CHAPTER 16 CHLORINE

Carl Wilhelm Scheele, a Swedish chemist, discovered chlorine in 1774. He did not understand that it was an element, but rather believed it to be a compound of oxygen. He produced the gas by reacting HCl(aq) with MnO_2(s) according to the reaction that we now know to be:

$$MnO_2(s) + 4\ H^+(aq) + 2\ Cl^-(aq) \rightarrow Mn^{+2}(aq) + Cl_2(g) + 2\ H_2O(l)$$

Scheele noted the bleaching power of the gas and within eleven years numerous patents appeared covering this process. Another scientist interested in chlorine was the French physician Claude Louis Berthollet. Several bleaching processes patented by Berthollet in 1785 are still used today.

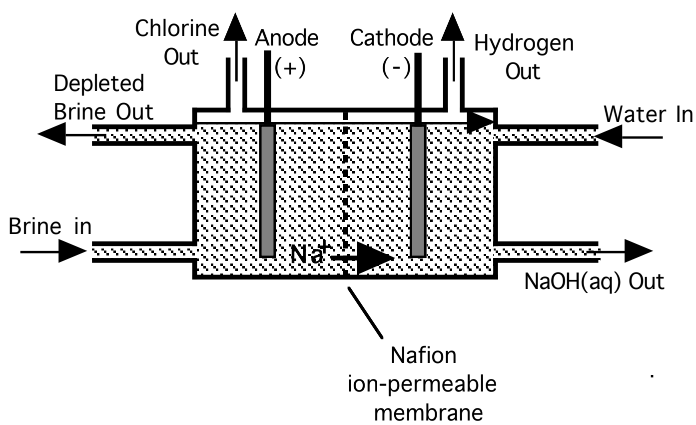
Sir Humphry Davy correctly identified Scheele's gas as an element in 1810 and he proposed the name ***chlorine***, which comes from the Greek word *khloros* which means yellow-green. Chlorine was used throughout Europe in the early 19th century as a disinfectant and germicide in order to control a cholera epidemic. Today, chlorine is used in virtually every country as a disinfectant of water supplies. Much of the chlorine produced is used in the manufacture of household bleach, NaOCl(aq). Industrial strength bleaches are used in pulp bleaching. Chlorine compounds are used to make dyes, textiles, medicines, insecticides, solvents, paints, and plastics. The plastic polyvinylchloride (PVC) is made from the monomer vinyl chloride, which ranks 15th in terms of quantities of chemicals manufactured in the USA.

Chlorine is a pale green-yellow gas with an unpleasant, bleach-like odor. Chlorine is a respiratory irritant to mucus membranes. It is detectable at 3.5 ppm, causes throat irritation at 15 ppm and coughing at 30 ppm. Exposure to Cl_2 at 1000 ppm (0.1%) is rapidly fatal. Chlorine was used as a trench warfare gas in 1915.

Chlorine has a melting point of -100.98 °C and a boiling point of -34.6 °C. The density of $Cl_2(g)$ is 2.898 g/L at 25 °C and 1 atm, 2.45 times greater than that of air. Chlorine is fairly soluble in water and colors it yellow-green. Under standard conditions, 3.1 volumes of Cl_2 will dissolve per 1 volume of water. At 10 °C, 14.6 g Cl_2 dissolve per L H_2O, corresponding to 4.62 volumes Cl_2 per 1 volume of water.

Chlorine does not occur in elemental form in nature. The vast majority is in the form of NaCl salt deposits that were produced from ancient seas. Sodium chloride is also the major salt present in the earth's oceans. In terms of natural occurrence in the earth's crust (which includes the oceans), chlorine ranks 20th at 0.065%. Chlorine is found in the minerals halite (NaCl), carnallite ($KMgCl_3 \cdot 6H_2O$), and sylvite (KCl). Like most of the minerals present in ocean and seawater, the sodium chloride present was carried there by rivers and run-off over the course of billions of years.

Chlorine has extensive uses in society and is one of the world's most important chemicals being manufactured on a large scale. Chlorine ranks 8th in terms of the quantities of chemicals manufactured in the USA. Industrial production of chlorine up through the 1970's and 80's involved the electrolysis of brine solutions, NaCl(aq), using an asbestos diaphragm cell and a mercury cathode electrode. For environmental reasons, this design has been all but replaced in modern countries by the Nafion ion-permeable membrane cell shown in the figure. The Nafion membrane is made of fluorine-containing polymers including Teflon. Its salient feature is to allow $Na^+(aq)$ ions to pass from one chamber to the other. In the left chamber brine solution enters the anode chamber where the chloride is oxidized to chlorine:



$$2\ Cl^-(aq) \rightarrow Cl_2(aq) + 2\ e^-$$

Pure water enters the cathode chamber where it is reduced to $H_2(aq)$ and $OH^-(aq)$:

$$2\ H_2O + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$$

Sodium hydroxide, NaOH(aq), another commercially important product, leaves the cathode chamber. The overall reaction is:

$$2\ H_2O + 2\ NaCl(aq) \rightarrow H_2(g) + 2\ NaOH(aq) + Cl_2(aq)$$

Suitability

All of these experiments are suited for use as classroom demonstrations. We do not advise these experiments for use as laboratory experiments conducted by high school students due to the toxicity of chlorine. Most of these experiments are suitable for university-level students, however, several of them are far better suited to be demonstrations. The following experiments are included in this chapter.

Experiment 1. Chlorine and sodium hydroxide form bleach
Experiment 2. Chlorine disproportionates in water to form acidic species
Experiment 3. Chlorine discolors the natural colors of fruit juices
Experiment 4. Testing colorfast fabrics
Experiment 5. Chlorine reacts with aqueous sodium sulfite
Experiment 6. Halogen activity series
Experiment 7. Chlorine and sodium form sodium chloride
Experiment 8. Hydrogen/chlorine rockets
Experiment 9. Chemiluminescence and singlet oxygen.
Experiment 10. Spectacular underwater fireworks
Experiment 11. Liquid and solid chlorine

Generally, the production of chlorine and the experiments that go with this gas should be conducted by individuals familiar and experienced with gas production using the syringe method introduced in Chapter 1. Chlorine has properties that make its proper use and handling more important than was the case for carbon dioxide, hydrogen and oxygen.

All of these experiments serve to review basic concepts of chemistry, especially chemical properties, chemical changes, writing and working with chemical formulas, chemical reactions, and writing balanced chemical equations. In addition to these review topics, chlorine forms an aqueous solution with sodium hydroxide (household bleach) that is a familiar household chemical.

Experiments 1 and 2 explore the disproportionation of chlorine in water and sodium hydroxide solutions — the formation of bleach. Experiments 3 and 4 demonstrate chlorine's ability to oxidize (called bleaching) natural and artificial pigments. Experiments 5 – 8 investigate the rich oxidation-reduction chemistry of chlorine. Experiments 9 and 10 are among the most spectacular in this book. Their main purpose is to demonstrate that light is a form of chemical energy. All of the first ten experiments involve oxidation-reduction chemistry. Experiment 11 simply demonstrates the phase changes for chlorine.

Background skills required

Students should be able to:

- ❖ generate a gas as learned in Chapter 1.
- ❖ know how to prevent accidental/unintentional discharge of gas.
- ❖ understand fundamental concepts of high school chemistry so that observations can be interpreted.

Time required

These experiments require more than one laboratory period if most are to be done by the students. Splitting the experiments between classroom demonstration and laboratory experiment is also a possibility. For example, during one 45-minute laboratory period, students could do:

Preparation of Chlorine
Experiment 1. Chlorine and sodium hydroxide form bleach
Experiment 3. Chlorine discolors the natural colors of fruit juices
Experiment 4. Testing colorfast fabrics
Experiment 5. Chlorine reacts with aqueous sodium sulfite

The remaining experiments could be performed as classroom demonstrations or selected experiments could be performed during a second laboratory period.

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.

PREPARATION OF CHLORINE[1]

We describe here two simple methods for generating chlorine using the In-syringe method learned in Chapter 1. Method A gives much better results, producing a syringe full of chlorine within 30 seconds while avoiding the use of 6 M HCl(aq). Method B goes not works quite as well, but has the advantage that it uses common household bleach.

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.

Toxicity

Chlorine has an irritating odor and is a poisonous gas. Concentrations of 4 ppm can be detected and 30 ppm will induce coughing. To put this in perspective, if 30 mL of Cl_2 were discharged into a volume of 1 m^3, the concentration of Cl_2 would be 30 ppm. Exercise caution when working with poisonous gases and vacate areas that are contaminated with unintentional discharges of gas.

Use a fume hood if available

The gas-generation and gas-washing steps should be carried out inside a working fume hood if possible.

Equipment

Microscale Gas Chemistry Kit (Chapter 1)
large vial cap, capable of holding 1 mL liquid and remain afloat (if Method B is used)

Chemicals

Method A	or	**Method B**
4 g NaOH		4 g NaOH
5 mL 2 M HCl(aq)		1.0 mL 6 M HCl(aq)
0.22 g $Ca(OCl)_2$(s)		3.0 mL household bleach

These quantities of reagents will produce approximately 55 mL of Cl_2. The production of Cl_2 is relatively fast and it typically takes 15 – 30 seconds to fill a syringe. The reactions for the two methods are:

$$\text{Method A: } Ca(OCl)_2(s) + 2\,HCl(aq) \rightarrow Ca(OH)_2(s, aq) + 2\,Cl_2(g)$$

$$\text{Method B: } 2\,HCl(aq) + NaOCl(aq) \rightarrow Cl_2(g) + NaCl(aq) + H_2O(l)$$

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[1] Content for this chapter first appeared as “Microscale Gas Chemistry, Part 10. Experiments with Chlorine” Mattson, B. M.; Harrison, B.; Lannan, J., ***Chem13 News***, **260**, October, 1997.

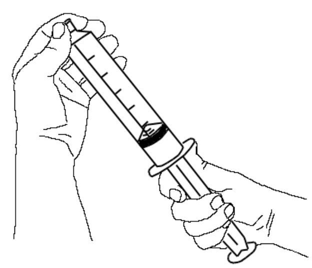
Preparation of Neutralization Solution

Prepare 100 mL of 1 M NaOH (4 g NaOH in H_2O to make 100 mL) in a 250 mL flask. Keep the flask stoppered when not in use. Label the flask "Neutralization Solution, 1 M NaOH." This solution will be used to neutralize excess reagents in the experiments.

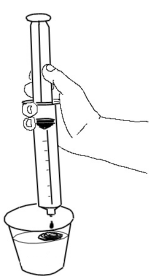
Preventing unwanted discharge of chlorine

Chlorine is a noxious gas and must not be discharged into breathable air. The use of syringes to generate such gas samples works exceptionally well and far better than any other method in preventing undesired discharges. There are two simple considerations to keep in mind whenever handling noxious gases:

(1) When opening the syringe (by removing the syringe cap), do so with the plunger slightly withdrawn so the contents are under reduced pressure. Use your thumb to maintain the plunger in this position as shown in the drawing. This will allow some air to enter the syringe but no noxious gas to escape.



(2) After the gas sample has been generated, discharge the used reagents into a cup containing the ***Neutralization Solution***.



Generating chlorine gas samples

The Cl_2 gas samples used in these experiments are generated by the In-syringe method described in Chapter 1. The following reagents (and quantities) are used.

	In the vial cap:	**In the weighing dish:**
Method A	0.22 g $Ca(OCl)_2(s)$	5 mL 2 M HCl(aq)
Method B	1.0 mL 6 M HCl(aq)	3.0 mL household bleach (6% NaOCl)

Method A

Generating chlorine by this method follows the same procedure that has been used in Chapter 1 (CO_2), Chapter 3 (H_2), and Chapter 4 (O_2). The solid calcium hypochlorite goes in the vial cap and is lowered by flotation. The liquid hydrochloric acid solution is drawn up into the syringe.

Method B

Unlike the reagents used to generate the other gases in this series, the reagent in the vial cap for Method B is a liquid and the reagent in excess. This assures that the reaction product will be acidic. A larger than normal vial cap is needed in order to hold 1 mL of reagent without sinking. If more than 3 mL bleach is used, the volume of gaseous $Cl_2(g)$ generated will *decrease*. The $Cl_2(g)$ will effervesce from the solution. If the plunger does not move easily in the barrel, gently pull the plunger outward every 10 seconds or so in order to accommodate the gas produced. Stop the gas generation after the syringe is full by removing the syringe cap while it is directed upwards. Rotate the syringe 180^o in order to discharge the reaction mixture into the **Neutralization Solution** and then recap the syringe. Fit the syringe cap over the syringe fitting.

Washing samples of chlorine

It is necessary to wash the Cl_2-filled syringes for some of these experiments. The gas-filled syringe is "washed" in order to remove traces of unwanted chemicals from the inside surfaces of the syringe before the gases can be used in experiments. To do this, draw 5 mL distilled water into the syringe without discharging any gas, cap the syringe and *gently* shake the water to dissolve the contaminants on the inside of the syringe. Remove the cap and discharge the water into the Neutralization Solution but not any of the gas. Chlorine is partially soluble in water, especially at high pH values. Some discoloration of the $Cl_2(g)$ present in the syringe should be expected from washing.

Disposal of chlorine samples

Unwanted samples of $Cl_2(g)$ can be discarded by drawing an equal volume of the **Neutralization Solution** into the syringe.

Teaching tips

1. Method A works much better than Method B. If Method B is used, the use of fresh bleach is necessary (Bleach has a short shelf-life.)
2. If >3 mL bleach is used (Method B), the volume of gaseous $Cl_2(g)$ generated will *decrease*!

Questions

1. Write the balanced equation for the reaction occurring in the syringe.
2. Determine the quantity of each reagent used and use the appropriate balanced chemical equation (Method A or B) in order to identify the limiting reagent. What quantity of $Cl_2(g)$, in moles is expected at 25 ^oC and standard pressure? With Method B, assume the density of bleach is 1 g/mL.
3. Assign oxidation numbers for chlorine in every species of the appropriate equation (either Method A or B). Determine the oxidizing and reducing agent.

EXPERIMENTS WITH CHLORINE

EXPERIMENT 1. CHLORINE AND SODIUM HYDROXIDE FORM BLEACH

Equipment

Microscale Gas Chemistry Kit

Chemicals

$Cl_2(g)$, 60 mL

3 M NaOH, 5 mL

Suitability

university lab, and classroom demonstration

Applications, Topics, Purpose

household chemicals, disproportionation, oxidation-reduction reactions, chemical changes, properties of chlorine, chemical formulas, writing balanced chemical equations, solutions, the dissolving process

Instructions

Add 5 mL 3 M NaOH to a weighing dish or small beaker. Generate a syringe full of $Cl_2(g)$. Washing the gas is unnecessary for this experiment. Draw the NaOH(aq) solution into the syringe and immediately cap the syringe. Vigorously shake the syringe to mix the chemicals. The plunger will be pulled inward as the Cl_2 reacts.

$$Cl_2(g) + NaOH(aq) \rightarrow NaOCl(aq) + NaCl(aq)$$

The resulting bleach solution can be washed down the drain with plenty of water — or used in Experiment 3 instead of $Cl_2(g)$.

Teaching tips

1. Chlorine disproportionates in this reaction to the oxidation states of +1 and –1.
2. The solution produced in this reaction can be used in Experiment 3 instead of $Cl_2(g)$.

Questions

1. What reaction took place in the syringe? What evidence indicated a chemical change took place during the demonstration? Does this evidence prove that a reaction took place or could there be an alterative explanation?
2. Assign oxidation numbers to the chlorine in every compound. What was oxidized? What was reduced?
3. Predict the reaction that would occur if the bleach solution were reacted with an acid such as HCl(aq). Hint: Review the reaction in Method B.

4. Chlorine is easily reduced to chloride. From Chapter 15 we learned that sulfur dioxide (and sulfites) are mild reducing agents. Write the oxidation-reduction reaction that would take place between chlorine and the sulfite ion to produce chloride and the sulfate ion under acidic conditions.

EXPERIMENT 2. CHLORINE DISPROPORTIONATES IN WATER TO FORM ACIDIC SPECIES

Equipment

Microscale Gas Chemistry Kit
pH meter

Chemicals

$Cl_2(g)$, 60 mL

Suitability

university lab and classroom demonstration

Applications, Topics, Purposes

drinking water, household chemicals, disproportionation, oxidation-reduction reactions, physical and chemical changes, properties of chlorine, chemical formulas, writing balanced chemical equations, solutions, solution equilibrium, acids-bases

Instructions

Add 50 mL distilled water to a plastic cup or small beaker. Generate a syringe full of $Cl_2(g)$. Position the pH meter in the distilled water. ***Slowly*** bubble 10 mL $Cl_2(g)$ through the water and observe the pH drop into the 3 - 4 range. The disproportion reaction produces the strong acid HCl(aq) and weak hypochlorous acid HOCl(aq):

$$Cl_2(aq) + H_2O(l) \rightleftharpoons HCl(aq) + HOCl(aq)$$

Teaching tips

1. This is the same reaction that occurs when chlorine is used to disinfect drinking water.
2. As with the previous experiment, chlorine disproportionates in this reaction to the oxidation states of +1 and –1.
3. The solution produced in this reaction can be discarded down the drain with plenty of water.
4. This makes a good demonstration. It is not "exciting", nor does it benefit the students to each perform it. Furthermore, doing it as a demonstration will minimize the chances for an accidental discharge of chlorine.

Questions

1. What was the starting pH and the final pH of your solution? Convert these values to $[H_3O^+]$. Determine the ratio of $[H_3O^+]_{solution}/[H_3O^+]_{water}$.

2. Compare the products in this experiment with the products in the previous experiment. Account for the differences in terms of acid-base reactions.

3. Why is this reaction called a *disproportionation*?

4. Classify each of the two products formed as either a strong acid, weak acid or neither.

Experiment 3. Chlorine discolors the natural colors of fruit juices

Equipment

Microscale Gas Chemistry Kit

Chemicals

$Cl_2(g)$, 60 mL

5 mL samples of various fruit juices such as cranberry juice, cherry drink, grape juice and tomato juice (ask students to bring samples)

Suitability

university lab, and classroom demonstration

Applications, Topics, Purpose

household materials, household chemicals, bleaching, dyes, oxidation-reduction reactions, physical and chemical changes, chemical reactivity of chlorine

Instructions

Obtain a number of samples of fruit juices such as cranberry juice, cherry drink, grape juice and tomato juice. Dilute each sample with an equal volume of water. Generate one syringe full of gas for each fruit drink to be tested. Wash the $Cl_2(g)$ samples. Draw about 5 mL of a fruit juice sample into a Cl_2-filled syringe and shake. The colors will change immediately or over a short period of time. Cranberry juice turns yellow-orange; cherry drink turns yellow; grape juice becomes bleached and tomato juice goes from the familiar red to pale yellow. Some food coloring dyes also react with $Cl_2(g)$.

Teaching tips

1. Ask students to bring samples from home.
2. Results for this experiment will vary; the dyes must be oxidized by chlorine in order for them to change colors.
3. It will take at least half of a syringe full of chlorine for each fruit drink because the concentration of the juices is quite high. Dilutions can “fine-tuned” for best results.

Questions

1. When we studied ammonia in Chapter 13 we found that many fruit juices underwent color changes when exposed to ammonia. What was the explanation?
2. When we studied sulfur dioxide in Chapter 15 we found that many fruit juices underwent color changes when exposed to sulfur dioxide. What was the explanation?
3. Chlorine causes a reaction unlike either of those encountered with ammonia or sulfur dioxide. What is the principle type of reaction caused by chlorine?

EXPERIMENT 4. TESTING COLORFAST FABRICS

Equipment

Microscale Gas Chemistry Kit
pieces of fabric
pieces of colored paper

Chemicals

$Cl_2(g)$, 60 mL

Suitability

university lab, and classroom demonstration

Applications, Topics, Purpose

household materials, household chemicals, bleaching, dyes, colored substances, physical and chemical changes, oxidation-reduction reactions, physical and chemical changes, properties of chlorine, chemical reactivity of chlorine,

Instructions

Chlorine gas from a syringe can be used to test colorfast dyes. Place pieces of fabric and or colored paper inside a clean syringe. Insert the plunger until about half of the air has been expelled. Connect this test syringe to a $Cl_2(g)$-filled syringe and transfer chlorine to the test syringe. Results for this experiment will vary; the dyes in the fabrics must be oxidized by chlorine in order for them to change colors. Some colorfast fabrics will resist color changes. Reds tend to turn pink, however.

Teaching tips

1. Ask students to bring samples from home.
2. Old laboratory books call for producing chlorine gas in a beaker and dropping fabric or paper with color marker lines on it into the beaker.
3. Although it is not as interesting, colored paper is very susceptible to the bleaching action of chlorine. Ahead of class, try the experiment on a variety of pieces of colored paper. Then cut the colored papers (that work) into small test strips for use by the students.
4. Suggest that each student or team use a different piece of fabric *and* several pieces of colored paper, work out the details and then share their results in a short presentation to the rest of the students.

Questions

1. Make a table of color changes encountered using the colored paper. What colors are the most likely to be oxidized by chlorine? What colors are the most stable
2. Many colors are a combination of two other colors. For example, green is often obtained by mixing blue and yellow; purple is obtained by mixing blue and red, orange is obtained by mixing red and yellow. Blue, red and yellow may have different sensitivities to bleaching by chlorine. Is there any evidence that a combination color, such as green, was partially bleached, i.e., the blue component was removed, but the yellow was not?

EXPERIMENT 5. CHLORINE REACTS WITH AQUEOUS SODIUM SULFITE

Equipment

Microscale Gas Chemistry Kit

Chemicals

$Cl_2(g)$, 60 mL

1 M $Na_2SO_3(aq)$, 60 mL

Suitability

university lab and classroom demonstration

Applications, Topics, Purpose

properties of chlorine, chemical reactivity of chlorine, chemical formulas, writing balanced chemical equations, oxidation-reduction reactions

Instructions

Prepare 60 mL 1 M $Na_2SO_3(aq)$ in a small beaker. Generate a syringe full of chlorine. It is unnecessary to wash the gas. Remove the syringe cap from the syringe and draw 5 mL of the sodium sulfite solution into the syringe. Keep the syringe positioned in the beaker of sulfite solution while gently rocking/swirling the syringe around to mix the solution with the gas. The level of solution will rise in the syringe as the gas reacts with the sulfite according to the equation:

$$Cl_2(g) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2\ Cl^-(aq) + HSO_4^-(aq) + H^+(aq)$$

An analogous reaction can be performed with bisulfite in place of sulfite, but the products are acidic enough to form unpleasant $SO_2(g)$ odors.

Teaching tips

1. Labs should have a bottle of aqueous (1 M) sodium hydrogen sulfite on hand to neutralize spilled bromine, and to destroy unwanted solutions of permanganate, chromates, dichromates, etc.
2. The level of solution will rise in the syringe as the chlorine gas reacts with the aqueous sulfite solution.

Questions

1. Suggest a way to eliminate residual $Cl_2(g)$ from aquariums. If you have a tank, check the ingredients in the product you use to remove residual $Cl_2(g)$.
2. Which reactant was oxidized in the given reaction? Which reactant was reduced?
3. Write and balance the oxidation-reduction reaction that occurs between the bisulfite ion and chlorine.

EXPERIMENT 6. HALOGEN ACTIVITY SERIES

Equipment

Microscale Gas Chemistry Kit
suitable cork or stopper for the medium test tube

Chemicals

$Cl_2(g)$, 60 mL
few crystals of NaBr or KBr
few crystals of NaI or KI
1 M $Na_2SO_3(aq)$, 5 mL

Suitability

university lab, and classroom demonstration

Applications, Topics, Purpose

oxidation-reduction reactions, chemical changes, properties of the halogens, chemical reactivity of the halogens, chemical formulas, writing balanced chemical equations

Instructions

The relative reduction potentials for chlorine, bromine and iodine are given here. Chlorine is highest in the ***activity series*** and is the most readily reduced.

$$Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq) \qquad E^o = +1.36\ V$$

$$Br_2(g) + 2\ e^- \rightarrow 2\ Br^-(aq) \qquad E^o = +1.07\ V$$

$$I_2(g) + 2\ e^- \rightarrow 2\ I^-(aq) \qquad E^o = +0.54\ V$$

In this experiment you will react aqueous bromide and iodide with chlorine. Add a few crystals of NaBr and NaI to separate medium test tubes. (KBr or KI can be used instead.) Add 3 - 5 mL of water to each to dissolve the crystals. Prepare a $Cl_2(g)$-filled syringe. Discharge 20 mL $Cl_2(g)$ into the test tube containing $Br^-(aq)$. Stopper the test tube and shake to mix gaseous and liquid reagents. Remove the stopper and set it upside down across the mouth of the test tube. The mixture immediately reacts to turn yellow-orange indicative of aqueous bromine:

$$Cl_2(g) + 2\ Br^-(aq) \rightarrow 2\ Cl^-(aq) + Br_2(aq) \qquad E^o = +0.29\ V$$

Repeat the above experiments with aqueous iodide solution. In this case, the solution initially turns dark brown and then over the course of one minute turns pale yellow with chunks of dark $I_2(s)$ crystals.

Solutions of Br_2(aq) and I_2(aq) produced can be treated with a few drops of 1 M Na_2SO_3(aq) until the solution is clear. The resulting clear solution can be poured down the drain with plenty of water.

Teaching tips

1. Emphasize the proper disposal of the Br_2(aq) and I_2(aq) solutions produced as per the last paragraph in the Instructions.

2. The purpose of the demonstration is to develop an activity series for the halogens; however, not enough information can be gained in the demonstration for students to do this. The periodic table will be needed to complete the activity series. The demonstration does illustrate that Cl_2(g) is a better oxidizing agent than bromine or iodine, but it does not differentiate the oxidizing abilities of these two elements. If your students have difficulty in developing an activity series, inform them that the halogens are oxidizing agents (easily reduced) with the best oxidizing agent found at the top of this family.

Questions

1. What was the color of the bromide ion in solution, Br^-(aq)? What is the color of elemental bromine? Was bromide oxidized or reduced in the reaction?

2. What was the color of the iodide ion, I^-(aq)? What is the color of elemental iodine in solution? Was iodide oxidized or reduced in the reaction?

3. Based on what you learned from the demonstration, would a reaction occur if chloride were mixed with aqueous bromine? Explain your reasoning.

4. Use the activity series you developed to determine which halogen, chlorine, bromine or iodine is the easiest to reduce. Which halide, chloride, bromide, or iodide is easiest to oxidize?

EXPERIMENT 7. CHLORINE AND SODIUM FORM SODIUM CHLORIDE

Equipment

Microscale Gas Chemistry Kit
suitable cork or stopper for the medium test tube
glass Pasteur pipet
Bunsen burner
ring stand and clamp
matches or lighter

Chemicals

Cl_2(g), 60 mL
sodium, Na, $^1/_4$ pea-sized, 0.25 g

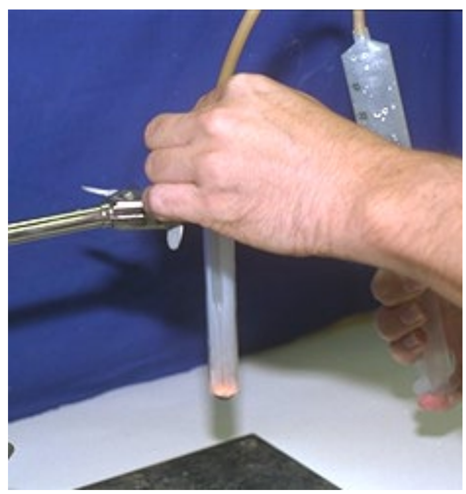
Suitability

university lab, and classroom demonstration

Applications, Topics, Purpose

oxidation-reduction reactions, formation of a salt, classification of matter, chemical properties of chlorine, energy and chemical change, chemical formulas, writing balanced chemical equations, classifying chemical changes, molecular/ionic structure

Instructions



This experiment is a modification of the method described in ***Chemical Demonstrations***.[1] Equip a 15 cm length of tubing with a glass Pasteur pipet. This eventually will be fitted onto the syringe and used to direct the Cl_2(g) onto molten sodium. Prepare a syringe full of Cl_2(g) and set it aside. Heat a small piece ($^1/_4$ pea-sized) of sodium in a large test tube using a gentle flame produced by a small burner. When the sodium has started to melt, remove the flame.

Use the syringe equipped with the tubing/glass pipet attachment to direct the Cl_2(g) gas in 5 mL increments over the molten sodium from a distance of about 1 cm. A bright, vigorous and short-lived reaction will result. The syringe helps control the direction and delivery of the chlorine gas. The process can be repeated in 5 mL increments of Cl_2(g) until all of the gas has been used. The reaction is:

$$2\ Na(l) + Cl_2(g) \rightarrow 2\ NaCl(s)$$

[1] Chemical Demonstrations, Vol. 2, p. 56, Summerlin, L., Borgord, C., & Ealy, J.

Clean-up

Allow the reaction to cool. The reaction mixture may contain unreacted sodium metal. Give this test tube to your instructor.

Teaching tips

1. The bright yellow fire is an indication that the reaction is proceeding as desired. If the yellow fireball goes out, the reaction has stopped and discharging additional chlorine should be stopped.

2. Be careful with clean-up. Unreacted sodium is likely present. Destroy the small amount of unreacted sodium by dropping the test tube into a 2 L plastic beverage bottle containing 500 mL water. Do not cap the bottle; do not direct the opening at anyone. Tip the bottle and contents in order so that water flows into the test tube. Alternatively, fill the test tube half-full with propanol or add 10 mL propanol to a beaker. After the bubbling stops (about 15 minutes), wash the solution down the drain with plenty of water.

Questions

1. What type of reaction took place? Oxidation-reduction? Precipitation? Acid-base reaction?

2. Sodium, chlorine and sodium chloride are examples of different types of substances: covalent molecules, ionic compounds and a metal. Match the substance with the type.

3. List properties of metallic, ionic and covalent molecules. Include generalizations, if possible, about melting point, boiling point, solubility in water, ductility, malleability, ability to conduct electricity, etc.

Experiment 8. Hydrogen-Chlorine Rockets

Equipment

Microscale Gas Chemistry Kit
several small test tubes
piezoelectric rocket igniter device (See: Appendix C)
Beral pipet, large stem, large body

Chemicals

Cl_2(g), 40 mL
H_2(g), 60 mL (See Chapter 3 for in-syringe preparation, or make oxygen in a gas bag — See Chapter 5)
universal indicator

Suitability

university lab, and classroom demonstration

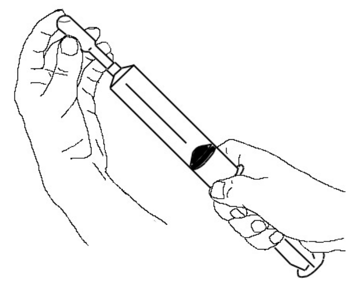
Applications, Topics, Purpose

kinetics, stoichiometry of reactions, activation energy, explosive mixtures, rocketry, types of chemical reactions, energy and chemical change, chemical reactions

Instructions

On several previous occasions (the first time was while studying oxygen), you filled and launched rockets using the method you will use here. You may want to review this procedure which is provided on page 65 and again in Appendix C. (A step-by-step color photo sequence on filling and launching rockets is available at our website.) Fill the pipet rockets completely with water and store them open-end down in test tubes filled with water. (Stand the test tubes somewhat upright by placing them in a plastic cup.)

Remove the cap from the Cl_2-filled syringe and slip the water-filled pipet rocket over the syringe fitting as shown in the figure. Bubble the $Cl_2(g)$ into the pipet rocket until it is about half full. Next, complete the water-displacement with $H_2(g)$ until the rocket is nearly filled. Leave some water in the pipet stem.

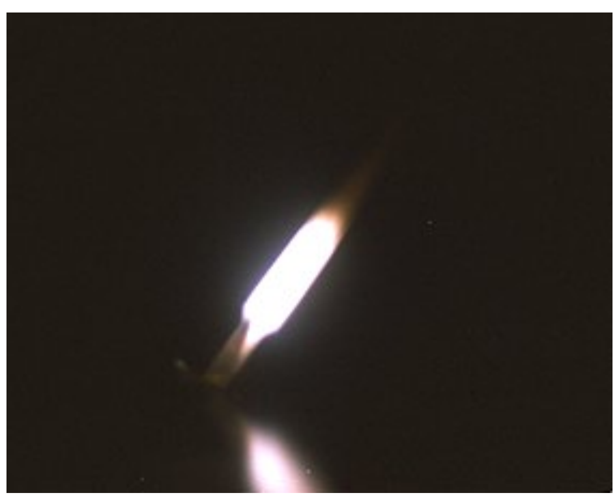


Position the rocket over the wire of the igniter. Water must remain in the stem because this serves as the propellant, but the ends of the wire leads must be above the water in the gas-filled region of the rocket. Trigger the igniter and the rocket will fly 5 m or more. The reaction is:

$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$$

Immediately collect the rocket test the pH of the gas inside by filling the rocket half-full with water and adding a few drops of universal indicator.

It is also possible to photochemically initiate the H_2/Cl_2 mixture with the flash from a camera, although it works best if the uv-filter is first removed. To do this, use a water-filled test tube as a launcher.



Teaching tips

1. A step-by-step color photo sequence on filling and launching rockets is available at our website.
2. Note: NEVER scale the H_2/Cl_2

reaction up or mix large quantities of these gases! Serious explosions can occur which can be photochemically triggered by room light or sunlight.

3. Provide a chart of indicator color vs. the corresponding pH to your students

Indicator Colors		
pH	**Universal**	**Red Cabbage**
4.0	Red	Red
5.0	Orange Red	Purple
6.0	Yellow Orange	Purple
7.0	Dark Green	Purple
8.0	Light Green	Blue
9.0	Blue	Blue-Green
10.0	Reddish Violet	Green
11.0	Violet	Green
12.0	Violet	Green
13.0	Violet	Green-Yellow
14.0	Violet	Yellow

Questions

1. Describe your experimental observations for this reaction. Did you notice the bright flash of light?
2. What were the results of the pH test of the gaseous reaction products present in the recovered rocket?
3. Why do these rocket reactions require a spark to initiate? Explain your answer using a reaction profile and a suitable energy of activation.

EXPERIMENT 9. CHEMILUMINESCENCE AND SINGLET OXYGEN

Equipment

Microscale Gas Chemistry Kit
large test tube
glass pipet

Chemicals

Cl_2(g), 60 mL
5 mL of 30% hydrogen peroxide
5 mL 6 M NaOH(aq)

Suitability

university lab, and classroom demonstration

Applications, Topics, Purpose

forms of energy, energy changes during reactions, chemiluminescence

Instructions

In this experiment you will observe the production of *singlet oxygen*, a high energy variant of O_2(g), and observe the energy release associated with its conversion to normal *triplet oxygen*. The conversion produces a chemiluminescent red glow (photochemical emission) with approximate wavelength of 630 nm. For a full discussion, please see Volume 1 of ***Chemical Demonstrations***.[2]

Equip a 15 cm length of tubing with a glass pipet. (The tubing fits inside the pipet stem.) Clamp a medium test tube (15 x 180 mm) in a ring stand and fill with 5 mL of 30% hydrogen peroxide. Generate a syringe full of Cl_2(g) and set it aside. Add 5 mL NaOH(aq) to the test tube containing the H_2O_2(aq). Hydrogen peroxide may start to decompose to O_2(g) before you add the chlorine. If the reaction starts to proceed at too fast a rate, it can be quenched by adding water from a squeeze bottle.

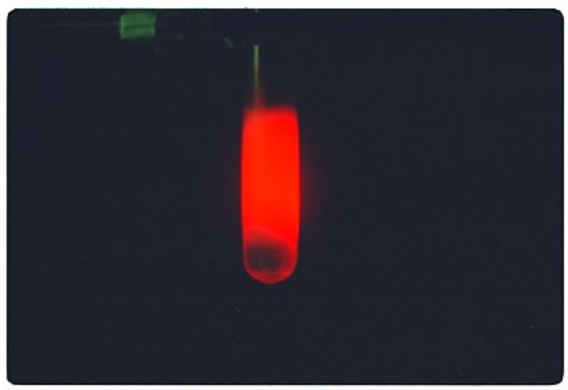
Remove the syringe cap from the syringe and equip the syringe with the tubing/gas dispersion apparatus. To perform the demonstration, carefully bubble chlorine gas slowly through the solution. With the lights off (completely darkened room), you can observe the spectacular red chemiluminescent glow near the gas dispersion tube.

The reactions are:

$$Cl_2(g) + 2\ NaOH(aq) + H_2O_2(aq) \rightarrow O_2(g,\ singlet) + 2\ NaCl(aq) + 2\ H_2O(l)$$

$$2\ O_2(g,\ singlet) \rightarrow 2\ O_2(g,\ triplet) + h\nu$$

Teaching tips



1. Use as a demonstration, not a laboratory activity.
2. The objective of the experiment is to illustrate that some reactions liberate energy as photons instead of heat.
3. In terms of molecular orbital theory, the first excited singlet state for oxygen corresponds to the two π^* electrons paired in the same MO ($^1\Delta_g$). The second excited state for singlet oxygen features one electron in each π^* orbital but with opposite spins ($^1\Sigma_g^+$). Triplet (normal) oxygen has two unpaired electrons, one in each π^* orbital.

Questions

1. The reaction emitted has wavelength 630 nm. What color does that represent?
2. Which form of oxygen, singlet or triplet, is higher in energy? Explain.
3. Given that the energy change for the following reaction is 92 kJ, determine if ΔH should be +92 kJ or –92 kJ for the following reaction:

$$2\ O_2(g,\ singlet) \rightarrow 2\ O_2(g,\ triplet)\quad \Delta H = ?$$

4. Which form of oxygen do we breathe?

[2] ***Chemical Demonstrations***, Vol 1., Shakhashiri, University of Wisconsin Press, 1983.

EXPERIMENT 10. SPECTACULAR UNDERWATER FIREWORKS!

Equipment

Microscale Gas Chemistry Kit
tape (electricians tape works well)

Chemicals

Cl_2(g), 60 mL
C_2H_2(g), 60 mL (Chapter 14)

Suitability

university lab, and classroom demonstration

Applications, Topics, Purpose

chemiluminescence, forms of energy changes, explosive mixtures, reaction kinetics

Instructions

Ethyne reacts with chlorine accompanied by spectacular flashes of fire. Prepare two 15 cm lengths of tubing. Tape the pieces together near one end as shown in the figure. The design will allow bubbles of ethyne and chlorine to come in contact under water. Generate a syringe full of ethyne and a syringe full of Cl_2(g). Connect the two syringes to the non-taped ends of the tubing. Simultaneously bubble C_2H_2(g) and Cl_2(g) into the water using small bursts of 5 mL at a time. The gases react to produce HCl(aq) and sooty carbon:

$$C_2H_2(g) + Cl_2(g) \rightarrow 2\ C(s) + HCl(aq)$$

Teaching tips

1. The taped tubing design will allow bubbles of ethyne and chlorine to come in contact under water.
2. Look for evidence of sooty carbon.
3. In addition to light, the other two forms or energy release are heat and electrical. Some reactions are entropy driven as well.

Questions

1. What kind of energy was released in the reaction? What are the other two types of energy associated with chemical reactions?
2. What is the composition of soot?
3. Would a similar reaction take place if chlorine and ethyne were directed towards each other in air rather than under water?
4. Sketch a reaction profile for the reaction between chlorine and ethyne. Give special attention to the height of the activation energy. Is it large or small?

EXPERIMENT 11. LIQUID AND SOLID CHLORINE

Equipment
- Microscale Gas Chemistry Kit
- cotton swab

Chemicals
- Cl_2(g), 60 mL
- liquid nitrogen

Suitability

university lab, and classroom demonstration

Applications, Topics, Purpose

matter, physical and chemical changes, properties of chlorine, energy and physical change, writing equations for phase changes, intermolecular forces

Instructions

This experiment requires liquid nitrogen. Place a Q-tip cotton swab into liquid nitrogen and then immediately place the swab against the side of a Cl_2(g)-filled syringe near the end with the syringe cap. It will be necessary to repeat the process several times. Soon chlorine will condense to a liquid near the point of contact and will stream down the side of the syringe barrel and vaporize. With continued application of liquid nitrogen to the same spot, solid chlorine will be formed and the plunger will be drawn inward. Avoid condensing so much of the chlorine that the plunger moves past the frozen spot.

Teaching tips

1. This makes a good demonstration. Be careful with liquid nitrogen.
2. Avoid condensing so much chlorine that the plunger moves past the frozen spot.

Questions

1. Write reaction equilibria for the two phase changes you observed.
2. Describe the appearance of liquid chlorine and of solid chlorine.
3. Why did the plunger move inward during the reaction? Was it because gases decrease in volume as they are cooled?
4. What intermolecular forces must be overcome when liquid chlorine becomes gaseous chlorine?

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.

SUMMARY OF MATERIALS AND CHEMICALS NEEDED FOR CHAPTER 16. EXPERIMENTS WITH CHLORINE

Equipment required

Item	For Demo	For 5 pairs	For 10 pairs
Microscale Gas Kit (See Chapter 1)	1	5	10
large vial cap*	1	5	10
small test tubes, 12 x 100 mm	3	15	30
Bunsen burner, small	1	5	10
fume hood**	1	1 – 3	2 - 5
pH meter	1	1 – 3	2 - 5
suitable cork or stopper for the medium test tube	1	5	10
glass Pasteur pipet	2	10	20
ring stand and clamp	1	5	10
matches or lighter	1	5	10
piezoelectric rocket igniter device	1	1 – 3	2 – 5
Beral pipet, large stem, large body	1	5	10

* capable of holding 1 mL liquid and remain afloat (if Method B is used)
** ideal, but not absolutely necessary

Materials required

Item	For Demo	For 5 pairs	For 10 pairs
tape (electricians)	1 roll	1 roll	1 roll
cotton swab	1	5	10
pieces of fabric	a	a	a
pieces of colored paper	3 - 4	3 - 4	3 – 4
fruit juices, various	a	a	a

a. students bring various samples

Chemicals required

Item	For Demo	For 5 pairs	For 10 pairs
hydrochloric acid, 2 M $HCl(aq)$*	30 mL	150 g	300 g
calcium hypochlorite, $Ca(OCl)_2(s)$*	1 g	5 g	10 g
hydrochloric acid, 6 M $HCl(aq)$**	5 mL	25 mL	50 mL
household bleach**	20 mL	100 mL	200 mL
sodium hydroxide	5 g	25 g	50 g
sodium hydroxide, 3 M NaOH	5 mL	25 mL	50 mL
sodium hydroxide, 6 M NaOH	5 mL	25 mL	50 mL
sodium sulfite, 1 M Na_2SO_3	60 mL	300 mL	600 mL
sodium bromide, NaBr***	< 0.1 g	< 0.1 g	< 0.1 g
sodium iodide, NaI***	< 0.1 g	< 0.1 g	< 0.1 g
sodium, Na(s)	0.25 g	1.25 g	2.5 g
magnesium	0.1 g	0.5 g	1 g
universal indicator****	< 1 mL	2 mL	3 mL
hydrogen peroxide, 30%	5 mL	25 mL	50 mL
calcium carbide, CaC_2	0.25 g	1.25 g	2.5 g
liquid nitrogen	25 mL	100 mL	200 mL

* Preparation of chlorine by Method A
** Preparation of chlorine by Method B
*** or KBr and/or KI
**** or cabbage juice (generally, you will need to use more cabbage juice than universal indicator

