Chemical Equilibrium and Le Chatelier's Principle

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It was then adopted for use with the SALS Device by Lisa Goetter.

Introduction:

This experiment has been adapted to enhance the lab experience of students who are blind or visually impaired. There are questions included throughout the experiment to help guide you through the lab.

The experiment uses 2 special tools: the SALS Device and a light box. If you are unfamiliar with using the SALS Device you may want to try one of our more basic laboratory experiments to practice with it before performing this experiment (see *Concentration and Color* http://research.chem.psu.edu/mallouk/ilab/experiments.html).

SALS Device Tips:

- Be sure that the SALS probe is at the same depth when taking readings of the solutions
- The solutions used throughout the experiment should be close to the same volume
- There are two memory spaces on the device: Memory 1 and Memory 2. Each Memory holds one tone, therefore whenever you save a tone in one of the memories any other tone previously saved to that same memory will be erased.
- Always save the beakers of solution in case you forget to save the tone or need to refer back to that solution at a later point in the experiment

10mL beakers are used frequently throughout this experiment. If you do not have access to 10mL beakers, test tubes large enough to accommodate the SALS probe can be used as long as the probe tip is fully submerged in the solution. The volumes of the solutions in this lab are intended for use with the 10mL beakers; however, the volumes may be adjusted if necessary. Be sure to adjust all measurements when changing the volume as the concentration needs to remain the same for each solution (in other words don't just add water to increase the volume, use the solution itself).

Purpose of the Experiment:

To gain an understanding of how equilibria react to externally applied changes.

To learn how to apply Le Chatelier's Principle in understanding observed changes

in an equilibrium mixture.

To practice making accurate observations.

To learn the distinction between changes in the position of an equilibrium and changes to the value of the equilibrium constant.

Materials:

Solid $CoCl_2 \cdot H_2O$

Concentrated (12M) HCl

6M HCl

10mL beakers

Pipet

Plastic pipette

Stir/hot plate

Ice

Large beakers

30mL beakers

Solid NaCl

6 M HNO_3

Solid $CuCl_2 \cdot 2H_2O$

6M NH_3

2 watchglasses

Deionized water

SALS Device

Light box

Clear plastic wrap

For Your Safety:

1. 12 M HCl (aq), 6 M HNO_3 (aq), 6 M NH_3 (aq) and 6 M NaOH (aq) are all strongly acidic or basic solutions. Flush skin that has been exposed to these reagents with water for at least 15 minutes. Remove any clothing that is contaminated with these acids or bases. If blistering occurs, seek a medical professional.

2. NH_3 (aq) has a strong odor. Work with NH_3 (aq) in the student hoods. Containers of NH_3 (aq) must be covered at all times. Use a watchglass to cover beakers that contain ammonia.

3. 12 M (concentrated) HCl gives off unpleasant fumes and should be worked with under the student hood as far as possible.

4. Solutions containing copper or cobalt ions should be washed off skin or clothing using excess water.

5. Gloves **must** be worn when cleaning up any spill that occurs during this laboratory period.

Disposal:

Flush all waste solutions down the sink with a large amount of water. Failing to dilute wastes properly may result in acid/base reactions in the sink and/or U-bend.

Preparing Yourself for this Experiment

You should prepare for this experiment by reading through the outline and considering which equilibrium you will be studying as you perform each step of the procedure. You will gain the most from this experiment if you think about what is happening at each step *while you are doing the experiment*. For this reason, this experiment has questions embedded within the text of the Experimental section. Make sure that you have answered all questions in a particular section before proceeding to the next set of experiments.

Theory

Most textbooks describe chemical equilibrium in terms of forward and reverse reactions and equilibrium constant expressions, but what do these descriptions have to do with a solution we can observe in a test tube? As you do this experiment think about how your observations are related to the mathematical expressions.

The following equilibrium equations represent colorful examples of equilibrium solutions.

$[Co(H_2O)_6]^{2+}(aq) + 4\ Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6\ H_2O\ (l)$

$[Cu(H_2O)_6]^{2+}\ (aq) + 2\ OH-\ (aq) \rightleftharpoons Cu(OH)_2\ (s) + 6H_2O\ (l)$

$Cu(OH)_2\ (s) + 4\ NH_3\ (aq) + 2\ H_2O(l) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2\ OH^-\ (aq)$

$[Cu(H_2O)_6]^{2+}(aq) + 4\ Cl\text{-}(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6\ H_2O(l)$

It is possible to approximate the position of equilibrium (product or reactant dominating) for each solution by noting the color of the solution. Using the SALS Device the color change can be heard when the equilibrium shifts. Since the extinction coefficients* for these coordination compounds are not identical (the extinction coefficient for $[CoCl_4]^{2-}$ (aq) is 100 times greater than the extinction coefficient for $[Co(H_2O)_6]^{2+}$ (aq)), your approximations will be just that – approximations. Also if more than one species is present in the same solution, the color of the solution will be a combination of the colors of the various species present.

*The extinction coefficient (ε in Beer's Law) is a measure of how strongly a compound absorbs light at a given wavelength.

Approximating the Position of an Equilibrium Mixture

The color and/or tone of each complex should be identified without any other complexes that would interfere with your interpretation before you attempt to estimate the position of the equilibrium. Thus, in the first equilibrium equation above, it is necessary to recognize $[Co(H_2O)_6]^{2+}$ (aq) without any $[CoCl_4]^{2-}$ (aq) present. Similarly, you will need to be able to recognize $[CoCl_4]^{2-}$ (aq) without any $[Co(H_2O)_6]^{2+}$ (aq) present. In order to recognize these solutions, you will prepare solutions that will force the predominance of each species (Part A and Part C). In each of the solutions, the equilibrium reactions will be occurring, but the concentration of one of the species will be much larger than the other because of the reaction conditions.

The Equilibrium Constant Expression

For the general equilibrium equation:

$$aA + bB \rightleftharpoons cC + dD$$

an equilibrium constant expression can be written as

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

Concentration Changes in Equilibrium Reactions

Great care must be taken when referring to changes taking place in an equilibrium mixture. The equilibrium constant, K, is just that, a constant at a given temperature. The value of K at a particular temperature is determined by the thermodynamics of the reaction.

Things to Think About:

In the preceding text, brackets, [ ], are used to represent two different concepts (in the equilibrium equations and in the equilibrium constant expression). What do the brackets represent in each instance?

Data Collection

This lab is written for use by blind and visually impaired students; however, each student may benefit from having a sighted partner to assist them throughout the lab.

A hot-water bath and an ice bath are needed in this experiment. It will be helpful to prepare these baths at the beginning of the laboratory period. A hot-water bath is prepared by heating a beaker of water with a hot plate or Bunsen burner until the water boils gently. Be careful with this hot water bath, since it could scald you. Similarly, an ice bath is prepared by placing ice and water in a beaker.

Things to Think About:

What are the equilibrium constant expressions for each equilibrium reaction?

How are solids or pure liquids represented in equilibrium constant expressions?

Initial Set-Up of Light Box and SALS Device

Cover light box with plastic wrap to protect it from spills. For extra protection we recommend the smaller beakers containing the solutions be placed inside a larger, empty beaker when using the light box (just make sure you consistently use the large beaker on the light box or do not use it). Also, be sure the room is dark enough to get a good reading – you may want to use the light box protector. Turn SALS Device on.

Note: Make sure all glassware is CLEAN as the amount of light that comes through determines the tone the SALS Device reads.

A. Observing the Colors of Some Coordination Compounds (Complex Ions)

The observations you make and the conclusions you reach in Parts A and C will be used in Parts B and D, respectively. Make sure that you decide which complex ion is responsible for the color of each solution before you proceed to Parts B and D. Also be sure to SAVE each beaker of solution from Parts A and C to use for comparison and identification of the complexes in Parts B and D.

Cobalt(II) Complexes

Prepare the following two solutions, then decide which complex ion, $[Co(H_2O)_6]^{2+}$ (aq) or $[CoCl_4]^{2-}$ (aq), is responsible for your observations.

Note: We recommend putting the smaller beakers of solution in a larger beaker as a safety precaution when using the light box.

1. Observe and record the color of solid $CoCl_2 \cdot 6H_2O$ with the help of your sighted partner. Now dissolve a few crystals in about 10mL of deionized water in a 10mL beaker; move the beaker to the light box, insert the probe, press play, and store the tone of this solution in Memory 1. *Note*: SAVE this beaker of solution.

2. Add 10mL of concentrated (12M) HCl to another 10mL beaker while working under the fume hood if you have one– BE VERY CAREFUL – wear GLOVES when handling 12M HCl. Add a few crystals of solid $CoCl_2 \cdot 6H_2O$ to the acid, then move the solution to the light box and insert the probe. Play the tone and store it in Memory 2. Note the difference between the tones in Steps 1 and 2. Be sure to cover this beaker with a watchglass when not in use as it gives off strong fumes. *Note*: SAVE this beaker of solution.

Note: Remember to store the tones after each step! This is how you will compare the differences between the colors.

B. Shifting Chemical Equilibria

Cobalt (II) Solutions

Set up five clean (10mL) beakers. Use a small, clean beaker to obtain 25mL of a 0.1M solution of $CoCl_2 \cdot 6H_2O$. With a pipet, deliver 2.0mL of this solution into each of the five beakers. Label them 1 through 5. Add 5mL of the same solution to beaker #5 to obtain a good reading from the SALS Device. Use the light box and SALS Device to listen to the tone beaker #5 produces and compare it to the tones saved from Part A in Memory 1 and Memory 2. Set beaker #5 aside and use it as a control for comparing the colors of the other four solutions when conditions have been changed.

Before you perform each procedure, write down the equilibrium involved and predict what you expect to happen in the beaker. [Please make an honest attempt at predicting the outcome of each procedure.] After the procedure, you may want to summarize your observations for each beaker in a table similar to the one shown below. You should prepare a new table for each beaker. An example is shown below.

Beaker #1

Initial conditions: $CoCl_2 \cdot 6H_2O$ dissolved in water

Equilibrium: $[Co(H_2O)]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$

Description of Conditions	Prediction of what will happen	Observations during and after procedure (colors or precipitate formations from sighted partner)	Predominant complex (major species)
initial solution			
add'n of conc. HCl			
add'n of H_2O			
heating to 100 $^\circ$C			
cooling to 0°C			

3. Beaker #1
   a. Wearing gloves, pipet 3.0mL of concentrated (12M) HCl into the beaker containing the cobalt solution. Move the beaker to the light box, insert the probe, play the tone. Use the two solutions saved from Part A as a comparison to determine the predominant species in the solution. Save this solution's tone in Memory 1.

   Note: Keep beaker covered with a watchglass when not in use.

b. Now add 1.0mL of deionized water to this beaker, move to the light box, insert the probe, play the tone, and save it in Memory 2. Based on the color/tone and its comparison to the solutions from Part A and Memory 1, what is the predominant species in solution now?

c. Carefully, place the beaker in the boiling water bath and allow it to remain for several minutes so that the solution is heated to 100˚C. Quickly transfer the beaker to the light box, insert the probe, and play the tone. Save in Memory 1. Compare it to the solutions from Part A and the solution from Step 3b in Memory 2. What is the predominant species now?

d. Place the beaker into the ice bath and leave it there for at least 3 minutes. Quickly transfer the beaker to the light box, insert the probe and play the tone. Compare this tone to the solutions from Part A and those saved in Memory 1 and 2. What is the predominant species?

Question:

Shifting Equilibria 1. Explain why the equilibrium concentrations of the cobalt species appeared to change (or not) at each step. Answer in terms of changes to the concentration of specific chemicals or changes in the value of equilibrium constant K.

4. Beaker #2
   a. Pipet an additional 5mL of 0.1M $CoCl_2 \cdot 6H_2O$ into beaker #2.

   b. Calculate and then add enough solid NaCl to beaker #2 so that you produce a saturated NaCl solution. Be careful not to add too much salt as any sitting at the bottom of the beaker will affect the tone produced by the SALS. Move the beaker to the light box, insert the probe, and play the tone. Save the tone in Memory 1. Decide which cobalt species predominates in solution by comparing to the solutions from Part A.

   c. Place beaker #2 into the boiling water bath. Leave in the water bath for approx. 1 minute, then quickly transfer to the light box, insert the probe, and play the tone saving it in Memory 2. Compare this tone to the solutions from Part A and Memory 1 to decide which cobalt species predominates.

   d. Do the same in the ice bath. Compare all tones to each other (ice bath solution, Memory 1, Memory 2, solutions from Part A).

Question:

Shifting Equilibria 2. Explain why the equilibrium concentrations of the cobalt species appeared to change (or not) at each step. Answer in terms of changes to the concentration of specific chemicals or changes in the value of equilibrium constant K.

5. Beaker #3
    a. Pipet 3.0mL of 6M HNO_3 into beaker #3. Move the beaker to the light box, insert the probe, play the tone, and save in Memory 1. Observe and record your comparisons to the solutions from Part A and decide which species predominates in this solution.

       Note: You may need to retest the solutions from Part A.

    b. Place this beaker into the boiling water bath, use the light box and SALS Device to decide which species predominates at 100˚C. Save this in Memory 2. Compare to the solutions from Part A and Memory 1. Record your observations and conclusions in your notebook.

    c. Now cool beaker #3 in an ice bath to 0˚C, record your observations, and, using the solutions from Part A, decide which species predominates in solution.

Question:

Why do it? Explain the purpose of the actions taken with beaker #3. What did you learn from this set of experiments? (*Hint:* compare your results to those in Step 3).

6. Beaker #4

   Pipet an additional 5mL into beaker #4 but do not add any reagent. Observe it at room temperature, 100˚C, and 0˚C by using the light box and SALS Device, and decide which species predominates at each temperature through comparison. Record your observations and conclusions.

Question:

Addition of Water. Use examples from your data to describe how the addition of water to a solution affects the position of the equilibrium. Explain why the addition of water changes the equilibrium position, even though [H_2O] does not appear in the equilibrium constant expression.

Question:

Temperature Dependence of Equilibrium Constant K. Use your observations to explain why it is important to include the temperature when reporting the value of K. Summarize the observations that you made as you changed the temperature of the cobalt solutions. Does the value of K for this equilibrium increase or decrease as the temperature increases? Does the value of ΔG° for the *forward* reaction as you have written it become more positive or more negative as the temperature *increases*?

C. Observing the Colors of Some Coordination Compounds (Complex Ions)

Copper(II) Complexes

Prepare the following four solutions, then decide which complex ion or salt, $[Cu(H_2O)_6]^{2+}$(aq), $[Cu(NH_3)_4(H_2O)_2]^{2+}$(aq), $Cu(OH)_2$ (s), or $[CuCl_4]^{2-}$ (aq), is responsible for your observations as this is how you will determine which species predominates in Part D. SAVE all solutions from this part for use in Part D.

7. Weigh 2g of solid $CuCl_2 \cdot 2H_2O$ into a small (30mL) beaker and record the color of the crystals. Add about 20mL of deionized water and swirl to dissolve the crystals. Pour this solution into three clean 10mL beakers. The amounts in each beaker should be roughly the same but need not be exact. Move one beaker to the light box, insert the probe, play the tone, and record the tone in Memory 1. This will stay in Memory 1 until Step 15 to use as a comparison for the other solutions. *Note*: SAVE this beaker of solution.

8. In the fume hood, fill a plastic pipette (eye dropper) with 6 M NH_3 and take it over to the light box with one of the 10mL beakers of solution from Step 7. (Again, we recommend placing the 10mL beaker in a larger beaker to protect both you and the light box from any spills). With the beaker on the light box and the probe inserted into the solution, add 3-4 drops of NH_3 at a time while holding down the play button. The solution will need to be stirred. After 2 rounds of adding $NH_{3,}$ save the tone in Memory 2. As the concentration of ammonia is changing, you will observe several different copper species so make careful observations. Continue adding NH_3 while the tone reaches its lowest point and then begins returning to a higher pitch. Add a few more rounds of NH_3 after hearing the change and then stop. This is when the solution will be clear. Save the final tone in Memory 2. *Note*: SAVE this beaker of solution.

Note: Cover this beaker with a watchglass while not in use to minimize the fumes.

Question:

Presence of a Solid. How would having a solid present in solution affect the tone?

9. To the second beaker from step 7, add about 20 drops of 6M NaOH. Move the beaker to the light box, insert the probe, and listen to the tone. Decide which species predominates. *Note*: SAVE this beaker of solution.

10. Pour the solution in the third beaker from Step 7 into a 30mL beaker. Measure approximately 10mL of 6M HCl and add to the solution. Stir, and then pour approx. 10mL of the solution back into a 10mL beaker. Then move to the light

box, insert the probe, and play the tone. Decide which species predominates.
Note: SAVE this beaker of solution.

D. Shifting Chemical Equilibria

Copper (II) Solutions

There are eight procedures listed below. Before you perform each procedure, write down the reaction and/or equilibrium process involved and predict what you expect to happen. Group your written equilibrium reactions(s), predictions, and the information asked for at each step below according to the step number.

11. Weigh 0.6 g of $CuCl_2 \cdot 2H_2O$ (s) into a 10mL beaker. Pipet 6mL of 6M HCl into the beaker and stir to dissolve the solid. Use the light box and SALS Device to hear the tone this solution produces. Save this in Memory 2. Then compare this tone with all four solutions from Part C to determine the predominant species in solution.

12. Obtain 8mL of 6M NH_3 (aq) in your graduated cylinder. Pour the solution from Step 11 into a 30mL beaker. SLOWLY, add 4mL to the beaker. Swirl to mix, move to the light box and listen to the tone, comparing it to the other solutions from Part C and record your observations. Using a plastic pipette, continue adding 6M NH_3 in 10 drop portions, mixing and recording observations made with the SALS Device until you have added the full 8mL. Fill a 10mL beaker approx. three quarters of the way full. Using the SALS Device, save the tone in Memory 2 and compare it to the solutions from Part C, what is the predominant species in solution?

Note: Keep this beaker covered with a watch glass when not in use.

13. Return all of the solution from Step 12 to the 30mL beaker. Add 10mL of 6M HCl to the beaker. Stir to mix. Pour approx. 10mL into a 10mL beaker. Use the light box and SALS Device to store this in Memory 2, make comparisons, and record your observations. Based on the tone and your comparisons with the solutions from Part C, what is the predominant species in solution?

14. Pour all of the solution (from both the 10mL and 30mL beakers) into a 50mL beaker. Add 30mL deionized water to it. Stir to mix. Fill a 10mL beaker approx. three quarters of the way full. Use the light box and SALS Device to make comparisons and record your observations. Based on your comparisons to the solutions from Part C, what is the predominant species in solution?

Question:

The Copper Complexes. Write a chemical equation for the reaction taking place in each of steps 12, 13, and 14. Identify the dominant copper species in the solution at the end of each step.

15. Take two 30mL beakers and pour approx. 15mL of the solution from step 14 into each beaker. Heat one beaker until the solution just boils. Place the other in an ice bath. Compare the hot solution to the cold one with the light box and SALS Device, saving the tones in Memory 1 and Memory 2. Based on their comparisons to each other and to the solutions from Part C, what is the predominant species in each solution?
16. Turn the heat up under the hot solution and boil it vigorously to reduce the volume to half or less what you started with. Pour this solution into a 10mL beaker and cool to room temperature. Using the light box and SALS Device compare and record your observations. Based on comparisons to the initial solutions and the two solutions from Step 15 (saved in Memory 1 and 2), what is the predominant species?

Question:

Shifting Equilibria 3. In step 15, what is the dominant copper species in solution at 0°C and at 100°C. Write a chemical equation for the equilibrium between these two copper species. Put the species found in the hot solution on the product side. Suggest a *brief* explanation for why the dominant copper species in solution is different at high and at low temperature. Consider what might be happening to the value of K.

Question:

Concentration Effects. What is the dominant copper species in solution after cooling in step 16? If this is not the same as the dominant species found in this same solution at room temperature *before* you reduced the volume, give an explanation for the change.

Question:

Thermodynamics and Equilibrium

(ii) Write the chemical equation for the equilibrium investigated in steps 3-5. Put the halogenated metal complex on the product side. For the equation *as you wrote it*, is the <u>forward</u> reaction *endothermic* or *exothermic*? Explain your choice.

(ii) Consider the equation you wrote in (i). Does the forward reaction represent an increase or a decrease in the overall *entropy* of the system? Is this a large or a small change in entropy?

(iii) Based on your answers to (i) and (ii), what would you expect the sign of ΔG° to be at room temperature?

(iv) Based on your answer to (iii) would you expect the value of K to be greater than or less than 1 at room temperature?

(v) Explain how your experimental observations support or contradict your answer to (iv).