## LeChâtelier's Principle and the Solubility of Carbon Dioxide

## LeChâtelier's Principle

## Introduction

When carbon dioxide gas dissolves in water, it forms a weakly acidic solution due to the following reversible reaction:

$$
2 \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{CO}_{2}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq})
$$

Equation 1
The hydrogen ion concentration in solution depends on the amount of dissolved carbon dioxide. In this demonstration, the effect of pressure and temperature on the solubility of carbon dioxide and on the position of equilibrium for this reversible chemical reaction will be studied by measuring the $\mathrm{H}^{+}$concentration at different pressures and temperatures.

## Concepts

- Reversible reaction
- Equilibrium
- LeChâtelier's Principle
- Acid-base indicator


## Materials

Bromcresol green indicator solution, $0.04 \%, 5 \mathrm{~mL}$
Carbon dioxide gas
(see the Supplementary Information section)
Ice
Seltzer water, 50 mL
Water
Color chart or pH reference strip for bromocresol green

Beaker, $50-\mathrm{mL}$
Beakers, 250-mL, 2
Hot plate
Pipet, graduated, Beral-type
Syringe, $10-\mathrm{mL}$
Syringe tip cap (septum)
Thermometer

## Safety Precautions

Avoid contact of all chemicals with eyes and skin. Follow all laboratory safety guidelines. Wear chemical splash goggles, chemicalresistant gloves, and a chemical-resistant apron. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information. Remember to wash hands thoroughly with soap and water before leaving the laboratory.

## Preparation

Prepare a boiling water bath and ice-water bath for use in Part B. To prepare a boiling water bath, fill a $250-\mathrm{mL}$ beaker about $2 / 3$-full with water, add a boiling stone, and heat at a medium-high setting on a hot plate. To prepare an ice-water bath, fill a second $250-\mathrm{mL}$ beaker about $3 / 4$-full with a crushed ice/water mixture.

## Procedure

## Part A. Effect of Pressure

1. Obtain about 10 mL of seltzer water in a $50-\mathrm{mL}$ beaker and add 1 mL of bromcresol green indicator using a graduated, Beral-type pipet. Swirl to mix the solution.
2. Draw about 2 mL of the seltzer/indicator solution into a $10-\mathrm{mL}$ hypodermic syringe and seal the syringe by pushing a tip cap firmly on its open end. Record the initial volume of liquid in the syringe. (The initial volume should be about $2 m L$.)
3. Compare the color of the seltzer/indicator solution with the bromcresol green color chart to determine the pH of the

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seltzer water. Record the initial pH of the solution. (The seltzer/indicator solution is yellow-green, corresponding to a pH of 4.0.)
4. Expand the volume of gas in the syringe by withdrawing the plunger until it stops. While holding the plunger in the withdrawn position, shake the solution until the seltzer no longer effervesces and its color no longer changes. Note: According to Boyle's Law, increasing the applied volume should decrease the pressure of the gas in the syringe.
5. Determine the pH of the solution in the syringe and record both the pH and the total volume of material (liquid plus gas) in the syringe. (The new pH increases at an expanded volume.)
6. Recall that pH and $\left[\mathrm{H}^{+}\right]$are inversely related-the higher the pH , the lower the hydrogen ion concentration. Write Equation 1 on the board or overhead projector. What effect does decreasing the pressure have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1? (Decreasing the pressure shifts the equilibrium shown in Equation 1 to the left, reducing the solubility of carbon dioxide gas and decreasing the bydrogen ion concentration.)
7. Note the volume of carbon dioxide gas in the syringe. Compress the mixture in the syringe while shaking until both the color and volume no longer change. Note: According to Boyle's Law, decreasing the applied volume should increase the pressure of the gas in the syringe.
8. Determine the pH of the solution in the syringe and record both the pH and the total volume of material (liquid plus gas) in the syringe. (The new pH is 4.0 at a compressed volume.)
9. What effect does increasing the pressure have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1? (Increasing the pressure shifts the equilibrium shown in Equation 1 to the right, increasing the solubility of carbon dioxide gas and increasing the hydrogen ion concentration.)
10. Repeat step 4 by withdrawing the plunger until it stops. While holding the plunger in the completely withdrawn position, shake the solution until the color of the solution no longer changes.
11. Determine the pH of the solution in the syringe at the increased volume and record both the pH and the total volume of material (liquid plus gas) in the syringe. (Equilibrium will reestablish itself to give a pH of approximately 4.4 at an expanded volume.)
12. Holding the syringe with the tip cap up, remove the tip cap from the syringe. Attach the syringe to the carbon dioxide source and draw in $3-4 \mathrm{~mL}$ of carbon dioxide gas. Reseal the syringe by firmly pressing the tip cap on its open end. Compress the mixture while shaking until the color of the solution no longer changes. Record the pH of the solution as well as the new volume of material after the mixture was compressed. (Increasing the $\mathrm{CO}_{2}(\mathrm{~g})$ concentration shifts the equilibrium shown in Equation 1 to the right, increasing the hydrogen ion concentration and lowering the pH .)
13. Discuss the results in terms of LeChâtelier's Principle.

## Part B. Effect of Temperature

14. Dispose of the solution in the syringe and obtain about 2.0 mL of fresh seltzer/indicator solution into the syringe. If the initial color of the solution has changed noticeably from Part A, prepare a new seltzer/indicator solution.
15. Holding the syringe with its open end upwards, draw carbon dioxide gas into the syringe from its source until the total volume of material in the syringe is about 5 mL . Seal the syringe by pushing the syringe tip cap firmly on its open end.
16. Compare the color of the seltzer/indicator solution with the bromcresol green color chart to determine the pH of the seltzer water. Record the initial pH of the solution, the total volume of all material in the syringe, and the temperature of the solution in the beaker. (The initial pH is 4.2 at a total volume of approximately 5 mL and an initial temperature of $21^{\circ} \mathrm{C}$.)
17. Remove the beaker of boiling water from the hot plate and place the syringe into the heated water.
18. Holding the syringe by the plunger, stir the hot water while shaking the mixture in the syringe up and down. Tap on the plunger a few times while shaking the solution to overcome the friction between the plunger and the sides of the syringe.
19. After several minutes, record the temperature of the water, the total volume of the mixture in the syringe, and the pH of the solution. (At a temperature of $100^{\circ} \mathrm{C}$, the volume increases and the pH increases to 4.6.)
20. What effect does increasing the temperature have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1? (Increasing the temperature shifts the equilibrium shown in Equation 1 to the left, reducing the solubility of carbon dioxide gas and decreasing the bydrogen ion concentration.)
21. Remove the syringe from the hot water and place it into the ice-water bath. Holding the syringe by the plunger, stir the
ice-water bath while shaking the mixture in the syringe up and down. Tap on the plunger a few times while shaking the solution to overcome the friction between the plunger and the sides of the syringe.
22. After several minutes, record the temperature of the water, the total volume of the mixture in the syringe, and the pH of the solution. (At a temperature of $5^{\circ} \mathrm{C}$, the volume decreases and the pH decreases to 4.0.)
23. What effect does decreasing the temperature have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1? (Decreasing the temperature shifts the equilibrium shown in Equation 1 to the right, increasing the solubility of carbon dioxide gas and increasing the hydrogen ion concentration.)

## Disposal

Please consult your current Flinn Scientific Catalog/Reference Manual for general guidelines on specific procedures governing the disposal of laboratory waste. The resulting solutions may be flushed down the drain with excess water according to Flinn Suggested Disposal Method \#26b.

## Tips

- Any unflavored, unbuffered seltzer will work as a source of dissolved carbon dioxide. Do not use soda water or club soda, which contains sodium bicarbonate. Club soda is essentially a buffered solution-its pH will not change.
- Prepare an aqueous $0.04 \%$ solution of bromcresol green by dissolving 1 g of bromcresol green, sodium salt in 250 mL of distilled or deionized water.
- The following information can be used to prepare a color chart for bromcresol green:

| Color | $\mathbf{p H}$ | $\left[\mathbf{H}^{+}\right], \mathbf{M}$ | Color | $\mathbf{p H}$ | $\left[\mathbf{H}^{+}\right]$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Yellow | 3.8 | $16 \times 10^{-5}$ | Dark green | 4.6 | $2.5 \times 10^{-5}$ |
| Yellow-green | 4.0 | $10 \times 10^{-5}$ | Blue-green | 4.8 | $1.6 \times 10^{-5}$ |
| Light green | 4.2 | $6.0 \times 10^{-5}$ | Blue | 5.0 | $1.0 \times 10^{-5}$ |
| Green | 4.4 | $4.0 \times 10^{-5}$ | Blue | 5.2 | $0.6 \times 10^{-5}$ |

- Alternatively, a pH reference strip for bromcresol green can be prepared to relate the color of the indicator solution and the pH . Prepare a series of acetic acid/sodium acetate buffers in the pH range 3.8-5.2 by mixing the appropriate volumes of 0.1 M acetic acid and 0.1 M sodium acetate, as shown in the following table. Obtain a $1 \times 8$-well microscale reaction strip and add 8 drops of buffer to each well in order from pH 3.8 to 5.2 (see below). Add 1 drop of bromcresol green indicator to each well and mix thoroughly using a toothpick.

| $\mathbf{p H}$ | Volume of 0.1 M <br> Acetic Acid | Volume of 0.1 M <br> Sodium Acetate |
| :---: | :---: | :---: |
| 3.8 | 3.0 mL | 22.0 mL |
| 4.0 | 4.5 mL | 20.5 mL |
| 4.2 | 6.6 mL | 18.4 mL |
| 4.4 | 9.3 mL | 15.8 mL |
| 4.6 | 12.3 mL | 12.8 mL |
| 4.8 | 15.0 mL | 10.0 mL |
| 5.0 | 17.6 mL | 7.4 mL |
| 5.2 | 19.8 mL | 5.3 mL |

- This demonstration requires about 10 mL of carbon dioxide gas. Almost any method of generating and dispensing the gas will work. See the Supplementary Information section for a sample procedure.


## LeChâtelier's Principle and the Solubility of Carbon Dioxide continued

## Discussion

This activity demonstrates the effect of pressure and temperature on three reversible reactions: the solubility of carbon dioxide in water, the reaction of dissolved carbon dioxide and water to form $\mathrm{H}_{2} \mathrm{CO}_{3}$, and the weak acid ionization of $\mathrm{H}_{2} \mathrm{CO}_{3}$ to give $\mathrm{HCO}_{3}^{-}$and $\mathrm{H}^{+}$ions. For simplicity sake in terms of classroom discussion, these reactions are combined into one equation in Equation 1. The position of equilibrium for this reaction can be determined by measuring the concentration of $\mathrm{H}^{+}$ions in solution. Seltzer water is used as a source of dissolved carbon dioxide, and the concentration of $\mathrm{H}^{+}$ions is estimated using bromcresol green as an indicator. The indicator is yellow when the pH is less than 3.8 , blue when the pH is greater than 5.2 , and various shades of green in the pH range 3.8-5.2. A sealed syringe is used to provide a closed system.

$$
2 \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{CO}_{2}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq}) \quad \text { Equation } 1
$$

The effects of pressure and temperature on the solubility of carbon dioxide gas can be explained in terms of LeChâtelier's Principle:
"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of its components, the system will tend to shift its equilibrium position so as to counteract the effect of this disturbance."
When the total pressure above the seltzer water/indicator solution is reduced (by increasing the applied volume), the indicator color changes from yellow-green to green, corresponding to a pH change from 4.0 to 4.4. Since a pH increase corresponds to a decrease in the hydrogen ion concentration, the results indicate that the equilibrium shown in Equation 1 is shifted to the left as the pressure decreases-the solubility of carbon dioxide decreases. This is in agreement with LeChâtelier's Principle. Carbon dioxide gas is forced out of solution, back into the gas phase, thus increasing the pressure of the gas in the closed system. The reverse effect is observed when the pressure is increased. The relationship between gas pressure and the amount of dissolved carbon dioxide illustrates an application of Henry's Law, which states that the amount of a gas dissolved in solution is proportional to the pressure of the gas above the solution. The effect of changing the temperature on the position of equilibrium for Equation 1 can also be explained in terms of a pressure effect, since increasing the temperature of a gas will increase both the volume and the temperature. In general, the solubility of a gas will be greatest at higher pressures and lower temperatures.

## Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):
Unifying Concepts and Processes: Grades K-12
Evidence, models, and explanation
Evolution and equilibrium
Form and function
Content Standards: Grades 5-8
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, properties and changes of properties in matter
Content Standards: Grades 9-12
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, structure of atoms, structure and properties of matter, chemical reactions

## LeChâtelier's Principle and the Solubility of Carbon Dioxide continued

Sample Data Table (Student answers will vary.)

## Part A. Effect of Pressure

| Step \# | Volume of Liquid Plus Gas | Indicator color | $\mathbf{p H}$ |
| :---: | :---: | :---: | :---: |
| $2 \& 3$ | 2 mL | Yellow-green | 4.0 |
| 5 | 4 mL | Green | 4.4 |
| 8 | 2 mL | Yellow-green | 4.0 |
| 11 | 4 mL | Green | 4.4 |
| 12 | 7 mL | Blue | 5.0 |

## Part A. Discussion Questions

1. What effect does decreasing the pressure have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1?
When the total pressure above the solution decreases the reaction shifts to the left to reestablish equilibrium, and the solubility of carbon dioxide is reduced.
2. What effect does increasing the pressure have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1?
Increasing the pressure increases the solubility of the carbon dioxide and the reaction shifts to the right.
3. Explain the results in terms of LeChâtelier's Principle.

In both cases, the change in reaction conditions causes the reaction to shift in such a way so that the effect of the change will be counteracted. Equilibrium is then reestablished under these new conditions.

## Part B. Effect of Pressure

| Step \# | Volume of Liquid Plus Gas | Indicator color | $\mathbf{p H}$ | Temp ${ }^{\circ} \mathbf{C}$ |
| :---: | :---: | :---: | :---: | :---: |
| 16 | 5 mL | Light green | 4.2 | $21^{\circ} \mathrm{C}$ |
| 19 | 9.5 mL | Dark green | 4.6 | $100^{\circ} \mathrm{C}$ |
| 22 | 4.5 mL | Light green | 4.2 | $1.5^{\circ} \mathrm{C}$ |

## Part B. Discussion Questions

4. What effect does increasing the temperature have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1?
Increasing the temperature shifts the equilibrium shown in Equation 1 to the left, reducing the solubility of carbon dioxide gas and decreasing the bydrogen ion concentration.
5. What effect does decreasing the temperature have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1?
Decreasing the temperature shifts the equilibrium shown in Equation 1 to the right, increasing the solubility of carbon dioxide and increasing the hydrogen ion concentration.
6. Explain the results in terms of LeChâtelier's Principle.

When the temperature increases, the volume of the gas phase increases. At increased volume, the concentration of carbon dioxide in the gas phase is reduced, causing the reaction to shift to the left to counteract this change. At lower temperatures, the volume decreases, the concentration of carbon dioxide in the gas phase increases, and the reaction shifts to the right to counteract the change.

## Supplementary Information

## Preparation of the Bromocresol Green Solution, 0.04\%

Dissolve 0.1 gram of bromocresol green in 14.3 mL of 0.01 M NaOH and dilute to 250 mL .
or dissolve 0.1 gram of bromocresol green, sodium salt, in 250 mL of water
or dissolve 0.1 gram in 250 mL of $95 \%$ ethanol
Preparation of the $1^{\prime} 8$ Colorimetric pH Strips
The colorimetric/pH standard consists of a $1^{\prime} 8$ reaction strip containing 2 drops of bromocresol green indicator and 8 drops of acetic acid/sodium acetate buffer in each well in pH 3.8 to 5.2 order. Seal each well with hot melt glue. When cool, write the pH of the glue bead with a dark-colored permanent marking pen.

## Preparation of the Buffers

Prepare the buffer by mixing the sodium acetate and acetic acid solutions together in a vial or small bottle.
0.2 M sodium acetate- 3.4 grams of $\mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \cdot 3 \mathrm{H}_{2} \mathrm{O} / 250 \mathrm{~mL}$ of solution
0.2 M acetic acid- 3.0 grams of glacial acetic acid $/ 250 \mathrm{~mL}$ of solution

| $\mathbf{p H}$ | Volume of 0.2 M <br> Sodium Acetate Solu- <br> tion | Volume of 0.2 M <br> Acetic Acid Solution |
| :---: | :---: | :---: |
| 3.8 | 3.0 | 22.0 |
| 4.0 | 4.5 | 20.5 |
| 4.2 | 6.6 | 18.4 |
| 4.4 | 9.3 | 15.8 |
| 4.6 | 12.3 | 12.8 |
| 4.8 | 15.0 | 10.0 |
| 5.0 | 17.6 | 7.4 |
| 5.2 | 19.8 | 5.3 |

## Dispensing the $\mathbf{C O}_{2} \mathbf{G a s}$

Since each student needs only $3-4 \mathrm{~mL}$ of $\mathrm{CO}_{2}$, almost any method of dispensing the gas will work. One method is to fill a plastic bag with gas either from a tank or generated from marble chips and HCl . Another method is to simply draw some of the gas into the syringe from the inside of the seltzer bottle. It may be helpful to shake the bottle to release $\mathrm{CO}_{2}$ from the supersaturated solution. Another method is to fill a large syringe and then allow the students to withdraw some of the gas from the syringe.

## Carbon Dioxide Generator

Carbon dioxide gas can be generated by the reaction of marble chips and 3 M hydrochloric acid in an Erlenmeyer flask equipped with a gas delivery tube. Use a 1-quart plastic freezer bag as a gas delivery apparatus, as described below.
To construct the gas delivery apparatus, cut a \#10, one-hole rubber stopper with a large, sharpened cork borer. The result is a stopper with a plug that can be removed (the plug has the original single hole in it). Remove the plug from the stopper and push the plastic bag through the hole in the stopper, leaving about 1 inch of the bag out of the opening. Place the smaller, one-hole stopper "plug" into the freezer bag opening. The freezer bag should now be held tightly between the walls of the two stoppers. Carefully insert the tapered end of a medicine dropper through the hole in the stopper plug. Attach a short piece of latex tubing over the wide end of the medicine dropper and place a pinch clamp over the latex tubing.
To fill the gas with carbon dioxide, first evacuate the plastic bag by attaching the latex tubing to an aspirator. When the bag has been evacuated, replace the pinch clamp on the tubing and then attach the end of the tubing to the gas delivery tube on the carbon dioxide generator. Remove the pinch clamp and slowly fill the bag assembly with carbon dioxide. The bag should be taut when filled, but not ready to burst. Remove the tubing from the gas generator and replace the pinch clamp. The bag contains a slightly pressurized sample of carbon dioxide gas.

## LeChâtelier's Principle and the Solubility of Carbon Dioxide continued

## Reference

Dean, John, Lange's Handbook of Chemistry, 13th. Ed., 1992, McGraw-Hill Book Company, New York, page 11-30. ibid, page 5-104.
Flinn ChemTopic ${ }^{\mathrm{TM}}$ Labs, Volume 15, Equilibrium, Cesa, I., Ed., Flinn Scientific, Batavia, IL, 2003.

## Flinn Scientific-Teaching Chemistry ${ }^{\text {TM }}$ eLearning Video Series

A video of the LeChâtelier's Principle and the Solubility of Carbon Dioxide activity, presented by John Mauch, is available in LeChâtelier's Principle, part of the Flinn Scientific-Teaching Chemistry eLearning Video Series.

The LeChâtelier's Principle and the Solubility of Carbon Dioxide is available from Flinn Scientific, Inc.

| Catalog No. | Description |
| :--- | :--- |
| B0064 | Bromcresol Green Indicator Solution, 0.04\% aqueous |
| LB1005 | Carbon Dioxide Gas, Lecture Bottle, 0.5 lb |
| AP1730 | Syringe, without Needle |
| AP8958 | Syringe Tip Cap |
| AP1724 | Reaction Strips, 8 Wells |
| AP1721 | Pipet, Beral-Type, Graduated |
| AP8870 | Thermometer |

Consult your Flinn Scientific Catalog/Reference Manual for current prices.
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## Equilibrium in a Syringe Student Worksheet

$$
2 \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{CO}_{2}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq})
$$

## Color Chart for Bromcresol Green

| Color | $\mathbf{p H}$ | $\left[\mathbf{H}^{+} \mathbf{]}, \mathbf{M}\right.$ | Color | $\mathbf{p H}$ | $\left[\mathbf{H}^{+}\right]$ |
| :--- | :---: | :---: | :--- | :---: | :---: |
| Yellow | 3.8 | $16 \times 10^{-5}$ | Dark green | 4.6 | $2.5 \times 10^{-5}$ |
| Yellow-green | 4.0 | $10 \times 10^{-5}$ | Blue-green | 4.8 | $1.6 \times 10^{-5}$ |
| Light green | 4.2 | $6.0 \times 10^{-5}$ | Blue | 5.0 | $1.0 \times 10^{-5}$ |
| Green | 4.4 | $4.0 \times 10^{-5}$ | Blue | 5.2 | $0.6 \times 10^{-5}$ |

## Data Tables

Part A. Effect of Pressure

| Step \# | Volume of Liquid Plus Gas | Indicator color | $\mathbf{p H}$ |
| :---: | :--- | :--- | :--- |
| $2 \& 3$ |  |  |  |
| 5 |  |  |  |
| 8 |  |  |  |
| 11 |  |  |  |
| 12 |  |  |  |

## Part A. Discussion Questions

1. What effect does decreasing the pressure have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1?
2. What effect does increasing the pressure have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1?
3. Explain the results in terms of LeChâtelier's Principle.

## Equilibrium in a Syringe Student Worksheet, cont.

## Part B. Effect of Pressure

| Step \# | Volume of Liquid Plus Gas | Indicator color | $\mathbf{p H}$ | Temp ${ }^{\circ} \mathbf{C}$ |
| :---: | :--- | :--- | :--- | :---: |
| 16 |  |  |  |  |
| 19 |  |  |  |  |
| 22 |  |  |  |  |

## Part B. Discussion Questions

4. What effect does increasing the temperature have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1?
5. What effect does decreasing the temperature have on the solubility of carbon dioxide gas and on the position of equilibrium for Equation 1?
6. Explain the results in terms of LeChâtelier's Principle.
