Experiment 1
Chemical Equilibrium and Le Châtelier's Principle

Goals

To become familiar with the law of mass action and Le Chatelier's Principle.

Discussion

Chemical equilibrium

A system at chemical equilibrium is one in which the concentrations of all the components of the equilibrium are constant over time. For example, if 1 M dinitrogen tetraoxide gas (a heavy but invisible gas) is placed in a container and heated to 100°C it is found that nitrogen dioxide (a poisonous brown gas responsible for the smog seen in cities) will be formed according to the equation:

$$\underset{\text{dinitrogen tetraoxide}}{N_2O_4\,(g)} \rightleftarrows \underset{\text{nitrogen dioxide}}{2NO_2\,(g)}$$

On the other hand, cooling the sample to a low temperature (–80°C) of will result in the formation of N_2O_4. By changing the temperature we can make the system "shift" to one side of the equation or the other. When we say that the system "shifts" to the left we mean that the reactant (N_2O_4) is produced in increasing amounts. When we say that the reaction "shifts" to the right we mean that the product (NO_2) is produced in increasing amounts.

The double arrow ($\rightleftarrows$) in the equation is used to indicate that the system is reversible. In a reversible reaction the system can react in the forward direction (→) or in the reverse direction (←). At room temperature (25°C), it is found that, over time, a mixture of NO_2 and N_2O_4 will result. The equilibrium concentrations of the two species will become:

species	**initial concentration at 25°C**	**equilibrium concentration at 25°C**
NO_2	0.00 mol/L	0.067 mol/L
N_2O_4	1.00 mol/L	0.967 mol/L

If we keep the temperature constant then these equilibrium concentrations will remain constant over time. The system is said to be in chemical equilibrium. When a system is in chemical equilibrium the concentrations of the reactants and products are constant.

Stressing a system at equilibrium

What happens if we take a system in chemical equilibrium and make a change to it? For example, suppose that we have a mixture of N_2O_4 at 0.967 M and NO_2 at 0.067 M. We then add some NO_2 to the system so that the concentration of NO_2 is now 1.00 M. What happens?

What is observed is that the mixture responds to the change that we made. The response is one which counteracts the change we made. The nitrogen dioxide will begin to react more rapidly and form more dinitrogen tetraoxide. After some period of time, the system will again stabilize and the concentrations will stop changing. We can calculate the new concentrations. Once the system reaches the new equilibrium the concentration of NO_2 will be 2.16 M and N_2O_4 will be 0.99 M. What happened?

The law of mass action

For the formation of N_2O_4 from NO_2 it is found that at 25°C the ratio $\dfrac{(\text{concentration of } NO_2)^2}{(\text{concentration of } N_2O_4)}$

is equal to about 0.0046 when the system is at equilibrium.

Sample calculation
Consider the initial mixture we looked at earlier. It was stated that at equilibrium the concentration of NO_2 was 0.76 M and the concentration of N_2O_4 was 0.12 M. Do these concentrations correspond to the ratio $\frac{(\text{concentration of } NO_2)^2}{(\text{concentration of } N_2O_4)} = 0.21$?

$$\frac{(0.12\,\text{M})}{(0.76\,\text{M})^2} = 0.2077 \approx 0.21$$

Since the ratio is equal to 0.21 we say that the system is at equilibrium because we find that once the ratio is equal to 0.21 the concentrations stop changing.

Now, what happens when the concentration of NO_2 is increased to 2.0 M as stated earlier? The system is no longer at equilibrium because NO_2 was added. Again, we can determine this by calculation. If the ratio $\frac{(\text{concentration of } N_2O_4)}{(\text{concentration of } NO_2)^2}$ is equal to 0.21 then the system is at equilibrium.

But for 2.0 M and 0.12 M the ratio is: $\frac{(0.12\,\text{M})}{(2.0\,\text{M})^2} = 0.03$ so the system is not at equilibrium. In order for the system to return to equilibrium it must form more N_2O_4 and, in the process, consume NO_2. The concentration of N_2O_4 will increase to and the concentration of NO_2 will decrease to .

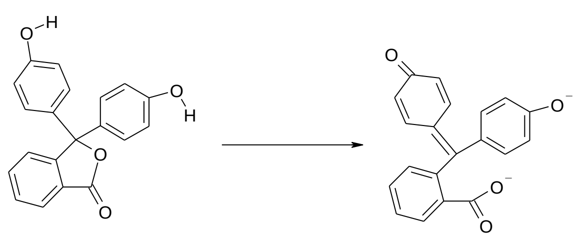
$$\underset{\text{nitrogen dioxide}}{2NO_2\,(g)} \rightarrow \underset{\text{dinitrogen tetraoxide}}{N_2O_4\,(g)}$$

These observations can be summed up by **Le Chatelier's Principle**: When a system at equilibrium is subjected to a disturbance, it will respond such that the effect of the disturbance is minimized.

Le Chatelier's principle is commonly observed in chemical reactions. In this experiment we will use two separate methods to disturb systems at chemical equilibrium.

1. Change the concentration of one or more species in the chemical equilibrium
2. Change the temperature of the system

Acid-base indicators
Acid-base indicators are materials that change color to reflect changes is solution acidity. For example, phenolphthalein is colorless in water when the solution is acidic (the concentration of H^+ ions is greater than the concentration of ^-OH ions). But when the solution becomes basic (the concentration of ^-OH ions is greater than the concentration of H^+ ions) phenolphthalein solutions are pink. The phenolphthalein is reflecting the acidity of the solution it is in.



colorless in acidic solution pink in basic solution

Cobalt complexes

Name	**Formula**	**Color**
cobalt(II) chloride	$CoCl_2$ (s)	light blue
cobalt(II) chloride hexahydrate	$CoCl_2 \cdot 6H_2O$ (s)	red
cobalt(II) ion	Co^{+2} (aq)	red
cobalt(II) chloride ion	$CoCl_4^{2-}$ (aq)	dark blue

Procedure

This experiment can be performed in pairs or as a demonstration by the instructor.

Part 1. Chemical equilibrium using acid-base indicators
Crystal Violet

$$\underset{\text{yellow}}{HCV}(aq) + H_2O(l) \rightleftarrows \underset{\text{violet}}{CV^-}(aq) + H_3O^+(aq)$$

1. Using a graduated cylinder add 5 mL of distilled or deionized water to a clean test tube. Add 2 to 3 drops of crystal violet indicator. Stir the solution using a glass stir rod.

What is the color of the solution? ___________________

Which form of crystal violet has a higher concentration in the solution, HCV or CV^-?_________________

Is the ratio $\frac{(\text{concentration of } CV^-)}{(\text{concentration of HCV})}$ large or small?__________________

2. Add a drop of 6 M hydrochloric acid solution to the test tube and stir the solution. Stir the solution using a glass stir rod.
What is the color of the solution now?______________________

Continue adding hydrochloric acid solution to the test tube one drop at a time, recording the color of the solution after each drop of hydrochloric acid solution is added. Be sure to stir the solution after each drop.

Drops of HCl solution	**Color**
0	

What can you conclude from your observations? What is the effect of adding hydrochloric acid solution to the crystal violet solution?

3. Add 6 M sodium hydroxide solution to the test tube. Follow the same procedure as in step 2.

Drops of NaOH solution	Color
0	

What can you conclude from your observations? What is the effect of adding the sodium hydroxide solution to the crystal violet solution?

Methyl Red: Methyl red is another common acid-base indicator. In solution it ionizes according to the equation**:**

$$\underset{\text{red}}{\mathrm{HMR\,(aq)}} \rightleftharpoons \mathrm{H^{+}\,(aq)} + \underset{\text{yellow}}{\mathrm{MR^{-}\,(aq)}}$$

1. Using a graduated cylinder add 5 mL of distilled or deionized water to a clean test tube. Add 2-3 drops of methyl red indicator.

What is the color of the solution?___________________________

Which species has a higher concentration in the solution, HMR or MR^{-}?______________________

Is the ratio $\dfrac{(\text{concentration of MR}^{-})}{(\text{concentration of HMR})}$ large or small?_________________________

2. Add either HCl (6 M) or NaOH (6 M) to the solution dropwise to change the color of the solution. Which one, HCl or NaOH, should you add?

____

Did the solution change color as you predicted?______________________

Part 2. Chemical equilibrium in cobalt complexes

Some ionic compounds exist as hydrates. They form weak bonds to water molecules. The attachment of these water molecules can affect the electronic structure of the compound and affect its color. An example is cobalt(II) chloride. Without the attached water molecules cobalt(II) chloride is a blue solid. When exposed to humid air, however, the salt forms a hydrate and turns a dark red. The compound is called cobalt(II) chloride hexahydrate and its formula is: $CoCl_2{\cdot}6H_2O$. This process can be represented by equation 1:

equation 1 $$\underset{\text{blue}}{CoCl_2(s)} + \underset{\text{from air}}{6H_2O(g)} \longrightarrow \underset{\text{dark red}}{CoCl_2 \cdot 6H_2O(s)}$$

By heating the hydrate water can be driven off:

equation 2 $$\underset{\text{dark red}}{CoCl_2 \cdot 6H_2O(s)} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftarrows}} \underset{\text{blue}}{CoCl_2(s)} + 6H_2O(g)$$

When dissolved in water the cobalt(II) chloride salt decomposes, resulting in the formation of the $Co(H_2O)_6^{2+}$ ion and a deep red solution. This process is represented by equation 3:

equation 3 $$\underset{\text{dark red crystals}}{CoCl_2 \cdot 6H_2O(s)} \xrightarrow[H_2O(l)]{} \underset{\text{red solution}}{Co(H_2O)_6^{2+}(aq)} + 2Cl^-(aq)$$

Alternatively, solutions high in chloride concentration can form the dark blue aqueous $CoCl_4^{2-}$ ion (equation 4):

equation 4 $$\underset{\text{red}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq) \rightleftarrows \underset{\text{blue}}{CoCl_4^{2-}(aq)} + 6H_2O(l)$$

In this part of the experiment we will test LeChatelier's Principle using the cobalt(II) chloride salt.

Procedure

1. Place a few crystals of $CoCl_2{\cdot}6H_2O$ into each of three test tubes.

2. Add 2 mL of water to the first test tube. Label the test tube (H_2O). Stir the crystals to dissolve them into solution.

What is the color of this solution?___________________

What is the dominant species of cobalt in this solution?_____________________

Explain your observations equation 3.____

____

3. Add 2 mL of 12 M HCl to the second test tube. Label the test tube (HCl). Stir the crystals to dissolve them into solution.

What is the color of this solution?___________________

What is the dominant species of cobalt in this solution?_____________________

4. Slowly add distilled or deionized water drop by drop with stirring, until no further color change occurs.

What is the color of the solution?___________________

What is the dominant species of cobalt in this solution? _____________________

Explain your observations using equation 4.____

____

5. Now put the test tube into a hot-water bath and observe the color of the solution.

What is the color of the solution at room temperature?______________________

What is the color of the solution in the hot-water bath?______________________

What is the dominant species of cobalt in the hot water bath? _____________________

6. Take the test tube out of the hot-water bath and place it in an ice bath. Observe the color of the solution.

What is the color of the solution in the ice bath?____________________

What is the dominant species of cobalt in this solution? _____________________

Explain your observations using the ideas presented in the Discussion section.

7. Add a few drops of distilled or deionized water to the contents of the third test tube from step 1. Add just enough water to wet the contents. Don't try to dissolve the salt.

What is the color of the solution?_________________________

What is the dominant species of cobalt in this solution? _____________________

8. Using a test tube holder, heat the contents of the test tube using a Bunsen burner until you are satisfied that all of the water has been driven off.

What is the color of the solution in the test tube?____________________

What is the dominant species of cobalt in this solution? _____________________

Explain your observation using equation 2.

____

____

9. Add a drop of distilled or deionized water to the contents of the test tube.

What is the color of the solution in the test tube?____________________

What is the dominant species of cobalt in this solution? _____________________

Explain your observation using equation 1 (note we are adding liquid water).________________________

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Part 3: Solubility and Complex Ion Equilibria of Zinc and Magnesium Ions

Both zinc (II) ions and magnesium (II) ions form insoluble hydroxide precipitates. However, these hydroxide precipitates are quite different in their properties, as this part of the experiment will show. For example, $Zn(OH)_2$ forms $[Zn(OH)_4]^{2-}$ with excess OH^- and $[Zn(NH_3)_4]^{2+}$ upon addition of NH_3. All hydroxide precipitates dissolve in acid. Hydroxide precipitates that react with bases are called **amphoteric** hydroxides.

When sodium hydroxide is added to a solution of zinc nitrate, $Zn(NO_3)_2$, the following reaction occurs.

$$Zn(NO_3)_2(aq) \ + \ 2NaOH(aq) \ \rightarrow \ Zn(OH)_2(s) \ + \ 2NaNO_3(aq)$$

Write the complete ionic equation and the net ionic equation for the above reaction:

Complete ionic equation:____

Net ionic equation:____

A magnesium ion solution has a similar reaction:

$$Mg(NO_3)_2(aq) \ + \ 2NaOH(aq) \ \rightarrow \ Mg(OH)_2(s) \ + \ 2NaNO_3(aq)$$

Write the complete ionic equation and the net ionic equation for the above reaction:

Complete ionic equation:____

Net ionic equation:____

Step 1: To each of three test tubes, add about 2 mL of 0.1 M $Zn(NO_3)_2$. To each test tube add one drop of 6 M NaOH and stir. Record what you see below.

Observation: ____

Step 2: To the first test tube from Step 1 above, add 6 M HCl drop by drop with stirring. To the second test tube add 6 M NaOH, again drop by drop with stirring. To the third test tube, add 6 M NH_3 one drop at a time with stirring. Record your observations below:

Addition of HCl ____

Addition of excess NaOH ____

Addition of NH_3 ____

Repeat steps 1 and 2 using a solution of 0.1 M $Mg(NO_3)_2$. Record what you observe below.

Addition of 1 drop NaOH ____

Addition of HCl ____

Addition of excess NaOH ____

Addition of NH_3 ____

Below write the equations for each of the steps above. (Your instructor will write these on the chalkboard. Copy them carefully).

For zinc hydroxide:

The addition of HCl ____

The addition of excess NaOH ____

The addition of NH_3 ____

For magnesium hydroxide:

The addition of HCl ____

The addition of excess NaOH ____

The addition of NH_3 ____

From your observations above, how is $Mg(OH)_2$ **similar** to $Zn(OH)_2$?

From your observations above, how is $Mg(OH)_2$ **different** from $Zn(OH)_2$? (Note that some cations form many complex ions and others do not.) Which metal hydroxide is an amphoteric hydroxide?

Part 4: The reactions and color changes of copper(II) hydroxide

The chemistry of copper (II) hydroxide, $Cu(OH)_2$, is somewhat different than that of the zinc and magnesium hydroxides you studied above. The color changes you will see are rather subtle so watch carefully. (Your instructor will write all the chemical formulas and equations on the chalkboard. Copy them carefully.)

Step 1: Into each of 3 test tubes, place 2 mL of a copper (II) sulfate solution. Record the color below.

Color of copper (II) sulfate solution ____

Step 2: To two of the test tubes, add one drop of 6 M NaOH. Record what happens below, including any color changes.

Addition of 1 drop NaOH ____

Molecular equation for the above reaction:____

Complete ionic equation for the above reaction:____

Net ionic equation for the above reaction:____

Note: Although we will not perform the experiment, if 6 M HCl were added to the copper(II) hydroxide precipitate formed in Step 2, the precipitate would dissolve just like the hydroxide precipitates of zinc and magnesium. All hydroxide precipitates dissolve in acid.

Step 3: Now add 6 M NaOH drop by drop to one of the test tubes from Step 2 above.
Record what happens below including any color changes.

Addition of excess NaOH ____

Molecular equation for the above reaction:

Step 4: To the other test tube containing the copper(II) hydroxide precipitate in Step 2 above, add 6 M NH_3 drop by drop. Record what happens below, including any color changes.

Addition of NH_3 ____

Molecular equation for the above reaction: ____

Step 5: To the remaining test tube from Step 1 containing the copper(II) sulfate solution, add one drop of 6 M NH_3. Don't stir. Record what happens below, including any color changes.

Addition of 1 drop of NH_3 ____

Complete ionic equation for the above reaction:____

Net ionic equation for the above reaction:____

Step 6: Now add 6 M NH_3 drop by drop to the test tube in Step 5 above. Record what happens below including any color changes.

Addition of excess NH_3 ____

Molecular equation for the above reaction (only for the dissolving of $Cu(OH)_2$):

____

From your observations above, discuss how solutions of copper(II) ions **differ** from those of Zn(II) and Mg(II) ions as regarding their reactions with sodium hydroxide and ammonia. Is $Cu(OH)_2$ amphoteric?

____

____

An Aside: Copper(II) sulfate in crystalline form actually has water of hydration, just as cobalt(II) chloride does. The formula is correctly written as $CuSO_4{\cdot}5H_2O$ and the name is copper(II) sulfate pentahydrate. Your instructor will show you some of the crystals and then heat them in a large test tube to drive off the water. A few drops of water will then be added to the dried solid. Record the color changes below. Note: In describing a solid whose water of hydration has been removed, the word "anhydrous" is sometimes added to the name. "Anhydrous" means "without water."

Color of crystalline copper(II) sulfate pentahydrate ____________________________

Color of the heated powder, copper(II) sulfate anhydrous ______________________
[The equation for the reaction is $CuSO_4{\cdot}5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(g)$]

Color of the heated powder after water has been added ________________________
[Adding water turns the copper(II) sulfate anhydrous back into copper(II) sulfate pentahydrate, but now it is probably in aqueous solution. The equation is $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4{\cdot}5H_2O(aq)$]

Hydroxide Properties Summary Table

Metal hydroxide	**Dissolves in excess OH^- (yes or no)**	**Forms complexes with NH_3 (yes or no)**	**Amphoteric? (yes or no)**
$Zn(OH)_2$			
$Mg(OH)_2$			
$Cu(OH)_2$			