, appreciable amounts of neighboring intermediates, appreciable amounts of varying intermediates, one intermediate, a fully deprotonated base.

***In-class Problem Set #4***

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

Before beginning this problem set, spend about twenty minutes discussing amino acids and zwitterions, hydrochloride salts, and common ligands such as EDTA and how they function.

Give the students about five minutes to think about what might be occurring and look up $K_f$ values for the complex. Spend about thirty minutes talking about metal-ligand complexes and chelates. Talk about $H_2O$ as a ligand and how a hydrated metal ion compares entropically to a metal chelated with EDTA. Briefly discuss the geometry of metal-ligand complexes and how the complexation stoichiometry varies depending on the metal ion and ligand. With the realization that the Kf value is large, groups are able to set up a table with initial amounts, a line for a complete reaction, and a line for the back reaction.

*What is the value of x for the back-reaction based on this $K_f$ expression?*

Examine the amount of uncomplexed calcium(II) to confirm that it is quite small.

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

*What affect will pH have on the ligand?*

Students should realize that $EDTA^{4-}$ is a base and that in the presence of an acid the protonated species will form. After groups have discussed this, state this to the class as a whole.

*How do we expect the formation of the calcium-EDTA complex to change based on this pH?*

Students should recognize that with increased amounts of protonated EDTA, according to LeChatlier's principle, the amount of calcium-EDTA that can form is reduced. After groups have discussed this, state this conclusion to the class as a whole.

*Can we now solve for the amount of uncomplexed calcium ion?*

I use a set of equilibrium constant tables that has an additional table that contains a listing of the fraction of EDTA that exists as $EDTA^{4-}$ ($\alpha$-values) reported for each half a pH unit. This table is on the same page as the Ka values for EDTA and Kf values for metals with EDTA.

Students see this table and invariably take the $\alpha$-value for pH 2 and multiply it the total concentration of EDTA to arrive at a concentration of $EDTA^{4-}$. They then tend to think that, since Kf is large, they can use the initial amount of calcium(II), calculated amount of $EDTA^{4-}$, and set up a table for a reaction that goes to completion. In the line of the table for the reaction at completion, they will list the complexed calcium as equivalent to the initial concentration of $EDTA^{4-}$ they just calculated, and show that $EDTA^{4-}$ goes to zero. At this time, it is important to point out to the entire class that the concentration of $EDTA^{4-}$ cannot go to zero, since there are large quantities of the protonated forms in solution that must redistribute to produce some finate amount of $EDTA^{4-}$. With this being the case, the students can appreciate that the amount of complexed calcium must be larger than they calculated, but are stumped about how to actually do the calculation. Some are now tempted to think that the presence of a buffer with a pH of 2 is insignificant because the large $K_f$ will shift the equilibrium towards the formation of the complex.

*At this point the concept of an α-value should be introduced.*

I spend about an hour introducing the concept of α-values. The first thing I point out is that having a table of $\alpha$-values for $EDTA^{4-}$ implies that the fraction of EDTA that exists in solution as $EDTA^{4-}$ only depends on the pH and has no dependence on the total concentration of EDTA, and that we need to show that this is the case.

*I ask the groups to write an expression for the fraction of EDTA that exists in solution as $EDTA^{4-}$.*

Most groups are able to write this expression without any difficulty. I write it on the board and then instruct them to take the reciprocal of this expression and examine how the equation now consists of a series of ratios of species. Write the reciprocal expression on the board.

*I now ask them if they can evaluate terms for each ratio that will only depend on the pH (or concentration of hydronium ion).*

Some groups realize that they will need to use the Ka expressions for EDTA to evaluate terms for the ratios. Others need to be prompted by asking them what else we know about the system or about EDTA. I also write the four dissociation reactions for EDTA on the board as a way of getting them to think about how we might evaluate these terms. Once they realize that the Ka expressions will need to be used, it can be pointed out that the ratio of $HEDTA^{3-}$ to $EDTA^{4-}$ can be evaluated using only Ka4. I ask them to use appropriate Ka expressions to evaluate that ratio as well as the ratio of $H_2EDTA^{2-}$ to $EDTA^{4-}$ and to then see if a pattern is emerging such that they can guess the forms of the final two ratios. They usually can guess the final two terms after seeing the pattern for the earlier two. We can then examine how the only variable in the expression is the concentration of hydronium ion. I then point out how we could do a similar process for any other of the protonated EDTA species in solution, arriving at a set of $\alpha$-value expressions for each species observed in the dissociation of EDTA. I then draw the axes of a graph on the board that has the value of $\alpha$ on the y-axis and pH from 0-14 on the x-axis.

*I then ask the groups to draw a plot for the $\alpha$-values for each species observed in a triprotic acid ($H_3A$, $H_2A^-$, $HA^{2-}$, $A^{3-}$).*

Remind them that the sum of the a-values for all four species must be 1 at every pH value. It also helps to have them think about the two extreme species (H3A and A3-) first and to think about what the plot of their $\alpha$-values would look like as a function of pH. Most groups are able to reason out that there should be a lot of H3A and not much A3- at highly acidic pH and the reverse of this at highly basic pH. Once they see that, they can usually rationalize that the intermediate species must have an $\alpha$-value that is low at highly acidic and highly basic pH with some maximum point at an intermediate pH. At this point, I show them examples of plots of α-values for different systems and we look at where the buffers are on the plots, how the plots vary with different species depending on the Ka values for the system, etc.

*Now we can ask how the α-value can be used to calculate the concentration of $EDTA^{4-}$ at a pH of 2?*

Groups can usually substitute the $\alpha$-value expression into the Kf expression for the reaction. I then show them how the $\alpha$-value, as a constant for the particular pH, can be brought up onto the side with Kf to create a conditional constant, and how the magnitude of the conditional constant is then used to determine whether or not the reaction goes to completion and what strategy we will use to actually calculate the equilibrium concentrations. We also write the reaction that is described by the conditional constant. We can now construct a table of initial and equilibrium values under the conditional reaction and calculate the amount of calcium complex that forms.

*Are there any other calcium complexes that can form with the ions present? Are they significant?*

The students will probably not think of hydroxide as a ligand, but remind them that since metals will exist in solution as cations, hydroxide can often form metal complexes. Have them look up the $K_f$ for calcium hydroxide and assess whether or not this is significant. Remind them that the system is buffered at a pH of 2.

*Evaluate a second conditional constant that incorporates in the complexation of calcium by hydroxide ion.*

I indicate that this will probably be a process analogous to what we just did for the protonation of EDTA and ask whether they think it might be possible to calculate an $\alpha$-value for the calcium ion. I also ask them what might be the variable in this expression and most realize it should likely be the concentration of competing ligand.

*Derive an expression for the $\alpha$-value for the calcium ion as a function of hydroxide.*

*Incorporate the $\alpha$-value into Kf and calculate a second conditional constant that accounts for both protonation of the EDTA and complexation of calcium by hydroxide.*

*What is the concentration of calcium EDTA complex in the solution?*

*What would a plot of complexation of calcium with EDTA look like as a function of pH?*

Students will often think that one of the extremes leads to maximized complexation, but challenge them to consider what would happen at an acidic pH and a basic pH. I show them a page in the accompanying text that has a compilation of the conditional constants for the calcium complex with EDTA to illustrate this trend.

*What if we had a metal that forms multiple hydroxide complexes such as cadmium? How do we factor hydroxide complexation?*

Students should realize that if they had an α-value for $Cd^{2+}$, they could find a conditional constant. Allow them time to derive the expression for $\alpha Cd^{2+}$ and find its value. Suggest also that they start with the terms that include Cd(OH)+ and Cd(OH)2 and see if they can see a pattern that would allow them to guess the final two terms. They may need help getting started but, as with the α-values for ligands, allow them to simplify the individual terms. I then show them a table from the text that shows the conditional constants for the cadmium complex with EDTA as a function of pH to illustrate the trend in complexation with pH.

*What if there were more competing ligands?*

Discuss how a total $\alpha$-value could be written with separate sets of terms for all competing ligands, emphasizing how we must know the concentration of uncomplexes ligand in the final solution to be able to calculate an $\alpha$-value.

***In-class Problem Set #5***

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

**a) No other simultaneous equilibria will occur.**

*What reaction is occurring and what is the equilibrium constant expression?*

Students should recognize that lead(II)phosphate will dissociate in water, but may have trouble remembering what the stoichiometric coefficients are in front of each ion. Allow the students a few minutes to write the correct reaction and $K_{sp}$ expression. Once everyone has the correct expression, spend a few minutes discussing sparingly soluble complexes, the solubility product, saturated solutions, and solubility.

*What two expressions equate the individual dissociated ions to the solubility of the solid?*

If students are struggling with this step, ask them something along the lines of:

*If I measured the concentration of free lead(II), what would that tell me about how many moles of the solid dissolved?*

Students may try to incorporate $K_{sp}$ into their expression or try to account for both ions in the same expression. Remind them that there is one expression for each ion. It may take about ten minutes for every student to have and comprehend the right expressions.

*What is the value of S?*

Students will probably not be able to answer this question on their own. Remind them of the two expressions they just wrote for S and that they also have a Ksp expression for the solution. Groups will eventually realize that the two expressions for S can be rearranged and substituted into the $K_{sp}$ expression leaving S as the only variable.

*Using the value for S, what is the concentration of free lead(II) in this system?*

Again, the students will not necessarily know how to approach this questions, but remind them that they have an expression which relates S to the concentration of each ion.

**b) The solution is buffered at a pH of 3 and you will need to consider the protonation of phosphate that can occur.**

*What will happen to the solubility of lead(II)phosphate at this pH?*

Allow the students a few minutes to consider this question. They should realize that as phosphate is protonated, the equilibrium will shift towards dissociated ions and thus the solubility is increased.

This is a chance to take some time to discuss the impact that acid rain has on metals in the environment. A good example is the increased solubility of aluminum leading to the precipitation of aluminum(III)hydroxide in fish gills.

*What two expressions equate the species in solution to the solubility of the solid?*

Groups usually realize that we will need an expression in terms of lead ion and phosphate species.

*Where did every mole of phosphate (protonated and deprotonated) come from? What is the S expression for the phosphate ion?*

Students should realize that every mole of phosphate must have come from the original lead(II)phosphate and that the S expression must be modified to include the total concentration of phosphate species present. They also realize that since we know the pH, and since we are considering total phosphate species, that an $\alpha$-value is likely used somehow to solve the problem.

*How would the α-value for $PO_4^{3-}$ help? What is the modified $K_{sp}$ expression that includes the α-value?*

Allow students a few minutes to consider how to factor the α-value into the S and Ksp expression. Summarize the final Ksp expression that includes the α-value at the board.

*What is the value of $\alpha PO_4^{3-}$?*

Have students write the correct expression for $\alpha PO_4^{3-}$. It may take them about five minutes to all have the correct expression. In order to save time, once they have written the correct expression give them the exact value of $\alpha PO_4^{3-}$ instead of having them evaluate it.

*What is the value of S?*

Students should all be able to calculate S. Discuss how the magnitude of S compares to that of part (a). What is the concentration of free lead(II)?

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

*What complexes can form? What is the modified expression for S for the lead species?*

By looking up $K_f$ values, students should realize that lead can form three soluble hydroxide complexes in water. They should recall from part (b) that they need to incorporate the total lead into the S expression and that knowing value of $\alpha Pb^{2+}$ will allow them to solve for S.

*What is the value of $\alpha Pb^{2+}$? What does the value of $\alpha Pb^{2+}$ tell us about the formation of hydroxide complexes?*

As with $\alpha PO_4^{3-}$, once they have written the correct expression, provide them with the exact numerical value. It should take them no more than five minutes to write the correct expression. The students should realize that with an α-value of approximately 1, there is essentially no complexation of lead with hydroxide.

*What would happen at a high pH? What does a plot of the solubility of lead(II)phosphate versus pH look like? What would happen to the solubility at highly acidic, intermediate, and highly basic pHs.*

Where is the solubility minimized? Spend about ten minutes discussing what can occur at extreme pH values and what factors determine the pH at which solubility is minimized. Also discuss methods that are used to remove metals as their insoluble hydroxide species (a common industrial strategy to remove toxic metals from waste streams) from solutions.

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

Allow the students ten minutes to think about how to approach this problem. Students may initially be tempted to find α-values for the ions at a pH of 7 forgetting that α-values are only valid for a constant pH. Allow them to calculate $\alpha PO_4^{3-}$ in order to demonstrate that the pH will change. Talk about how in order for the pH to remain constant, we would have to make unrealistic assumptions such as no $H_3O^+$ or $OH^-$ reacting or both sets of competing reactions consuming exactly the same amount of $H_3O^+$ and $OH^-$. Discuss how this is an example where there are no simplifying assumptions that we can make and that the only way to solve this problem is to solve a set of simultaneous equations.

*How many unknown variables are there in this system? What are the equations?*

Students may have a surprising amount of trouble counting the unknowns. Once they have all agreed on a number, challenge them to come up with the same number of equations to relate those unknown variables. They may need some assistance figuring out what sorts of equations will be helpful. Remind them that something like $K_{sp}$ is an equation that relates some of the unknown variables. Allow them about five minutes to come up with as many equations as they can. They may be tempted to list the S expressions as equations, but remind them that doing so would introduce S as a new variable. They will most likely come up with eight or nine on their own but not know about a mass and charge balance. Point out that equating the two S expressions is the mass balance for the system.

*Ask them whether there is something else besides mass needs to be balanced in a solution?*

Groups usually realize that the solution needs to be neutral so that the change must be balanced.

*What is the expression for the charge balance for the system?*

Instruct them to write all of the cations on one side and all of the anions on the other. Make sure that they correctly account for ions with charges other than one. Many groups put the coefficient in the wrong place in their initial attempt at writing a charge balance – they want to take a 3- ion and divide its concentration by three rather than multiplying it by three. A good example is to ask them to consider Na3PO4 dissolving in water and to write a charge balance for only that species, keeping in mind the relationship between the concentrations of the ion.