Experiment 5: LeChatelier's Principle

I. Introduction

The purpose of this lab is to look at several different chemical systems at equilibrium and observe how the system reacts to changes in various concentrations and temperatures. LeChatelier's Principle is a qualitative method of evaluating how a system at equilibrium should respond to changes.

LeChatelier's Principle: When a system is disturbed, it will react (or shift) in such a way as to minimize (or counteract) the effect of the disturbance.

In this experiment, we will be exploring factors that can disturb reactions and "shift" the reaction either right or left.

For example, we can look at the first equilibrium reaction, the dissolving of salt in water,

Equilibrium reaction: $NaCl(s) \leftrightarrow Na^{+}(aq) + Cl^{-}(aq)$

What it means to be at equilibrium: Firstly, dissolving reactions don't generally list water explicitly. Water appears in the above reaction only in the state designator "(aq)". Secondly, when this reaction is at equilibrium, the concentrations of each aqueous species does not change with time (definition of equilibrium). Solids do not appear in equilibrium constant expressions, so we can write,

$K = [Na^+] [Cl^-]$

Thirdly, the concept of dynamic equilibrium states that the rate of the forward reaction is equal to the rate of the reverse reaction. The only way that can be accomplished is for this solution to be a saturated solution of NaCl(aq). If it's less than saturated, then as soon as we put some more solid into solution, it would immediately dissolve, making the rate of the forward reaction faster than the rate of the reverse reaction. If the solution is supersaturated, then the rate of the reverse reaction is faster than the rate of the forward reaction and some NaCl(s) will precipitate.

Disturbances to equilibrium: All of the reactions in this lab will be at equilibrium as given. We will then alter the reaction system in some way so that we can watch how the reaction reestablishes, or gets back to, equilibrium. How the reaction gets back to equilibrium will be described by LeChatelier's Principle. For example, if we added 12**M** NaOH to a saturated solution of NaCl(s), as described above, the 12**M** NaOH will increase the $[Na^+]$ ions in solution. According to LeChat (as I'm sure his friends called him), the reaction seeks to counteract the increase in $[Na^+]$ by reacting away some of those Na⁺ ions to produce more NaCl(s). Put another way, the reaction shifts left toward making more reactants as it uses up the extra Na⁺ ions from the NaOH. As evidence of this, we see a white precipitate form.

This brings up a few questions:

(1) How does this shift relate to the equilibrium constant? It turns out that the value of K_c for the dissolving of NaCl(s) is $K_c = 45$. Therefore, a saturated solution of NaCl(s) has concentrations of Na⁺ and Cl⁻ ions of 6.7**M** each at equilibrium. When we add 12**M** NaOH, the [Na⁺] is increased to some value greater than 6.7**M**. Therefore if we calculated a reaction quotient Q_c , it would be greater than K_c , and the reaction would shift left to make more reactants, the same answer we arrived at using LeChat.

(2) What happens to the OH^- ion? Nothing. It acts as a spectator ion as far as the equilibrium reaction we're interested in. Certainly, the pH of the solution increases because OH^- acts as a base, but, to put it bluntly, we don't care about that right now.

(3) How does the concentration of Na^+ ions change overall? Na^+ ions were added to the solution in the 12**M** NaOH. Then some relatively small percentage of those Na^+ ions were reacted away as the reaction shifted left. Overall effect: net increase of Na^+ ions.

(4) How does the concentration of Cl^- ions change? Since the reaction shifted left, this acts to decrease the concentration of Cl^- ions in solution.

II. Experimental

A. Equipment Needed:

Chemicals in lab: Solid: NH₄Cl. Saturated solutions: NH₄Cl, NaCl. Solutions: 0.1M CoCl₂, 0.1M FeCl₃, 12M HCl, 6M HNO₃, 0.1M K₂CrO₄, 0.1M KSCN, 0.1M AgNO₃, 10% NaOH, 3M H₂SO₄, phenolphthalein

Equipment in lab: Micropipettes, test tubes, beakers, stir rods, hot plates, ice

B. Waste Disposal:

1. All colored solutions (except the pink phenolphthalein solution) used in this experiment should be disposed of in the proper waste container. (usually in the hood)

2. All NaCl, NH₄Cl and pink phenolphthalein solutions should also be <u>disposed of in a different</u> <u>container!</u>

C. Experimental considerations

1. Be very careful with the acids and bases in this lab. Also, most colored solutions (in addition to possible chemical damage) can stain your clothing and skin.

2. Concentrated 12 M HCl should be worked with only in the hood. Once it's been added, you can go back to your work area.

D. Before Starting Experimental Work (Before Class)

- 1. Write the purposes of the lab. Include a definition of the principle that we are studying in this experiment.
- 2. Write out all 6 of the equilibrium reactions that we will be studying
- 3. For this experiment only, please cut off the borders of the following pages, tape them into your notebook, so that you can write your answers directly on these handouts. Be sure the pages are permanently attached to your notebook before entering any data. Each person should answer the questions as they go and have your completed experiment signed off before you leave the lab.

E. Experimental Procedures

Procedure 1. Saturated Sodium Chloride Solution.

A NaCl solution is saturated (and at equilibrium) when all of the NaCl that can dissolve has dissolved. The easiest way to ensure that the solution is saturated is to place the solution in contact with excess solid NaCl. The equilibrium reaction for saturated sodium chloride solution:

Equilibrium reaction: NaCl(s) \leftrightarrow Na⁺(aq) + Cl⁻(aq)

Take 2–3 mL (1/4 full) of saturated sodium chloride solution in a test tube and add concentrated 12 **M** HCl drop-wise until you observe a reaction. (Perform the reaction in the hood!)

- 1. Observation:
- 2. The concentration of which species initially changed by adding 12 M HCl?
- 3. Did it increase or decrease?
- 3. According to LeChatelier's Principle, which way should the reaction shift?
- 4. Correlation of observation & prediction?

Procedure 2. Saturated Ammonium Chloride Solution.

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Equilibrium reaction: NH_4Cl(s) + heat \leftrightarrow NH_4^+(aq) + Cl^-(aq)
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Fill 2 test tubes with 2–3 mL of saturated ammonium chloride solution in each test tube. To the first test tube, add concentrated 12 **M** HCl drop-wise until you observe a reaction.

- 1. Observation:
- 2. The concentration of which species initially changed by adding 12 M HCl?
- 3. Did it increase or decrease?
- 4. According to LeChatelier's Principle, which way should the reaction shift?
- 5. Correlation of observation & prediction?

Equilibrium reaction: $NH_4Cl(s) + heat \leftrightarrow NH_4^+(aq) + Cl^-(aq)$

To the second test tube, place it in an ice bath. Let it sit there for several minutes. Stir it occasionally.

- 1. Observation:
- 2. Cooling the test tube removes heat and shifts the equilibrium. According to LeChatelier's

Principle, which way should the reaction shift?

3. Correlation of observation & prediction?

Procedure 3. Iron(III) Chloride plus Potassium Thiocyanate.

Equilibrium reaction: $Fe^{3+}(aq) + SCN^{-}(aq) \leftrightarrow FeSCN^{2+}(aq)$ Pale Yellow Colorless Red/Orange

Using a graduated cylinder, prepare a stock solution to be tested by adding 4 drops each of 0.1 M iron(III) chloride and 0.1 M KSCN solutions to 20 mL of distilled water and mix. Pour about 2-3 mL of this stock solution into each of four test tubes.

Use the first test tube as a control for comparison.

Add 1 mL of 0.1 M iron(III) chloride solution to the second tube and record the color change.

- 1. Observation:
- 2. The concentration of which species initially changed?

3. Did it increase or decrease?

4. According to LeChatelier's Principle, which way should the reaction shift?

5. Use **color** evidence to correlate observation & prediction?

Equilibrium reaction: $Fe^{3+}(aq) + SCN^{-}(aq) \leftrightarrow FeSCN^{2+}(aq)$

Add 1 mL of 0.1 **M** KSCN solution to the third tube and record the color change.

1. Observation:

2. The concentration of which species initially changed?

3. Did it increase or decrease?

4. According to LeChatelier's Principle, which way should the reaction shift?

5. Use **color** evidence to correlate observation & prediction?

Equilibrium reaction: $Fe^{3+}(aq) + SCN^{-}(aq) \leftrightarrow FeSCN^{2+}(aq)$

Add 0.1 **M** AgNO₃ solution drop-wise (less than 1 mL) to the fourth test tube until almost all of the color has disappeared. The white precipitate formed consists of both AgCl and AgSCN. In class we talk about decreasing the concentration of an ion and how this shifts the reaction. In practice one way to decrease the concentration of an ion in solution is to react it away by forming a precipitate such as AgSCN(s). This decreases the concentration of SCN⁻ ion in solution.

- 1. Observation:
- 2. The concentration of which species changed (i.e., what did Ag⁺ react with)?
- 3. Did it increase or decrease?
- 4. According to LeChatelier's Principle, which way should the reaction shift?

5. Use **color** evidence to correlate observation & prediction?

Now add 0.1 M KSCN (up to 1 to 2 mL) to the fourth test tube.

1. Does the orange color return? Why?

Procedure 4. Potassium Chromate with Nitric Acid and Sulfuric Acid.

Equilibrium reaction: $2 \operatorname{CrO_4^{2-}}(aq) + 2 \operatorname{H^+}(aq) \leftrightarrow \operatorname{Cr_2O_7^{2-}}(aq) + \operatorname{H_2O}(l)$ Yellow Orange

Pour about 3 mL of 0.1 **M** potassium chromate solution into each of two test tubes. Add about 2 drops 6 **M** nitric acid to one tube and about 2 drops of 3 **M** sulfuric acid to the other until a color change is noticeable. Observe the results.

- 1. Observation: _____
- 2. The concentration of which species initially changed?
- 3. Did it increase or decrease?
- 4. According to LeChatelier's Principle, which way should the reaction shift?
- 5. Use color evidence to correlate observation & prediction?

Equilibrium reaction: $2 \operatorname{CrO}_4^{2-}(\operatorname{aq}) + 2 \operatorname{H}^+(\operatorname{aq}) \leftrightarrow \operatorname{Cr}_2 \operatorname{O}_7^{2-}(\operatorname{aq}) + \operatorname{H}_2 O(1)$

Now add 10% NaOH solution drop-wise to each test tube until the original color of potassium chromate is restored. Observe the results.

- 1. Observation:
- 2. The concentration of which species initially changed?
- 3. Did it increase or decrease?
- 4. According to LeChatelier's Principle, which way should the reaction shift?
- 5. Use **color** evidence to correlate observation & prediction?

Procedure 5. Cobalt(II) Chloride Solution with Hydrochloric Acid and Ammonium Chloride.

Equilibrium reaction:

 $Co(H_2O)_6^{2+}(aq) + 4 Cl^{-}(aq) \leftrightarrow CoCl_4^{2-}(aq) + 6 H_2O(l)$ Pink Blue

Place about 2 mL (no more) of 0.1 M cobalt(II) chloride solution into each of three test tubes.

The first tube is a control for color comparison.

To the second tube, add about 3 mL of 12 M HCl drop-wise until you notice a color change. Record the results.

- 1. Observation:
- 2. The concentration of which species initially changed?
- 3. Did it increase or decrease?
- 4. According to LeChatelier's Principle, which way should the reaction shift?
- 5. Use **color** evidence to correlate observation & prediction?

6. State whether the concentration of each of the following substances was increased, decreased or remained the same when the concentrated HCl was added to the cobalt chloride solution (think carefully about Cl^{-}):

 $Co(H_2O)_6^{2+}(aq) + 4 Cl^-(aq) \leftrightarrow CoCl_4^{2-}(aq) + 6 H_2O(l)$ Pink Blue $Co(H_2O)_6^{2+} Cl^- CoCl_4^{2-}$

To the third test tube, add about 1.5 g of solid ammonium chloride and shake to make a saturated salt solution. As the ammonium chloride dissolves, feel the outside of the test tube and note any temperature and/or color changes.

7. Observation:

Place the first (control) and third test tubes in a beaker of boiling water, stir occasionally with a stir rod.

8. Observation:

Cool both tubes under tap water.

9. Observation:

10. Explain why heating caused NH₄Cl to dissolve (based on equilibrium reaction for dissolving of NH₄Cl given in Procedure 2) and why this leads to the shift in equilibrium reaction of the cobalt compounds. Use "LeChatlier" language.

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Procedure 6. A Solution of an Indicator.

The indicator phenolphthalein is a <u>weak acid</u> and can be represented with the formula HIn.

Equilibrium reaction: $HIn(aq) \leftrightarrow H^{+}(aq) + In^{-}(aq)$ colorlesspink

Prepare a phenolphthalein solution by adding 1 drop of phenolphthalein to 5 mL of water in a test tube and mix.

To this tube, add 6M or 10% NaOH until there is a color change. The NaOH creates a basic solution.

- 1. Observation:
- 2. The concentration of which species changed (i.e., what did NaOH react with)?
- 3. Did it increase or decrease?
- 4. According to LeChatelier's Principle, which way should the reaction shift?
- 5. Use **color** evidence to correlate observation & prediction?

6. For phenolphthalein, what is the main species present in a basic solution,

HIn or In⁻?

7. In contrast, what is the main species present in an acidic solution?

III. Further Instructions

A. In Class Work

Answer all of the questions. (Write your answers as you do each procedure, don't wait until the end.)

B. Experimental Summary: before you leave lab

Which example of LeChatelier's Principle (ie, which procedure) was the most difficult to understand (choose one)? Re-explain it in a paragraph as your experimental summary. Do not pick Procedure 5 because you have already had to explain it in question 10 of that procedure. Use "LeChatlier" language.