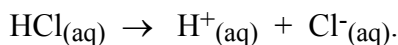


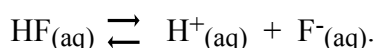
Chemical Equilibrium

Introduction

As you know from your growing experiences in Chemistry 2B, one of the major topics of the course is the area of chemistry known as Chemical Equilibrium. In Chemistry 2A you were exposed to reactions which essentially went to completion that is all the reactants were converted to products. An example of this type of reaction is when HCl is dissolved in water. You know that hydrochloric acid not only dissolves in water but that it also essentially completely dissociates. That is, a 1.0 M HCl solution is often described as being 1.0 M in both the hydrogen ion (or hydronium ion) and the chloride ion. We might write this situation as:



The analogous situation does not occur when the weak acid HF is dissolved in water. While a 1.0 M HF solution certainly does contain the hydrogen (or hydronium) ion and the fluoride ion, it also contains a significant quantity of HF in solution. We might write this as:



Note the symbol we use to indicate that the acid is not completely dissociated. We say that a chemical equilibrium is established in this reaction, and in all reactions which occur but which do not go essentially to completion. Most reactions do not go to completion but instead stop at a chemical position in which both reactants and products are still present. Chemical equilibrium is thus often thought of as a point of chemical balance between the "reactants" and "products".

One of the important aspects of chemical equilibrium is that it can be established by either starting with reactants or products. That is, the equilibrium point can be established in either direction. This illustrates that chemical equilibrium is dynamic in that reactants are reacting to form products at the same time that products are reacting to form reactants. It is the dynamic competition between these two processes that allows the point of equilibrium to be established.

What would happen if you suddenly placed some additional reactant into a system at equilibrium? Clearly this would affect this dynamic balance and cause a change in the resulting chemical equilibrium position. In fact, when these types of experiments are done it is always observed that the equilibrium will shift in such a way to reduce the concentration of the added reactant, or to "relieve the stress" of the added reactant. This behavior was summarized by Henri Louis Le Chatelier in 1884 and is generally referred to as Le Chatelier's Principle: When a stress is applied to a chemical system at equilibrium, the equilibrium shifts in a direction that reduces the effect of the stress. In this qualitative experiment you will be exposed to a number of different chemical systems that reach equilibrium and you will observe the effect of an added stress on each system. Note that it is important to make good observations in the experiment and carefully consider the results you draw from each experiment and how they relate to the equilibrium topics you are studying in lecture. **As preparation for this experiment you should read Chapter 16 of Petrucci et. al., 8th ed., paying special attention to section 16.6.**

Safety: Remember to wear gloves and use caution whenever handling acids and bases. WEAR YOUR GOGGLES!

In preparation for the Strong Acid Titration Experiment, each student must obtain about 4.5 grams of potassium acid phthalate, KHP, in a vial and dry it in an oven at 110° C for 2 hours. Place the vial of KHP in a small, beaker to keep it from spilling. Label your beaker using a graphite pencil in the white frosted area. Cover the beaker with a watch glass and place it in the oven. After two hours, remove your beaker from the oven. While keeping the watch glass on top of the beaker, let it cool until it is warm but safe to handle. Remove the watch glass and place the beaker containing the uncapped vial in a desiccator.

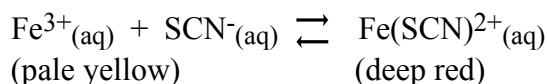
YOU WILL WORK INDIVIDUALLY ON THIS EXPERIMENT.

The questions for this experiment are integrated with the procedure. Write your answers to these questions in your laboratory notebook as you do the experimental procedure.

Experimental Procedure

Part I. Equilibria of Complex Ions

In this procedure, you will study the properties of a chemical system containing a complex ion. Many metal ions will bond with ions and molecules to form species called complex ions. An example of such a system is the combination of iron(III) ion with thiocyanate ion (SCN⁻). When these two species are mixed they establish an equilibrium in water which can be described as:



Thus, the system will change color depending on the quantity of the complex ion present. In this part of the experiment, you will observe the change in the equilibrium position by adding various chemicals.

1. Place 3 mL of 0.1 M KSCN into a 100 mL beaker. Add 3 mL of 0.1 M Fe(NO₃)₃. Now add 70-80 mL of water to dilute the solution and reduce the resulting color. Observe the color of the solution. Make sure that you can see through the solution; if the color is too dark you will have trouble noting color changes as you proceed. You may continue to dilute the solution if it looks too dark. The volume given here is a general guideline.
2. Place 5 mL of the resulting solution into 4 separate test tubes.

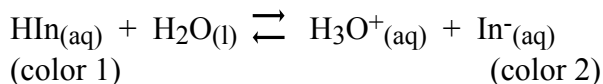
3. To the first test tube add 1.0 mL of 0.1 M Fe(NO₃)₃ solution. Observe the color change.
4. To the second test tube add 1.0 mL of 0.1 M KSCN solution. Observe the color change.
5. To the third test tube slowly add 6 M NaOH solution drop wise. Observe any changes. You will notice two changes. The color change indicates a shift in the equilibrium, but why is there an equilibrium shift? You should address this in Question A below.

Clean-Up: All solutions can be discarded down the drain.

Question A: Compare the color of the solution in each of the four test tubes. Explain the color changes in terms of the equilibria described above and what you believe happened in Step 5.

Part II. Equilibria of Acid/Base Indicators

In this procedure, you will study the properties of two acid-base indicators, phenolphthalein and methyl orange. Many indicators are weak acids that establish equilibrium in water:



Thus, indicators can be thought of as dyes which change color depending on whether they are in a protonated (HIn) or unprotonated (In⁻) form. In this part of the experiment you will observe the change in the equilibrium position of the indicators by adding acids and bases to solutions that contain these indicators.

1. Place 3 mL of deionized water into six test tubes. Add two drops of phenolphthalein to three of the test tubes and two drops of methyl orange to the other three test tubes. Observe the color of the solutions.
2. Add two drops of 6 M HCl to one test tube containing each indicator. Observe any color change.
3. Add 4 drops of 6 M NaOH to another test tube containing each indicator. Observe any color change.

Question B: What are the colors of the protonated and unprotonated forms of phenolphthalein?

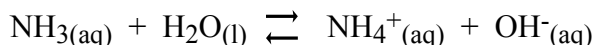
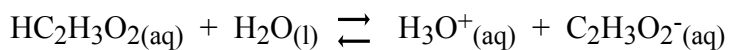
Question C: What are the colors of the protonated and unprotonated forms of methyl orange?

Question D: Write the equilibrium expression for each indicator as shown above for HIn. Be sure to indicate the color of each form. Use Hph for the protonated form of phenolphthalein and Hmo for the protonated form of methyl orange.

Clean-Up: All solutions may be discarded down the drain and the test tubes should be rinsed with deionized water.

Part III. Equilibria of Weak Acids and Bases

In this procedure, you will study the equilibrium properties of weak acids and bases. As described in the chapter on acids and bases, weak acids and bases establish equilibrium with water. In this part you will study this concept by using an acetic acid/acetate ion equilibrium system and the ammonia/ammonium ion equilibrium system. The pertinent equilibria for each system are:



In this part of the experiment, you will observe the change in the equilibrium position through the use of the indicators used in Part I.

Procedure for the acetic acid/acetate ion equilibrium

1. Place 3 mL of 0.1 M acetic acid into three test tubes. You will make this solution from 6 M stock solution. Add two drops of methyl orange to each test tube. Observe the color of the solutions.
2. To one of these test tubes add 1.0 M $\text{NaC}_2\text{H}_3\text{O}_2$ a few drops at a time and observe any color changes. Remember to mix the solution well after each addition. To another test tube, add **6M** acetic acid a few drops at a time and observe any color changes. Again, mix well after each addition. Repeat this step with another sample to confirm your results.

Question E: Explain your observations using both the equilibria presented above and the one involving the indicator. What color change did you observe? How is the acetic acid/acetate ion equilibrium affected by adding acetate ion? How does this change affect the concentration of H_3O^+ ? How does the change the concentration of H_3O^+ affect the Hmo/mo⁻ equilibrium?

Procedure for the ammonia/ammonium ion equilibrium

- Place 3 mL of 0.1 M ammonium hydroxide into the other three test tubes. You will make this from 6 M stock solution. Add two drops of phenolphthalein indicator to each tube. Observe the color of the solutions.
- To one of these test tubes add 1 M NH₄Cl a few drops at a time and observe any color changes. Remember to mix the solution well after each addition. Add more **6M** ammonium hydroxide to the test tube a few drops at a time. Mix well after each addition and note any color changes.

Question F: Explain your observations using both the equilibria presented above and the one involving the indicator.

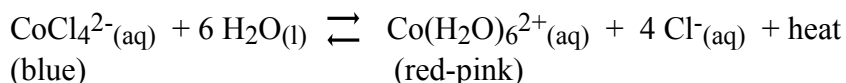
- To another test tube containing ammonium hydroxide, add 6 M HCl a few drops at a time and observe any color changes. Remember to mix the solution well after each addition.

Question G: Explain your observations using both the equilibria presented above and the one involving the indicator.

Clean-Up: All solutions can be discarded down the drain.

Part IV. Temperature Effects on Equilibria

In this procedure, you will again study the properties of a chemical system containing a complex ion. The system in this study of the temperature effects on equilibria can be described as:



You will note that "heat" has been shown to be a "product" of the reaction as it is read from left to right. In other words, as the reaction occurs from left to right the system gives off energy in the form of heat. Thus the system will change color depending on whether heat is added or removed from the system. In this part of the experiment you will observe the change in the equilibrium position by adding and removing heat.

- Use a hot plate to heat a beaker of water to boiling. **DO NOT USE A BUNSEN BURNER** to heat the beaker of water. You will need to share your hot plate.
- Place 3 mL of saturated solution of cobalt chloride solution into two test tubes. Place the test tube into a beaker of boiling water until it turns blue. Observe the color change.

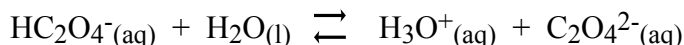
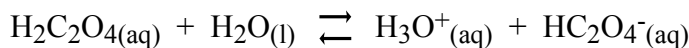
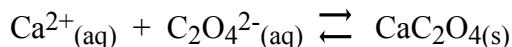
- Pull out one of the test tubes and allow it to cool to room temperature. Slowly immerse this test tube into another beaker containing a water-ice mixture. Observe the color change. If you have trouble seeing the color change, dilute the cobalt solution a little, reheat it and try again.

Question H: Explain the color changes in terms of the equilibria described above.

Clean-Up: Place the solution into the metal ion waste container located in the fumehood.

Part V. Equilibria of Precipitation Reactions

In this procedure, you will study the properties of two chemical systems involving the oxalate anion, $\text{C}_2\text{O}_4^{2-}(\text{aq})$. The chemical sources of the oxalate ion are calcium oxalate, $\text{CaC}_2\text{O}_4(\text{s})$, and the weak diprotic acid, oxalic acid, $\text{H}_2\text{C}_2\text{O}_4(\text{aq})$. This system is particularly interesting because 3 simultaneous equilibria occur in water. The equilibria in water that are important can be described as:



Clearly, this is a more complex system than we have thus far encountered. However, we should be able to qualitatively understand the system. For example, if you wanted to precipitate the calcium with oxalate would you want the solution to be basic or acidic based on the equilibria described above? Take a guess! Now let's see if you are right.

- Mix 4 mL of 0.1 M CaCl_2 with 4 mL of deionized water in a small beaker. Split the resulting solution into three approximately equal portions in three separate test tubes.
- Add 12 drops of 0.25 M $\text{Na}_2\text{C}_2\text{O}_4$ solution to one of the test tubes containing calcium chloride. Observe the results.
- Add 6 drops of 0.5 M $\text{H}_2\text{C}_2\text{O}_4$ solution to one of the other test tubes containing calcium chloride. Observe the results.

Question I: Even though you added the same stoichiometric amount of oxalate ion to these test tubes you have observed differing amounts of precipitate. Why?

- Now add 10 drops of 6 M HCl to the solution of calcium chloride and oxalic acid. Observe the results.

Question J: Explain the results in terms the equilibria discussed above.

5. Now slowly add 20 drops of 6 M NH_4OH to this test tube until a change occurs.

Question K: Explain the results in terms the equilibria discussed above.

6. You may wonder if the precipitate in Step 5 is really an oxalate or a hydroxide precipitate. This can be checked by adding 20 drops of 6 M NH_4OH to the solution in the last remaining test tube containing calcium chloride. Observe the results.

Question L: Do you believe the precipitate is calcium oxalate or calcium hydroxide? Explain.

Question M: If you wanted to precipitate calcium with oxalate, would you want the solution to be acidic or basic? Explain your answer using your observations.

Clean-Up: All solutions from this part may be washed down the drain.

