# Le Châtelier’s Principle

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## Introduction

Le Châtelier’s principle applies to a chemical system that is initially at equilibrium. W*hen a change is made to such a system, the equilibrium position will shift so as to counteract the change*. Suppose a solution contains the species chromate, CrO42-, and dichromate, Cr2O72-, in equilibrium, with some concentration of reactants and some concentration of products present.

 2CrO42–(aq) + 2H3O+(aq) ⇌ Cr2O72–(aq) + 3H2O(l)(aq) Eq (1)

 yellow orange

To this solution is added a few drops of a concentrated solution of Na2CrO4(aq). The task is to predict whether adding the Na2CrO4(aq) to the mixture will result in the reaction shifting to the left, to the right, or staying the same (that is, to predict how the equilibrium position will shift). To understand how Na2CrO4(aq) is related to this equilibrium requires recognizing that sodium salts **dissociate**: Na2CrO4(aq) → 2Na+(aq) + CrO42-(aq). So, adding Na2CrO4(aq) increases the concentration of CrO42– in the solution. According to Le Châtelier’s principle, the reaction will shift to counteract what was done to it, so the reaction will shift to the right, which will lower the concentration of CrO42–.

It is not easy to predict the color change in this case. Adding yellow Na2CrO4(aq) to the beaker would, of course, make the solution more yellow. But, the shift in the reaction to the right would make the solution more orange.

Suppose that AgNO3(aq) was added to the original equilibrium mixture. Neither Ag+ nor NO3– is directly involved in the equilibrium. However, in this case the silver ion will react with the chromate ion (CrO42–): 2Ag+(aq) + CrO42–(aq) → Ag2CrO4(s). So, adding AgNO3(aq) to the equilibrium mixture will precipitate the chromate ion, making its concentration in solution less. The reaction will shift to counteract that change, which corresponds to shifting to the left. Shifting to the left corresponds to a decrease in the concentration of Cr2O72–, so less orange would be present after adding AgNO3(aq).

Suppose that a few drops of concentrated phosphoric acid, H3PO4(aq), were added to the original equilibrium mixture. The problem is to figure out what H3PO4 has to do with the equilibrium being studied. There is no phosphate in that equilibrium. However, in solution H3PO4 dissociates: H3PO4 → H+(aq) + H2PO4–(aq). And, H+(aq) is the same thing as H3O+(aq), so adding H3PO4 to a solution increases the concentration of hydronium ion, H3O+. Consequently, the reaction would be expected to shift to the right, consuming some of the hydronium ion that was added; the solution would become less yellow, since CrO42– decreases on shifting to the right, and more orange, since Cr2O72– increases.

Suppose a few drops of concentrated NaOH(aq) are added to the equilibrium. The equilibrium does not show OH– ion. However, hydroxide reacts with hydronium ion (that is, base neutralized acid): OH–(aq) + H3O+(aq) → 2H2O(l). So, adding hydroxide ion will decrease the concentration of hydronium ion, H3O+. The reaction will shift to counteract what was done to it; that is, it will shift to the left, becoming more yellow and less orange.

For some equilibria, all of the components may be colorless, as in Eq (2), so a shift in the position of the reaction cannot be seen.

 H3PO4(aq) + H2O(aq) ⇌ H3O+(aq) + H2PO4–(aq) Eq (2)

However, if the reaction is an acid-base reaction, as this reaction is, the shift may be made visible by adding an acid-base indicator. Suppose an indicator is used that is green in acid and yellow in base (this is **not** the indicator used in this lab). To figure out which side of the reaction corresponds to which color, look for the side that has H+ (or hydronium ion, H3O+) on it. If the reaction shifts to that side, the indicator color will shift to become more like the color of its acid form, Eq (3).

 H3PO4(aq) + H2O(aq) ⇌ H3O+(aq) + H2PO4–(aq) Eq (3)

 yellower greener

This reaction produces hydronium ion, so if the reaction shifts to the right, the solution will become more acidic and the indicator will become greener. If it shifts to the left, some of the hydronium ion would be consumed, making the solution less acidic, and so more basic, and so yellower.

Some reactions may produce OH–, instead of H+. In that case, if the reaction shifts to the side producing OH–, the solution will become more basic, and the indicator will shift to the color of its basic form.

Let us predict if this reaction mixture would get yellower or greener if a few drops of concentrated H3PO4(aq) were added to it. The H3PO4(aq) is on the reactants side, so the equilibrium would shift to the right to consume some of the added material. Shifting to the right produces more H3O+(aq), making the solution more acidic, so the indicator would be predicted to become greener.

Le Châtelier’s principle also applies to chemical reactions involving heat. Heat can be added or removed from a reaction by heating or cooling the reaction mixture. If heat is added to the mixture by raising the temperature, the equilibrium will shift to produce less heat; if heat is removed from the mixture by lowering the temperature, the reaction will shift to produce more heat. This will be used to determine if a reaction is exothermic or endothermic. To do this, heat is included in the previous reaction. It is placed on one side of the reaction, then the evidence is examined to see if that is the correct side. In the following reaction, it is placed on the reactants side (that corresponds to the reaction being endothermic).

 heat + H3PO4(aq) + H2O(aq) ⇌ H3O+(aq) + HPO4–(aq) Eq (4)

 yellower greener

Suppose that on heating this system the indicator became more yellow. Adding more heat should have shifted the reaction to the right to consume some of the added heat, resulting in the solution becoming greener, not yellower. Therefore, the heat was placed on the wrong side: heat must be a product, not a reactant, and the reaction must be exothermic. The correct equation is the following:

 H3PO4(aq) + H2O(aq) ⇌ H3O+(aq) + H2PO4–(aq) + heat Eq (5)

 yellower greener

## Procedure

### Caution: As always, wear safety glasses while performing this experiment. Concentrated acid, which causes burns, will be used.

### Preparation

Hot and cold water baths:

Start heating a 150 mL beaker about half-full of tap water to near-boiling on a hot plate. (Do not boil the water so that it won’t splatter on you.)

Fill another 150 mL beaker with about half full with ice. Add water to make a slush (having water present improves cooling, because an object will have a greater contact area with a liquid than with ice).

Label four 15 × 125 mm test tubes as follows:

 NaHSO4 Na2SO4 MgCl2 NaOH

Place the tubes in a test tube rack.

### Equilibrium of a Weak Acid, HSO4–

HSO4–(aq) + H2O(l) ⇌ H3O+(aq) + SO42–(aq) Eq (6)

1. Eq (6) is the net ionic equation for the equilibrium to be examined in this section. Copy that reaction to the data sheet. (Please don’t reverse the reaction; then “left” and “right” on the data sheet would get reversed!) The acid-base indicator used in this part is thymol blue, which becomes yellow-orange as a solution becomes more basic, and pinkish as a solution becomes more acidic. Below the net ionic equation, **write the indicator color change** expected after the reaction has shifted to the left and to the right, as in Eq (3). Then, answer the two questions about how the color would change if the equilibrium shifted.
2. **Prepare storage solutions.** Transfer about 5 mL of the provided NaHSO4 solution to the test tube labeled “NaHSO4”. Transfer about 5 mL of the provided Na2SO4 solution to the test tube labeled “Na2SO4”. Place a disposable plastic transfer pipet into each tube.
3. **Transfer NaHSO4 to the 24-well plate.** Using the disposable pipet, transfer about 10 drops of the NaHSO4 solution into wells A1, A2, and A3, and 20 drops to wells A4 and A5.
4. **Add indicator.** Add 1 drop of the thymol blue indicator from the dropper bottle to each of the five wells. Mix the solution with a toothpick (some people mix by swirling the 24-well plate on the desk top, but that is apt to cause a spill). More toothpicks are on the front desk. Record the color of these solutions, which are at equilibrium.

**Figure 5**. 24-well plate. Notice the letters along the side and numbers along the top, which allow each well to be identified. For example, the bottom right well is D6. Picture by Joseph Elsbernd, on Flickr; creative commons SA-BY.

#### Adding Na2SO4

1. **Add Na2SO4 to a well.** With the pipet, add one drop of the Na2SO4 solution to well A1. Mix the solution with a toothpick. Probably not much change in color is observed, so add a drop more with mixing until a color change is observed. Record the color change.

For example, if the indicator had originally been pink, the color change might be “less pink” or “more pink”. If the color had been purple, the color change might be “redder” or “bluer”, or “more blue” or “less red”.

1. **Analyze.** Compare that color change to the colors written under the equation in step 1, and record on the data sheet the direction the reaction shifted. Explain the direction of the shift on the data sheet using Le Châtelier’s principle. Here is a template for creating these explanations.

 Adding \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (the reagent) increases/decreases the concentration of \_\_\_\_\_\_\_\_\_\_\_ (one of the species involved in the reaction). To counteract this change, the reaction shifted to the left/right, which increased/decreased the concentration of \_\_\_\_\_\_\_\_\_\_\_\_ (the species that the indicator responds to), resulting in the indicator color becoming \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.

#### Adding NaHSO4

1. **Add NaHSO4 to a well.** Since NaHSO4 is already in the well, to increase its concentration, solid NaHSO4 will be added. With a microspatula, add a crystal of NaHSO4 to well A3 (well A2 is the color with nothing added, for comparison). Mix the solution with a toothpick. Add crystals with mixing until a color change is observed. Record the color change.
2. **Analyze.** Based on the color change, record on the data sheet the direction the reaction shifted on adding NaHSO4 solution to well A3. As before, explain the direction of the shift on the data sheet using Le Châtelier’s principle.
3. **Clean the pipets.** Fill a beaker with tap water, and use it to rinse out the two pipets a couple of times, then rinse them with deionized water. The rinse water can be placed in the waste container in the hood that is labelled “Discarded HSO4- mixtures”. Get as much of the liquid out of the pipets as possible.

#### Changing the Temperature

1. **Place a mixture in the hot-water bath.** Draw the solution in well A4 into a pipet. Invert the pipet, and tap it or swirl it to get all the liquid out of the stem and into the bulb. (Be careful: squeezing the pipet may expel a drop of the liquid in an unexpected direction, like towards your eye.) Place the pipet bulb-down into the hot-water bath.
2. **Place a mixture in the cold-water bath.** Draw the solution in well A5 into the other pipet. Likewise, get all the liquid out of the stem and into the bulb. Place the pipet bulb-down into the cold-water bath.
3. **Equilibrate.** Swirl the mixtures in the pipets for a minute or two to speed up the heat transfer. When the color has largely stopped changing, record the changes in color of the two solutions.
4. **Reverse the process.** Exchange the pipets in the two baths to see whether the color changes are permanent, or whether the process can be reversed.
5. **Analyze.** From the color change, determine whether the reaction shifted to the left or to the right on heating. Based on the direction the reaction shifted on heating, determine whether heat is a reactant or product in this reaction. Rewrite the net ionic equation, including heat in the reaction, as in Eq (4) and Eq (5). State whether this is an exothermic or endothermic reaction.
6. **Clean up.** Take the 24-well plate and a bottle of deionized water over to the hood containing the waste containers. Dump the contents of the plate into the “Discarded HSO4- Reaction Mixtures” container. Rinse the plates with the deionized water, letting the water run into the waste container. Be careful to completely rinse out any crystals of NaHSO4 that may remain. Dry the plate with a “Lab Wipe” tissue paper.

Empty the two test tubes into the waste container, and rinse with deionized water from a squirt bottle.

Empty the two pipets into the waste container, and rinse them two or three times with deionized water. Get most of the liquid out of the pipets.

Throw the toothpicks into the “Discarded Toothpicks” container.

### Equilibrium of a Slightly Soluble Salt, Mg(OH)2

Mg(OH)2(s) ⇌ Mg2+(aq) + 2OH–(aq) Eq (7)

Eq (7)is the net ionic equation for the equilibrium to be studied in this section. However, rather than starting with Mg(OH)2, that solid will be made by mixing MgCl2(aq) and NaOH(aq).

1. **Prepare storage solutions.** Use a graduated cylinder to transfer about 10 mL of the provided 1.0 *M* MgCl2(aq) solution to the test tube previously labeled “MgCl2”. Transfer about 10 mL of the provided 0.5 *M* NaOH(aq) solution to the tube labeled “NaOH”. Place one of the disposable plastic transfer pipet that you just cleaned into each tube.
2. **Transfer MgCl2 to the 24-well plate.** Transfer 5 drops of the MgCl2 solution into wells B1, B2, B3, and B4. Place a toothpick in each well for future use.

**Caution**: As always, wear safety glasses while performing this experiment. Sodium hydroxide, NaOH is very hazardous. If you get NaOH on your skin, rinse with water until it stops feeling soapy. Likewise, HCl can cause burns. If you get HCl on your skin, rinse it off with water.

1. **Transfer NaOH to the 24-well plate.** Transfer 20 drops of the NaOH solution into wells B1, B2, B3, and B4. Mix with the toothpicks. Write a complete chemical reaction for what was observed in cells B1 and B2.
2. **Net ionic equation for the equilibrium.** In the data sheet, record the net ionic equation, Eq (7), for the equilibrium involving Mg(OH)2.

#### Adding HCl

1. **Add concentrated HCl to a well.** The concentrated HCl is stored in the hood. Take the plate to the hood and add 1 drop of concentrated HCl to well B1. Mix the solution with a toothpick. If not much change is observed, add a drop more with mixing until a change is observed. Describe this change in the data sheet.
2. **Analyze.** State on the data sheet which component of the equilibrium reaction has its concentration directly changed by adding HCl(aq). (The HCl is assumed to react with something in the solution, rather than with the solid.) Based on the observed change, record on the data sheet the direction the reaction shifted on adding conc. HCl solution to well B1. Explain the direction of the shift on the data sheet using Le Châtelier’s principle.

#### Adding Na4EDTA

1. **Add Na4EDTA to a well.** Add 1 drop of Na4EDTA to well B2. Mix the solution with a toothpick. Probably not much change will be observed, so continue adding drops, mixing after each drop, until a distinct change is observed (this reaction may take a couple of minutes of stirring). Record the change on the data sheet.

EDTA stands for ethylene diamine tetraacetic acid, Fig. 7. It is available as a sodium salt, Na4EDTA. EDTA wraps around metal ions, like Ca2+, Mg2+, and Co2+, as shown in the structure on the right. Although the ion stays in solution, the EDTA prevents it from reacting with OH–, so in effect, EDTA lowers the concentration of Mg2+ ion.

**Figure 7.** Structure of EDTA (left), and a metal atom surrounded by an EDTA ion (right).

1. **Analyze.** State on the data sheet which component of the equilibrium reaction has its concentration changed by adding Na4EDTA(aq) to the mixture. Based on the observed change, record on the data sheet the direction the reaction shifted on adding Na4EDTA. Explain the direction of the shift on the data sheet using Le Châtelier’s principle.

#### Changing the Temperature

1. **Add indicator.** Add 1 drop of phenolphthalein indicator from the dropper bottle to the solutions in wells B3 and B4. Mix the solutions with the toothpicks. Record the color if this indicator solution, which is at room temperature, on the data sheet.

The acid-base indicator used in this part, phenolphthalein, becomes pink as a solution becomes more basic, and colorless as a solution becomes more acidic.

Also, below the net ionic equation for this equilibrium (step 4) write the indicator color change expected after the reaction has shifted to the left and to the right, as in H3PO4(aq) + H2O(aq) ⇌ H3O+(aq) + H2PO4–(aq) Eq (3).

1. **Clean the pipets.** Fill a beaker with tap water, and use it to rinse out the two pipets a couple of times, then rinse them with deionized water. The rinse water can be placed in the waste container in the hood that is labelled “Discarded Mg(OH)2 Reaction Mixtures”. Get as much of the liquid out of the pipets as possible.
2. **Place a mixture in the hot-water bath.** Draw the solution and solid in well B3 into a pipet. Carefully expel the liquid from the pipet back into the well to help suspend the solid in the liquid, then draw the liquid back into the pipet. Invert the pipet, and tap it or swirl it to get all the liquid out of the stem and into the bulb. (Be careful: squeezing the pipet may expel a drop of the liquid in an unexpected direction.) Place the pipet bulb-down into the hot-water bath.
3. **Place a mixture in the cold-water bath.** Likewise, draw the solution in well B4 into the other pipet. Place this pipet bulb-down into the cold-water bath.
4. **Equilibrate.** Swirl the mixtures in the pipets occasionally to speed up the heat transfer. After three or four minutes, record the changes in color of the two solutions.
5. **Reverse the process.** Exchange the pipets in the two baths to see whether the color changes are permanent, or whether the process can be reversed.
6. **Analyze.** From the color change, determine whether the reaction shifted to the left or to the right on heating. Based on the direction the reaction shifted on heating, determine whether heat is a reactant or product in this reaction. Rewrite the net ionic equation, including heat in the reaction, as in Eq (4) and Eq (5). State whether this is an exothermic or endothermic reaction.
7. **Clean up.** Take the 24-well plate and a bottle of deionized water over to the hood containing the waste containers. Dump the contents of the plate into the “Discarded Mg(OH)2 Reaction Mixtures” container. Rinse the plates with the deionized water, letting the water run into the waste container. Be careful to completely rinse out any solid Mg(OH)2 that may remain. Dry the plate with a “Lab Wipe” tissue paper.

Empty the two test tubes into the waste container, and rinse with deionized water from a squirt bottle.

Empty the two pipets into the waste container, and rinse them two or three times with water, and put them in the trash.

Throw the toothpicks into the “Discarded Toothpicks” container.