CHAPTER 3 HYDROGEN

HENRY CAVENDISH[1] IS CREDITED with having first isolated and studied hydrogen as a true chemical element in 1766. He produced the gas, which he called *inflammable air* by reacting hydrochloric acid with metals. Although others, including John Mayow and Robert Boyle also knew of the reaction between metals and acid, Cavendish is given credit for the discovery because he was the first to systematically study the properties of the gas. In the late 18th century, Antoine Lavoisier recognized the substance as an element and later named it *hydrogen* from the two Greek words meaning "water-forming".

Henry Cavendish

Hydrogen is a colorless, odorless, and tasteless gas that is insoluble in water. Very little molecular hydrogen, H_2, can be found in nature. The most familiar compound of hydrogen is water which is $^2/_{18}$ or 11% hydrogen by mass but $^2/_3$ hydrogen by atom count. Hydrogen makes up over 92% of all the atoms of the Universe. Our sun consists of 30% by mass hydrogen.

Hydrogen is the lightest of all known molecular substances. Even helium has a molar mass that is twice as large. As a result, the density of hydrogen is very small (0.0824 g/L at 25 ^oC and 1 atm) and is over 14 times smaller than that of air. Another result of having such a small molar mass is that hydrogen's melting point (-259.14 ^oC or 14.0 K) and boiling point (-252.5 ^oC or 20.7 K) are extremely low.

The most readily used source of hydrogen is natural gas. Methane is combined with steam at 1000 ^oC to produce hydrogen and carbon monoxide. The mixture of CO and H_2 is called ***synthesis gas*** or just ***syn gas***.

---

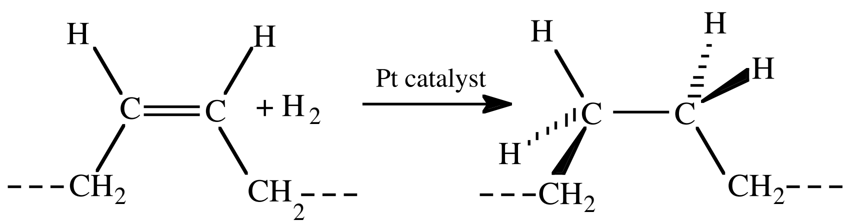
[1] To learn more about Henry Cavendish, visit our gas website, http:// mattson.creighton.edu/Microscale_Gas_Chemistry.html and click on "History of Gas Chemistry"

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3\ H_2(g) \qquad \Delta H^o_{rxn} = +206\ kJ$$

The major industrial use of hydrogen in terms of mass used is in the synthesis of ammonia by the Haber process. Over 16 million tons of ammonia are produced annually in the USA and most of this is used for fertilizer.

$$3\ H_2(g) + N_2(g) \rightarrow 2\ NH_3(g)$$

Hydrogen is also used to ***hydrogenate*** oils in the food industry. Vegetable oils contain numerous double bonds and are called polyunsaturated oils. These double bonds react with hydrogen in the presence of a catalyst. The product is margarine which has properties of a solid and is called a saturated fat.



Hydrogen is used in the manufacture of methanol, which in turn is used in many industrial applications including the plastics and adhesives industries. It is also used to prepare metals from their oxides at elevated temperatures. The process is expensive so that only precious metals are produced this way.

$$MO_x + x\ H_2(g) \rightarrow M(s) + x\ H_2O(g)$$

Suitability

The following experiments are included in this chapter:

Part 1. Experiments with Hydrogen

Experiment 1. Traditional test for hydrogen
Experiment 2. Hydrogen forms explosive mixtures with air
Experiment 3. Reversible conversion of copper metal and copper(II) oxide
Experiment 4. Reduction of iron(III) oxide with hydrogen

Part 2. Demonstrations and Advanced Experiments with Hydrogen

Experiment 5. Effusion of hydrogen is faster than air
Experiment 6. Hydrogen burns with a gentle flame
Experiment 7. Incomplete combustion of hydrogen
Experiment 8. Disappearing/reappearing candle flame
Experiment 9. Calcium and calcium hydride produce hydrogen in reactions with water
Experiment 10. Deuterium isotope effect

The first four experiments are designed for use by all levels of students (from middle school age through university level). Very little prior knowledge is required. Students with more experience will understand the experiments at a higher level than beginning students, but will also enjoy these experiments. These experiments are appropriate when discussing chemical compounds, chemical formulas, chemical reactions, the mole, as well as a variety of topics including physical and chemical changes.

Experiments in Part 2 are best performed as classroom demonstrations. They address particular concepts usually encountered later in the first year chemistry course. Experiment 5 should be done with the gas laws to demonstrate effusion. Experiment 6 demonstrates chemical reactivity of hydrogen. Experiment 7, similar in design to Experiment 6, demonstrates part of the reaction mechanism for hydrogen combustion by trapping a reaction intermediate. Experiment 8 is a very impressive classroom demonstration; a candle flame appears to be extinguished as a syringe full of hydrogen is lowered over the burning candle. As the syringe is raised, the candle re-ignites. The process can be repeated several times. Experiment 9 works well with a discussion of the chemical reactivity of alkaline earth metals and/or metal hydrides. Experiment 10 is the only advanced topic experiment and is used to demonstrate the deuterium isotope effect.

Background skills required

Students should be able to:

- generate a gas as learned in Chapter 1
- measure quantities of liquid reagents
- use a balance
- use a Bunsen burner

Time required

Students should be able to generate hydrogen and perform the four experiments in Part 1 in a single 45 minute laboratory period.

Preparation of hydrogen in a "gas bag"

Large samples of $H_2(g)$ can be prepared conveniently in 1 L food storage bag. See Chapter 5 for details.

Website

This chapter is available on the web at website:

http://mattson.creighton.edu/Microscale_Gas_Chemistry.html

Instructions for your students

For classroom use by teachers. Copies of all or part of this document may be made for your students without further permission. Please attribute credit to Professors Bruce Mattson and Mike Anderson of Creighton University and this website.

Microscale Gas Chemistry Kits

Each pair of students will need certain equipment in order to prepare gases and perform experiments with the gases. We recommend organizing this equipment in 8 cup plastic food storage containers. Each kit should contain:

- two 60 mL plastic syringes with a LuerLOK fitting
- two Latex LuerLOK syringe caps
- two plastic vial caps
- one 15 cm length of Latex tubing
- one 3 cm length of Latex tubing
- one plastic pipet
- one clear plastic beverage cup (250 mL/9 oz)
- one small plastic weighing dish
- one small test tube (12 x 100 mm)
- one medium test tube (18 x 150 mm)
- one birthday candle

All of this will fit into the food storage container. In addition, each pair of students will need a wide-mouth beverage bottle for draining and supporting their syringes. Ordering information for kit materials is given at the end of this chapter and in Appendix E.

PREPARATION OF HYDROGEN[1]

General Safety Precautions

Always wear safety glasses. Gases in syringes may be under pressure and could spray liquid chemicals. Follow the instructions and only use the quantities suggested. **CAUTION!** Hydrogen forms explosive mixtures with air.

Toxicity

Hydrogen is relatively non-toxic; however, it is a simple asphyxiant if inhaled in very large quantities. We will not be generating large quantities of hydrogen.

Equipment

Microscale Gas Chemistry Kit

Chemicals (needed for each syringe full of hydrogen produced)

0.05 g solid Mg turnings or ribbon (approximately 6 cm ribbon = 0.05 g)
3 - 5 mL 2 M HCl(aq)

This quantity of magnesium will produce approximately 50 mL of H_2. The production of H_2 is ***very*** fast and it typically takes less than 30 seconds to fill a syringe. The reaction is:

$$Mg(s) + 2\ HCl(aq) \rightarrow H_2(g) + MgCl_2(aq)$$

Generating hydrogen gas samples

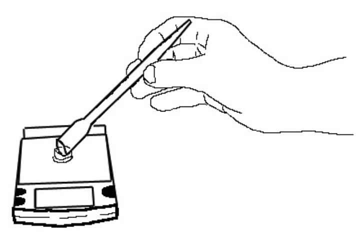
Samples of hydrogen are generated by the In-Syringe Method as described in Chapter 1 and repeated here.

1. Wear your safety glasses

2. Measure out the solid reagent

(Use 0.05 g Mg to make H_2)

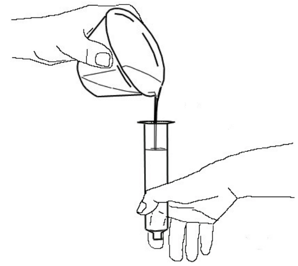
Place the solid reagent into the vial cap. It may be difficulat to measure out such a small amount of magnesium. Your teacher may tell you how to estimate this quantity. For example, use **x** turnings or use **x** cm Mg ribbon corresponds to 0.05 g, rather than having you measure the amount on a balance.



[1] Content for this chapter first appeared as "Microscale Gas Chemistry, Part 3. Experiments with Hydrogen" Mattson, B. M., ***Chem13 News***, **253**, December, 1996.

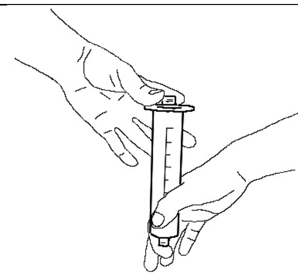
3. Fill the syringe barrel with water

Fill the barrel with water. Place your finger over the hole to form a seal. Fill completely to the top.



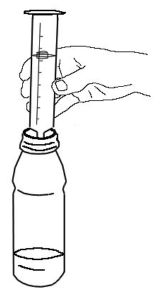
4. Float the vial cap

Float the vial cap containing the solid reagent on the water surface. This is easiest if the syringe barrel is filled completely to the top with water.



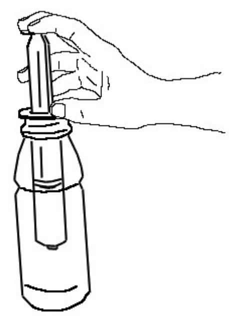
5. Lower the cap by flotation

Release the seal made by finger to lower the cap into the syringe barrel without spilling its contents. Option: Allow the syringe to drain into a wide mouth beverage container. When successfully completed, the cap should rest upright on the bottom of the syringe with all reagent still in the cap.



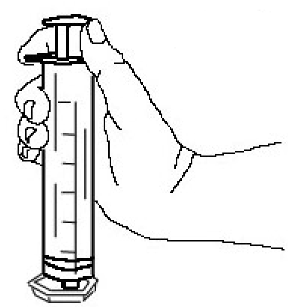
6. Install the plunger

Install the plunger while maintaining the syringe in a vertical position. The plunger has a plastic "rib" near the rubber seal that snaps past the "catch" — a small ridge just inside the mouth of the syringe. Usually it takes a firm push to move the rib past the catch. After that, the plunger should move smoothly. The plunger should fit snugly against the rim of the vial cap.



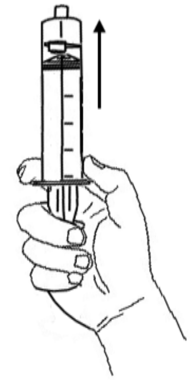
7. Draw aqueous reagent into syringe
(Use 3 – 5 mL 1 M HCl to make H_2)

The aqueous reagent, measured into a small weighing dish, is drawn into the syringe while maintaining the vertical position of the syringe. The vial cap with the solid reagent should float on the solution.



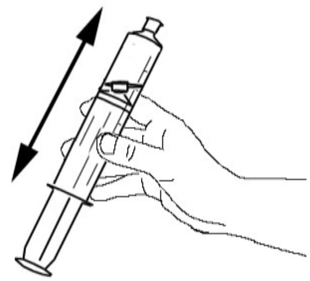
8. Minimizing the quantity of air prior to reaction because hydrogen and air form explosive mixtures.

This procedure is used when there is excess air in the syringe before the reaction begins. Carefully rotate the syringe so as not to let the vial cap spill ints contents. With the syringe opening directed upward, carefully push the plunger inward until the air is mostly gone. Install the syringe cap by turning or pushing it on.



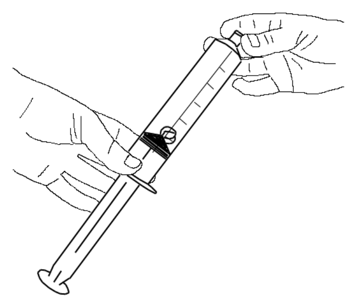
9. Generate the gas

Hold the syringe so that the cap is up. Shake the syringe in order to mix the reagents. As the liquid reagent splashes into the vial cap, gas generation will commence and the syringe plunger should move outward. It is sometimes necessary to gently help the plunger move up the barrel.



10. Remove cap to stop gas collection

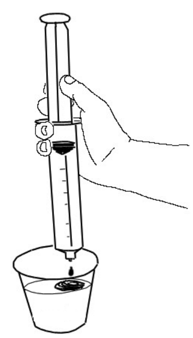
Keep the cap up! After the plunger has reached the desired mark (usually 60 mL), remove the syringe cap and leave it off through Step 11. The syringe is under positive pressure so there will be a tiny gas release sound.



11. Discharge reagents

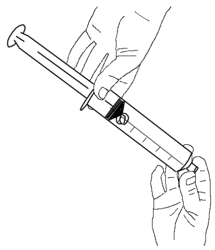
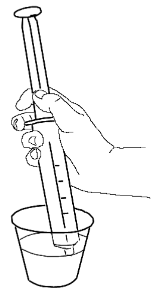
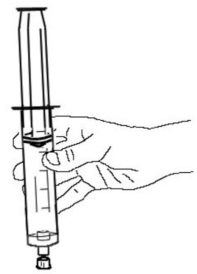
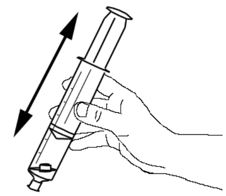
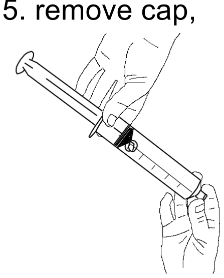
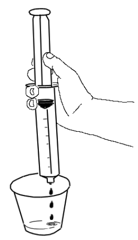
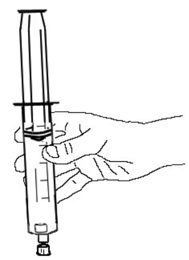
Turn the syringe 180^{o} and discharge the liquid reagent into the plastic cup over half-filled with water in order to dilute the reactants. Immediately cap the syringe with the syringe cap to prevent loss of gas by effusion.

Caution: Always use Steps 9, 10, and 11 as described. Never remove the syringe cap with the cap end directed downward: Reagents will spray out of the syringe onto your hands.



12. Wash away contaminants

The gas-filled syringe may be "washed" in order to remove traces of unwanted chemicals from the inside surfaces of the syringe before the gas is used in experiments. To wash a gas:

1. Remove the syringe cap (with H_2, keep tip downward) 	2. draw 5 mL water into the syringe, 	3. cap the syringe, 	4. shake syringe to wash inside surfaces, 
5. remove cap, 	6. discharge water only, and finally 	7. recap the syringe. 	8. Repeat? One rinse is usually enough.

Disposal of hydrogen samples

Unwanted hydrogen samples can be safely discharged into the room.

Teaching tips

1. The generation of hydrogen is a rapid reaction and should be practiced before showing your students.
2. Hydrogen is the only gas for which diffusion is a major concern. When the syringe cap is off, keep the opening directed downward to minimize loss of hydrogen through the hole.
3. If magnesium ribbon is being used, measure the mass of a 25 cm length. Determine the mass per cm and use that to cut pieces of desired mass instead of using a balance. If magnesium turnings are being used, measure the mass of x turnings, measure the mass and divide the mass by x. Use this to estimate how many turnings each preparation should take – as an alternative to measuring out such small amounts of magnesium.

Introductory Questions

1. What is the formula for hydrogen gas?
2. Why should you hold the syringe with the opening down when the cap is off?
3. What was the volume of hydrogen you actually obtained in your syringe?

Questions

4. Was the reaction exothermic or endothermic?

5. How accurately can you read the syringe?

6. What about the position of the plunger before the reaction started (due to the volume of air and solution already present before the reaction started)? Should this volume be subtracted?

Advanced Questions

7. Determine the number of moles of magnesium you used to prepare your hydrogen.

8. Use the molar concentration of HCl and the volume used to determine the number of moles of HCl you used to make hydrogen gas.

9. Write the balanced chemical equation for the reaction occurring in your syringe.

10. Which is the limiting reactant, Mg(s) or HCl(aq)?

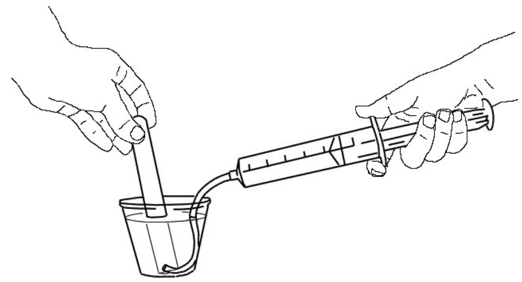
11. Using the ideal gas law and your answer to the previous question, what volume of gas is predicted? (Assume the temperature is 25 ^{o}C and standard pressure)

PART 1. HYDROGEN EXPERIMENTS FOR STUDENTS

EXPERIMENT 1. TRADITIONAL TEST FOR HYDROGEN

Equipment

Microscale Gas Chemistry Kit
Match or lighter
a coin



Chemicals

$H_2(g)$, 20 mL

Suitability

middle school lab, high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

chemical properties of gases, combustion reactions, gas density, characterization of gases, energy changes

Instructions

Affix a candle to a coin. Melt a drop of wax from a candle onto a coin and immediately push the base of a candle into hot wax so that the candle stands vertically.

Part 1. Fill the test tube with water and place it upside down in the cup of water. Light the candle. Connect the long piece of tubing (15 cm) to the fitting on the syringe. Displace the water with H_2 as shown in the figure above. Remove the test tube from the water, keeping it open-end downward, and move the open end near a lit candle. A BARK! sound will confirm the presence of hydrogen.

Part 2. Repeat the experiment using a test tube half-filled with air and half-filled with hydrogen. To do this, start with a test tube half-filled with air and half-filled with water and then displace the water with hydrogen. A much louder BARK! will result.

Teaching tips

Show students how to invert water-filled test tubes without loss of water. Filling the cup to nearly full makes it easier.

Introductory Questions

1. Hydrogen is much lighter than air. What other gas is also lighter than air? Hint:

2. What is the purpose of collecting the gas under water — by displacing the water in a test tube as was done in this experiment?

3. Hydrogen is an element with the atomic symbol H. It exists in nature as a molecular substance with the formula H_2. Oxygen does exactly the same thing. Write the atomic symbol for oxygen and write the formula of the molecular substance it forms.

Questions

4. Why was the test tube containing hydrogen gas stored upside down in the water?

5. Suppose you had two unlabeled test tubes, one that contained hydrogen and the other carbon dioxide. Suggest an experiment you could do to determine what gas was in each tube.

6. Why was the hydrogen-air mixture considerably louder than that of pure hydrogen?

7. Sketch what would happen to the hydrogen gas if you were to rotate the test tube so that the open end was directed upward.

Advanced Questions

8. What familiar product formed when you ignited the $H_2(g)$?

9. Write and balance the equation for the reaction that takes place when hydrogen burns (explodes) in air?

EXPERIMENT 2. HYDROGEN FORMS EXPLOSIVE MIXTURES WITH AIR

Equipment

Microscale Gas Chemistry Kit
Match or lighter

Chemicals

$H_2(g)$, 50 mL
3% dish soap solution

Suitability

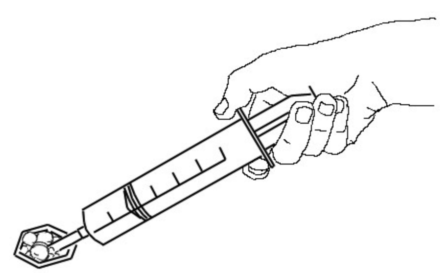
middle school lab, high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

combustion reactions, kinetics, chemical properties of gases, activation energy

Instructions

Part 1. Fill a small plastic weighing dish with 3% dish soap. Generate hydrogen using quantities listed above. Discharge the aqueous solution and equip the syringe fitting with a 3 cm length of tubing. (If you must store the syringe for even a few minutes, use the syringe cap.) Place the free end of the tubing into the soap solution and slowly discharge some of the hydrogen. Once a rounded mound of bubbles has been produced, remove the tubing and ignite the bubbles. A mild BARK! will occur as the hydrogen undergoes a comparatively gentle "explosion".



Part 2. With a syringe half-full of hydrogen, draw in an equal volume of air and repeat the experiment. This time, when the mixture is ignited, a louder, more definite explosion occurs.

Teaching tips

1. The hydrogen and air mixture produced in the syringe is an explosive mixture.
2. 3% dish soap solution is prepared my adding 3 g dish soap to enough water to make 100 mL.

Introductory Questions

1. What difference did you notice between Parts 1 and 2 in the experiment? Explain.
2. What is the purpose of the soap solution?
3. Why should extreme care be exercised when working with hydrogen gas?

Questions

4. What are the two major gases found in the air? Which one is reacting with hydrogen in this experiment?
5. If one bubble of hydrogen and one bubble of air were side-by-side and ignited, would the bang be louder or not as loud than if the same amount of gas were contained in a single bubble?
6. Would the explosion be louder if oxygen were used instead of air — with the same amount of hydrogen? Air is 21% oxygen.

Advanced Questions

7. Write the balanced chemical equation for the reaction occurring in this experiment.
8. Suggest an experiment to determine what mixture produces the loudest bang from a hydrogen/air mixture using the soap bubble solution.

EXPERIMENT 3. REVERSIBLE CONVERSION OF COPPER METAL AND COPPER(II) OXIDE

Equipment

- Microscale Gas Chemistry Kit
- small Bunsen burner
- glass Pasteur pipet
- ring stand and clamp
- match or lighter
- wooden stick such as a kabob skewer — must be able to fit into the pipet

Chemicals

- copper wool such as a ChoreBoy kitchen scrubbing pad
- hydrogen, $H_2(g)$, 50 mL

Suitability

middle school lab, high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

Preparation of metals, preparation of an ionic substance, types of solids, oxidation/reduction

Instructions

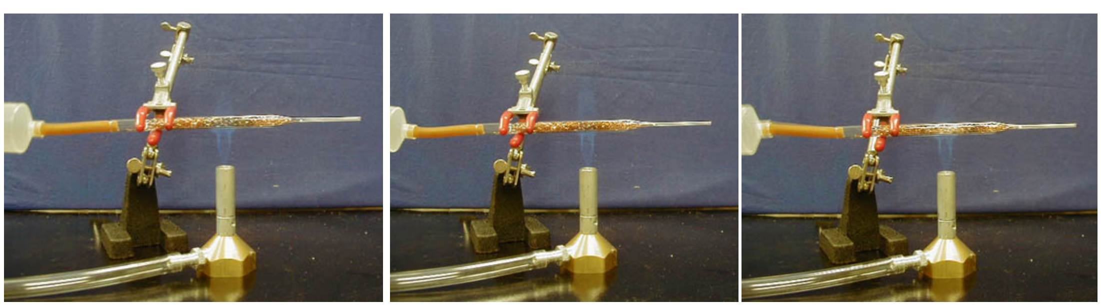
Use a wooden stick to position a 0.50-g plug of copper wool into a glass pipet. Clamp the pipet in a horizontal position.

Part 1. Heat the Cu/pipet for 30 s and then slowly pass 60 mL air through the pipet while continuing to hold the pipet in the flame. The copper will quickly turn black. The reaction is:

$$2\ Cu(s) + O_2(g) \rightarrow 2\ CuO(s)$$

Part 2. Connect the H_2-filled syringe to the pipet. Heat the CuO/pipet and then slowly pass the hydrogen gas through the pipet while continuing to hold the pipet in the flame. Water droplets should appear inside the stem of the pipet. The reaction is:

$$2\ CuO(s) + H_2(g) \rightarrow 2\ Cu(s) + H_2O(l)$$



Teaching tips

1. Tell students that hot glass looks like cold glass! Burns from touching hot glass are treated with aloe vera.

2. The terms ***oxidation*** and ***reduction*** are omitted from this experiment for use at introductory levels. Add them to your discussion if appropriate.

3. One purpose of this experiment is to draw attention to the four fundamental types of substances — metals, ionic compounds, molecular compounds and network covalent compounds. Students will work with all four in this experiment. (SiO_2, the primary component of the glass pipet, is a network-covalent compound.)

4. You may wish to construct the pipet devices for the students. These can be stored and used again.

Introductory Questions

1. Give the formulas for (a) copper(II) oxide, (b) elemental copper, (c) molecular hydrogen and (d)water, all of which were encountered in this experiment.

2. What did you observe that indicates to you that a reaction has taken place?

3. Do you think this reaction could be repeated over and over without consuming the copper — or will the copper eventually be used up?

Questions

4. How do you know that the conversion of copper to copper(II) oxide and then copper(II) oxide to copper is reversible?

5. Why is it necessary to heat the Cu in order for it to react?

Advanced Questions

6. The four fundamental types of substances are: metals, ionic compounds, molecular compounds and network covalent compounds. What fundamental type of substances id each of the following? (a) hydrogen; (b) copper; (c) copper(II) oxide; (d) water; and (e) silicon dioxide (the predominant component of the glass pipet)

7. Three of the four fundamental types of substances are almost always solids under standard conditions. Which type can be solid, liquid or gas under standard conditions?

8. These reactions can be discussed in terms of oxidation and reduction chemistry. Determine the oxidizing agent and reducing agent in each of the two reactions given in the instructions.

EXPERIMENT 4. REDUCTION OF IRON(III) OXIDE WITH HYDROGEN

Equipment

Microscale Gas Chemistry Kit
glass disposable pipet
Bunsen burner
Matches or lighter
Magnet
"000" steel wool

Chemicals

H_2 (g), 40 mL
Fe_2O_3(s), 0.25 g

Suitability

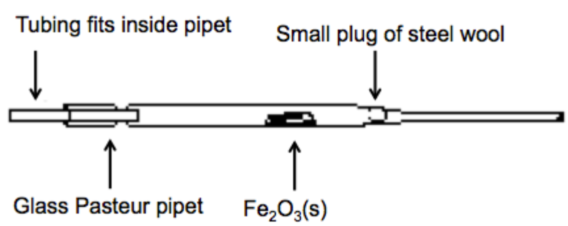
middle school lab, high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

magnetic properties of metals, preparation of a metal from an ore, oxidation/reduction.

Instructions

Prepare the pipet device as shown at right using 0.25 g Fe_2O_3. Test the Fe_2O_3 by holding a magnet above it through the glass. Heat the Fe_2O_3 for 30 s and then slowly pass H_2 gas through the pipet while continuing to hold the pipet in the flame. The powder will quickly darken and water droplets should appear inside the stem of the pipet. Remove the heat and allow the pipet to cool. Hold a magnet above the mound of solid metallic powdered iron. The reaction is:



$$Fe_2O_3(s) + 3\ H_2(g) \rightarrow 2\ Fe(s) + 3\ H_2O(g)$$

Teaching tips

1. Tell students that hot glass looks like cold glass! Burns from touching hot glass are treated with aloe vera.
2. If an analytical balance is available, one can determine the mass of the Fe_2O_3(s) used and the mass of the pipet/ Fe_2O_3(s) before and after the reaction. The

difference is the mass of oxygen lost during the reaction. A very close comparison between the predicted and observed mass loss is possible.

Introductory Questions

1. What does the “2” and “3” mean in the formula Fe_2O_3?

2. What did you observe that indicates to you that a reaction has taken place?

3. How does the magnet tell us that a reaction has taken place? Why will this test not work for every reaction?

4. Substances that are attracted to a magnet are called ferromagnetic. Is Fe_2O_3 ferromagnetic? Is Fe?

Questions

5. Write the chemical reaction that has taken place in sentence form: *“Iron(III) oxide and …)”*

6. Calculate the rate of hydrogen flow in mL/min.

Advanced Questions

7. Why is it necessary to heat the Fe_2O_3 in order for it to react?

8. Calculate the number of moles of Fe_2O_3 used in the pipet. Calculate the number of moles of H_2 passed through the pipet. Which reagent was in excess?

9. As the reaction between oxygen and iron took place, a bright white glow may have been observed. Does this indicate an exothermic or endothermic reaction?

Clean-up and storage

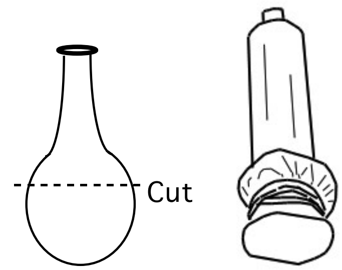
At the end of the experiments, clean the syringe parts, caps and tubing with water. Rinse all parts with distilled water if available. Be careful with the small parts because they can easily be lost down the drain. **Important:** Store plunger out of barrel unless both are completely dry.

PART 2. DEMONSTRATIONS AND ADVANCED EXPERIMENTS WITH HYDROGEN

EXPERIMENT 5. EFFUSION OF HYDROGEN IS FASTER THAN AIR

Equipment

Microscale Gas Chemistry Kit
Balloon, 25 cm diameter
rubber bands, two heavy duty scissors



Chemicals

$H_2(g)$, 60 mL

Suitability

classroom demonstration

Applications, Topics, Purpose

gas density, effusion/diffusion, kinetic molecular theory of gases

Instructions

Cut the end off of a large balloon as shown above. Generate $H_2(g)$, discharge the aqueous reagents and then cap the syringe. With the syringe cap directed ***upward as in the figure above (so that hydrogen does not escape)***, remove the plunger and secure the balloon over the syringe opening with a rubber band as in above. Gather the balloon so that the rubber is taut over the syringe opening. Use a second rubber band as well. The rubber bands must be wound quite tightly in order to prevent hydrogen loss.

Clamp the syringe in position with balloon end up (opposite of that shown in the figure). Within 30 minutes there should be visible evidence that the balloon is being pushed into the syringe barrel. By the next day, the balloon is drawn in by a very noticeable amount. After 3-5 days, the balloon will be extensively drawn into the syringe barrel. The experiment can be continued for weeks.

Teaching tips

1. No chemical reaction occurs with this experiment.
2. Noticeable results of the experiment are not immediate. If there is no evidence that the balloon being pulled into the syringe after several hours, it is likely that the balloon has not been tightly sealed to the syringe.
3. This experiment shoud be done as a demonstration because of the time involved.

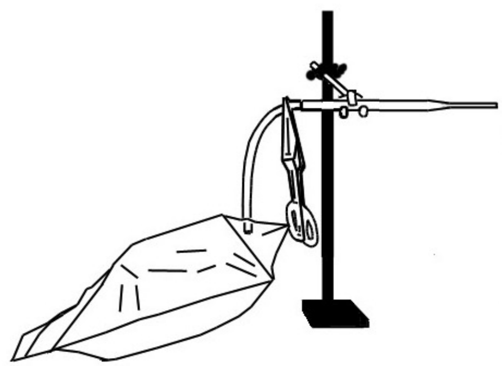
Questions

1. Why is the balloon being pushed into the syringe? What is pushing the balloon inward?
2. What does the word *effusion* mean? What is the difference between diffusion and effusion? If you do not know, look these terms up in a dictionary.
3. Predict what would happen if this experiment were repeated with a syringe filled with CO_2(g) instead of hydrogen.

EXPERIMENT 6. HYDROGEN BURNS WITH A GENTLE FLAME

Equipment

Microscale Gas Chemistry Kit
Glass disposable pipet
Matches or lighter
Food storage bag, 1 L / 1 quart
hemostat (or pinch clamp)
ring stand and clamp



Chemicals

Chemicals to generate hydrogen

Suitability

classroom demonstration

Applications, Topics, Purpose

explosive mixtures, combustion, simple reactions

Instructions

In Chapter 5 we describe the use of a plastic food storage bags for generating and storing larger quantities of gas. Like most gases, hydrogen can be generated inside the "gas bag" which consists of a length of tubing inserted into a food storage bag. See Chapter 5 for construction details. Assemble the apparatus as shown in the figure. Use a 15 cm length of tubing to connect the gas bag to the pipet.

Use the gas bag to discharge hydrogen at a constant, controlled rate in order to sustain a small flame. Keep the gas bag away from flames. Open the hemostat (or pinch clamp) and ignite the gas issuing from the pipet. Gently press down on the gas bag to control and sustain the flame. To stop the combustion, pinch the tubing shut.

The flame is "gentle" because of the lack of oxygen in the fuel. The flame is yellow because of the sodium in the glass; hydrogen normally burns with a blue flame.

Teaching tips

1. Do this experiment as a demonstration to reduce the chance for an explosion. Follow the instructions exactly.

2. Hydrogen forms explosive mixtures with air.

Questions

1. From Experiment 2, you learned that hydrogen and air form explosive mixtures. How does the design of this experiment prevent an explosion?

2. Write and balance the chemical reaction that takes place in both this and Experiment. 2

3. In Experiment 2, we deliberately created an explosive mixture of hydrogen and air and then ignited the mixture. Why are we so concerned about the same sort of explosive mixture in this experiment and have designed the experiment so that an explosion does not take place?

Advanced Questions

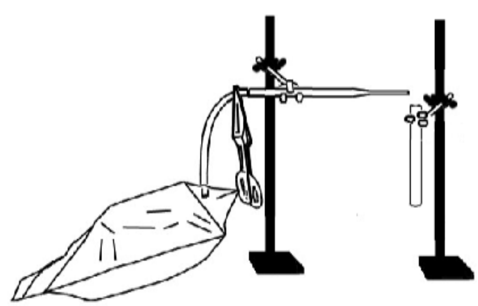
4. When hydrogen burns, we see a flame. When hydrogen/air mixtures explode we do not see a flame. Why?

5. What would happen if one were to hold a piece of glass above the flame at a safe distance (so it is not heated by the flame)?

EXPERIMENT 7. INCOMPLETE COMBUSTION OF HYDROGEN

Equipment

Glass disposable pipet
Matches or lighter
Food storage bag, 1 L / 1 quart
hemostat (or pinch clamp)
Latex tubing, 1/8-inch (3.175 mm) ID, 20 cm length
ring stands (2) and clamps (2)
test tubes, 18 x 150 mm (2)
graduate cylinders, 10 mL and 100 mL or volumetric flasks, 10 mL and 100 mL



Chemicals

Hydrogen or chemicals to generate hydrogen in a bag (Ch 5)
potassium permanganate, 0.010 g
starch, potato
potassium iodide, 1.66 g
ice chips

Suitability

University lab and classroom demonstration

Applications, Topics, Purpose

Reaction intermediates, radicals, reaction mechanism, combustion processes

Instructions prior to the demonstration:

This experiments builds on the previous experiment. The combustion of hydrogen in air is quite complex with at least 28 mechanistic steps and twelve reaction species. Most of the species involved are radical (having unpaired electrons) in nature. Among the various species generated, a few are stable (full octet), including hydrogen peroxide. In a normal hydrogen flame, the hydrogen peroxide goes on to further oxidation resulting in water. In this classroom demonstration, a hydrogen flame is played across the face of an ice cube and the combustion is quenched in an incomplete state. The solution that results contains aqueous hydrogen peroxide that can be tested with two simple chemical tests.

In Chapter 5 we describe the use of a plastic food storage bags for generating and storing larger quantities of gas. Like most gases, hydrogen can be generated inside the “gas bag” which consists of a length of tubing inserted into a food storage bag. See Chapter 5 for construction details. Assemble the apparatus as shown in the figure. Use a 20 cm length of tubing to connect the gas bag to the pipet. Obtain hydrogen from a compressed cylinder if available; it is convenient and the purity is good. Connect the Latex tubing directly to the gas regulator. Adjust the pressure to 100 kPa (1 atm, 15 psi) using the gas regulator knob. Use the flow valve to slowly discharge the desired amount of gas into the plastic gas bag. Do not overfill the gas bag. Seal the gas bag shut with the hemostat pinching the tubing as shown in the Figure.

Prepare a 6.3×10^{-4} M $KMnO_4$ solution by dissolve 0.010 g $KMnO_4$ per 100 mL solution. Next, prepare a starch-iodide solution: Make a slurry of 1 g potato starch in 20 mL distilled water in a small beaker. Heat the slurry with stirring until the color goes from the opaque white to a translucent gel. Remove from heat. Prepare 1.0 M KI solution: dissolve 1.7 g potassium iodide, KI, in 10 mL water. For each demonstration, mix 3 mL KI(aq) with 1 mL starch.

Instructions for the demonstration:

A hemostat stops the flow of hydrogen until one is ready to begin. When it is time for the demonstration, one simply removes the hemostat and ignites the hydrogen issuing from the pipet. The flame is small and often difficult to see, but the heat it produced is easily detected 10 cm away and a piece of paper brought near the flame will ignite. Occasionally, the hydrogen flame will appear yellow due to the sodium in the glass pipet. Using the hemostat, an ice chip is held in front of the flame at close range so that the flame plays across the ice. The test tube is adjusted so that the drippings can be collected. It takes less than one minute to obtain 3 – 5 mL of solution. The flame will often burn a hole through the ice chip. The exact amount of solution collected can be determined by measuring the mass of the test tube before and after collection.

Testing the solution for hydrogen peroxide.

The use of a control is always important. In this case, simply fill a second test tube with a quantity of distilled water equal to the amount of drippings collected.

Potassium permanganate test.

To each test tube, add several drops of dilute potassium permanganate solution (approx. 6.3×10^{-4} M $KMnO_4$). This will turn the distilled water pink-purple. In the test tube containing hydrogen peroxide, the permanganate will slowly, over the course of a minute or two, oxidize hydrogen peroxide to O_2(aq), but at this low concentration, bubbles are not noticed. Permanganate is reduced to either colorless (Mn^{+2}) or to a yellow-brown color (Mn^{+4}), however, no precipitate of MnO_2 is detected. One may continue to add an equal number of drops of the $KMnO_4$ solution to both solutions until the test tube comprised of drippings starts to persist with a purple color. Color photographs of these results are available at our gas chemistry website.

Potassium iodide test.

Add 10 drops of a 1.0 M potassium iodide/starch solution to a test tube of collected drippings and to the control solution. The solution with the drippings containing hydrogen peroxide will become faintly blue within a minute and will continue to darken to an intensely deep blue over a period of five minutes. The solution should turn blue indicating the presence of I_3^-(aq) produced by the reaction between KI(aq) and H_2O_2(aq)[2] Color photographs of these results are available at our gas chemistry website.

$$I^-(aq) + H_2O_2(aq) + H^+(aq) \rightarrow HOI(aq) + H_2O(l)$$
$$HOI(aq) + 2\, I^-(aq) + H^+(aq) \rightarrow I_3^-(aq) + H_2O(l)$$
$$2\, I_3^-(aq) + starch \rightarrow starch\text{-}I_5^- + I^-(aq)$$

[2] Shakhashiri, B. Z., ***Chemical Demonstrations, A Handbook for Teachers of Chemistry***, volume 4, pg 42.

Discussion

The idea for this experiment is quite old. In Partington's 1950 Textbook of Inorganic Chemistry, he describes the formation of small amounts of aqueous hydrogen peroxide by "playing" a hydrogen flame across an ice cube.[3]

The combustion of hydrogen is familiar to most students of chemistry:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$

Possible mechanisms for this reaction have been studied for over 30 years.[4] Reactions that take place in a flame are usually very complicated and varied. For example, a recent article investigating the mechanism of hydrogen combustion proposed two mechanisms that involved twelve chemical species and 34 different reactions.[5] Despite the complicated subtleties of these mechanisms, a few simple mechanistic reaction steps are fundamental in understanding hydrogen combustion. A reaction of primary importance is the thermal dissociation of the H_2 bond:

$$H_2(g) \rightarrow 2\ H\cdot(g) \qquad \Delta H = +436\ kJ$$

Reactions such as this are unheard of under normal laboratory temperatures but are important and common at the temperature of a flame. In this case, atomic hydrogen, H·, is formed. Atomic hydrogen, also called the "hydrogen radical" because of its unpaired electron, is extremely reactive towards a variety of species including molecular oxygen:

$$H\cdot(g) + O_2(g) \rightarrow HO_2\cdot(g)$$

In this prominent reaction, the H· radical produces the $HO_2\cdot$ radical, a high-energy intermediate that is involved in at least five other reactions with species including OH·, H·, ·O·, and another $HO_2\cdot$, all "normal" components of the gas mixture in a hydrogen/air flame. The reaction between OH· and $HO_2\cdot$ produces water, the final product of hydrogen combustion:

$$OH\cdot(g) + HO_2\cdot(g) \rightarrow H_2O(g) + O_2(g)$$

The reaction between two $HO_2\cdot$ groups, however, produces hydrogen peroxide:

$$HO_2\cdot(g) + HO_2\cdot(g) \rightarrow H_2O_2(g) + O_2(g)$$

Hydrogen peroxide is not a normal product of hydrogen combustion, but rather a reaction intermediate that can undergo further high-temperature reactions with either H· or OH·:

---

[3] J. R. Partington; ***Textbook of Inorganic Chemistry***, Macmillan. This text was first published in 1921 and continued through at least six editions with the 6th edition copyrighted 1950.

[4] A literature search produced over ten matches for "hydrogen" + "combustion" + "mechanism". Many were done by the Russians over the last 30+ years. In the following study, kinetic rate constants for several "elementary processes" of hydrogen combustion were determined: Balakhnin, V. P.; Gershenzon, Y. M.; Kondrat'ev, V. N.; Nalbandyan, A. B.; ***Dolk. Akad. Nauk SSSR*** (1966), 170(5), 1117 – 20.

[5] Brown, N. J.; Li, G.; Koszykowski, M. L.; ***International Journal of Chemical Kinetics*** (1997), 29(6), 393 – 414. This article provides a full discussion of the process of hydrogen combustion.

$$H_2O_2(g) + H\cdot(g) \rightarrow HO_2\cdot(g) + H_2(g)$$
$$H_2O_2(g) + OH\cdot(g) \rightarrow HO_2\cdot(g) + H_2O(g)$$

As demonstrated by the second of these reactions, H_2O is ultimately produced as the final product of hydrogen combustion in air. Under certain conditions, $H_2O_2(g)$ can survive as a reaction byproduct.

In addition to these reactions, $H_2O_2(g)$ can undergo O-O bond dissociation to produce OH· radicals:

$$H_2O_2(g) \rightarrow 2\ OH\cdot(g)$$

As we saw above, OH·(g) is an important species that reacts with $HO_2\cdot(g)$ to produce $H_2O(g)$.

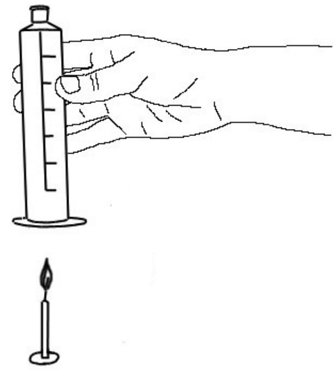
Teaching tips

1. Place a small weight such as a test tube wire rack on the hydrogen gas bag to increase the flow.
2. Do not make direct contact between the pipet and the ice cube. The flame will go out and water will plug the pipet stem. Sometimes it is hard to re-light it after this happens.
3. With use, the pipet melts closed and the flame becomes smaller and smaller. Replace the pipet after every few uses.
4. A YouTube movie of the reaction is available: (https://www.youtube.com/watch?v=pp8kC-aGbK4&feature=em-upload_owner).

Questions

1. What are the "normal" products of combustion when a hydrocarbon burns? When pure carbon burns? When pure hydrogen burns?
2. What causes the yellow color seen in the hydrogen flame?
3. Draw Lewis dot structures for the three principle radical species described above, H·, OH·, and $HO_2\cdot$.

EXPERIMENT 8. DISAPPEARING/REAPPEARING CANDLE FLAME



Equipment

Microscale Gas Chemistry Kit

Chemicals

magnesium turnings or ribbon, 0.10 g
hydrochloric acid, HCl(aq), 5 mL of 2 M

Suitability

classroom demonstration (all levels — including middle school)

Applications, Topics, Purpose

explosive mixtures, combustion, simple reactions

Instructions

Affix a candle to a coin with a drop of molten wax. Generate hydrogen using 0.10 g magnesium turnings or ribbon and 5 mL of 2 M HCl(aq) instead of the usual quantities. This will generate more than a syringe full of hydrogen. As the plunger reaches the top of the syringe barrel and is almost ready to pop out of the barrel, stop the reaction by discharging the aqueous solution into the plastic cup. Immediately cap the syringe with the syringe cap. Light the candle and turn off the room lights. With the cap directed upward, remove the plunger from the syringe barrel and immediately lower the syringe carefully but quickly over the top of the candle flame as shown in the figure. *As soon as the flame goes out, **raise the syringe.*** The candle should re-ignite. This experiment takes some practice. Once perfected, it makes an interesting magic trick.

Teaching tips

1. There are several possible explanations. Most likely, the wick is glowing hot enough to re-ignite the hydrogen once enough air is available again. In pure hydrogen, the candle does not burn. Hydrogen needs oxygen to burn.

2. A YouTube video of this experiment is available (http://www.youtube.com/watch?v=ZAK-4Ahm8i4). This is a good way to see how it is done.

Questions

1. Discuss possible explanations with other students. Agree upon the most plausible explanation.

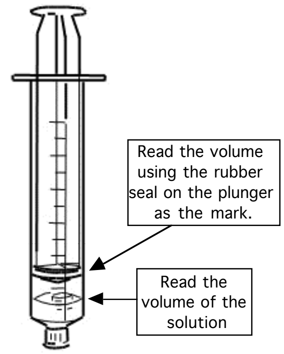
2. What, if anything, is wrong with other explanations that have been proposed?

3. Are all flames visible? Can a substance burn without a visible flame?

EXPERIMENT 9. CALCIUM AND CALCIUM HYDRIDE PRODUCE HYDROGEN IN REACTIONS WITH WATER

Equipment

Microscale Gas Chemistry Kit



Chemicals

Calcium metal, free of oxide, < 1 g
Calcium hydride, CaH_2, < 1 g

Suitability

college prep high school lab, university lab, and classroom demonstration

Applications, Topics, Purpose

Chemical reactions, oxidation of metals, oxidation-reduction reactions, Part A: reactivity of alkaline earth metals, Part B: hydrides, reactivity of hydrides

Instructions

Part A. A sample of fresh calcium, free of oxide coating, should be used. The exact mass (between 0.03 - 0.04 g) is determined using an analytical balance. The calcium is placed in a *dry* vial cap and lowered into the syringe. The liquid reagent is 20 mL of distilled water. Record the initial volume mark on the syringe barrel. Use the outer rubber ring on the plunger as a convenient reference as shown in the figure. Perform the reaction by shaking the syringe. The solution will bubble as hydrogen is produced and will eventually become cloudy due to $Ca(OH)_2(s)$ which is only sparingly soluble in water. The reaction is:

$$Ca(s) + 2\,H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$

Record the final volume mark and determine the volume of hydrogen by subtracting the volume of air originally present. The volume is quite close to what is expected from stoichiometry and ideal gas calculations. An ideal gas laboratory experiment could be developed that utilizes this procedure.

The 20 mL of solution now contains suspended calcium hydroxide solid and a small amount of dissolved calcium hydroxide. A variety of experiments can be performed with the solution. Add a few drops to an indicator solution to show that the pH is high. Discharge 10 mL of the solution into a plastic cup. Add just enough 1 M HCl(aq) to the cloudy suspension to produce a clear solution of aqueous calcium chloride:

$$Ca(OH)_2(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + 2\,H_2O(l)$$

As another variant, the calcium hydroxide suspension can be allowed to settle in the syringe where contact with air is avoided. After a few hours, the suspended $Ca(OH)_2(s)$ has settled producing a clear solution of limewater, $Ca(OH)_2(aq)$. Limewater has a number of uses as a reagent; it is used to test for $CO_2(g)$ and is used with alum to enhance settling of turbid water.

Part B. Repeat the experiment using between 0.03 - 0.04 g CaH_2 instead of calcium metal. The reaction is:

$$CaH_2(s) + 2\ H_2O(l) \rightarrow Ca(OH)_2(s) + 2\ H_2(g)$$

Teaching tips

1. If the calcium metal is not fresh, make sure the oxide coating has been scraped off.
2. Scraps of calcium and calcium oxide should be destroyed by reaction with water or any acidic solution. Do not place scraps of calcium metal or calcium hydride in the trash! A fire may result. Add small amounts of unwanted calcium metal and/or calcium hydride to a large quantity of water in order to destroy them.

Questions

1. Describe the appearance of the calcium metal before the reaction.
2. Describe the appearance of the calcium hydride before the reaction.
3. What is the formula of calcium hydride? Is calcium hydride ionic, covalent, metallic, or network covalent?
4. Describe your observations of the reaction between calcium metal and water (and between calcium hydride and water if Part B was done).
5. What class of reaction describes this (these) reaction(s)?
6. How might the product gas be tested?

EXPERIMENT 10. DEUTERIUM ISOTOPE EFFECTS[6]

Equipment

Microscale Gas Chemistry Kit

Chemicals

Bromphenol blue solution, < 2 mL
5 M H_2SO_4 Solution, < 2 mL
3.33 g D_2O
Magnesium turnings, < 1 g

Suitability

university lab and classroom demonstration

Applications, Topics, Purpose

chemical kinetics, isotopes and chemical reactivity

Instructions

The rates of chemical reactions are often dependent on the isotopes of the elements involved. This occurs because compounds containing heavier isotopes have slower average molecular speeds in both the gas phase and in solution. This phenomenon can be demonstrated as follows.

You will need two syringe assemblies for this experiment. They should be labeled "H_2O" and "D_2O." In two plastic weighing dishes measure out equimolar amounts of reagents as per the table:

Reagent:	**Weighing Dish 1: H_20 Solution**	**Weighing Dish 2: D_2O Solution**
Water (0.167 moles of each)	3.00 g H_2O	3.33 g D_2O
Bromphenol blue solution	10 drops	10 drops
5 M H_2SO_4 Solution	7 drops	7 drops
Calculated D/H Mole Ratio	0.0/1.0	3.0/1.0

Place 0.20 g of magnesium turnings in each of two vial caps. Draw ***all*** of the solutions into their respective syringes and install the syringe caps. Hold both syringes in the same hand and vigorously shake the syringes to mix the solutions. Within 2-3 minutes the color in the syringes begins to turn blue as the acid is consumed. The color change occurs in the H_2O syringe well before it does in the D_2O syringe.

The chemical equation for the reaction of magnesium with sulfuric acid is:

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

[6] This experiment is based on one published by Binder and Eliason, ***Journal of Chemical Education***, **63,** 536 (1986)

In the syringe with the $D_2O(l)$, hydrogen ion exchange between H^+ and D^+ is nearly instantaneous. Because the ratio of D/H is approximately 3:1 we can think of sulfuric acid as having the formula D_2SO_4 and thus the reaction is:

$$Mg(s) + D_2SO_4(aq) \rightarrow MgSO_4(aq) + D_2(g)$$

Teaching tips

1. The rate of a chemical reaction depends to a small extent on the isotope used. Heavier isotopes move slower than lighter isotopes of the same element. When these isotopes are part of a compound, the differences can be extremely small. However, in the case of H_2O vs. D_2O, the difference in molar mass is 18 g/mol vs. 20 g/mol — a difference of over 10%. The reaction with D_2O should be noticeably slower. This phenomenon is called *the deuterium isotope effect*.

2. The bromphenol blue indicator is yellow at the start of the experiment when the pH is lower and change to a blue color (a higher pH) when the experiment is complete.

Questions

1. What does the word *isotope* mean?

2. What is the difference between H and D? Write their isotope symbols using $^{m}{}_{Z}E$ notation, where m is the atomic mass number, Z is the atomic number and E is the element symbol.

3. Hydrogen has a third isotope, $^{3}_{1}H$ called tritium. Tritium is extremely rare and radioactive. How would the rate of reactions involving tritium compare to those involving deuterium and regular hydrogen? Rank the three of these isotopes in order of rate of reaction from slowest to fastest.

Summary of Materials and Chemicals Needed for Chapter 3. Experiments with Hydrogen.

Equipment required for Part 1: Student Experiments (Experiments 1 – 4)

Item	For Demo	For 5 pairs	For 10 pairs
Microscale Gas Kit (See Chap 1)	1	5	10
candle affixed to coin	1	5	10
Bunsen burner, small	1	5	10
glass Pasteur pipet	1	5	10
magnet	1	5	10
matches or lighter	1	5	10
ring stand and clamp	1	5	10

Materials required for Part 1: Student Experiments (Experiments 1 – 4)

Item	For Demo	For 5 pairs	For 10 pairs
copper wool such as a ChoreBoy scrubbing pad	a	a	a
“000” steel wool	a	a	a

a. one pad will be enough for entire group

Chemicals required for Part 1: Student Experiments (Experiments 1 – 4)

Item	For Demo	For 5 pairs	For 10 pairs
Mg turnings or ribbon	1 g	5 g	10 g
2 M HCl(aq)	20 mL	100 mL	200 mL
3% dish soap solution	10 mL	50 mL	100 mL
Fe_2O_3(s)	0.25 g	2 g	5 g

Equipment required for Part 2: Advanced Experiments and Demonstrations (Experiments 5 – 9)

Item	For Demo
balloon, 25 cm diameter	1
glass disposable pipet	1
matches or lighter	1
hemostat (or pinch clamp)	1
ring stands and clamps	2

Materials required for Part 2: Advanced Experiments and Demonstrations (Experiments 5 – 9)

Item	For Demo
balloon, 25 cm diameter	1
rubber bands, two heavy duty	1
scissors	1
food storage bag, 1 L / 1quart	1

Chemicals required for Part 2: Advanced Experiments and Demonstrations (Experiments 5 – 9)

Chemicals required for Part 2, Demonstrations:

Item	For Demo
Mg turnings or ribbon	2 g
2 M HCl(aq)	10 mL
potassium permanganate, $KmnO_4$	1 g
potassium iodide, KI	1 g
potato starch	1 g
calcium metal, free of oxide	< 1 g
calcium hydride, CaH_2	< 1 g
bromphenol blue solution	< 2 mL
5 M H_2SO_4 solution	< 2 mL
deuterium oxide, D_2O	4 mL

