PART 6

ADVANCED GASES

OVERVIEW TO PART 6

PART 6. ADVANCED GASES

The two gases described here and the experiments that go with them should be conducted by individuals familiar and experienced with gas production using the syringe method introduced in Part 1. These two gases are considered “advanced gases” for different reasons. Silane is an extremely pyrophoric gas and great caution must be exercised to prevent unintentional fires. For hydrogen sulfide, it is its offensive odor and high toxicity that warrant the “advanced” classification.

CHAPTER 26 SILANE

SILANE WAS FIRST PREPARED IN 1857 by Friedrich Wöhler and H. Buff by reacting HCl(aq) with Al-Si alloy or Mn_2Si.[1] Silane, SiH_4, is also called silicon tetrahydride, silicane and monosilane. Silane does not occur in nature.

Silane is a colorless, flammable gas with a repulsive odor. Silane has a melting point of -185 ^oC and a boiling point of -111.8 ^oC. It is insoluble in water and most organic solvents. The density of SiH_4 is 1.3128 g/L at 25 ^oC and 1 atm — 11% greater than that of air.

Silane is used to produce ultra-pure silicon for use in the semiconductor applications. Tetrahalosilanes are used in the industrial production of silane and related silicon hydrides. For example, $SiCl_4$, is reduced to SiH_4 by lithium hydride, sodium hydride or lithium aluminum hydride, $LiAlH_4$. The reaction with lithium hydride is:

$$SiCl_4(g) + 4\ LiH(s) \rightarrow SiH_4(g) + 4\ LiCl(s)$$

Suitability

All of these experiments are suited for use as classroom demonstrations. The techniques described herein are more advanced than those used in the first ten parts of this series. Individuals attempting these experiments should be experienced with the simpler syringe/gas techniques. These experiments are not suitable for use as laboratory experiments conducted by first year high school students. Advanced students or students with special laboratory skills could be allowed to perform these experiments under close supervision by the instructor.

The following experiments are included in this chapter:

[1] (a) ***Ann. 102***, 128 (1857); (b) ***Ann.*** **106**, 56 (1858)

Experiment 1. Silanes react with air
Experiment 2. Silane reacts with oxygen
Experiment 3. Silane reacts with chlorine
Experiment 4. Thermal decomposition of silane
Experiment 5. Reaction with aqueous potassium hydroxide

Most of these experiments/demonstrtations serve to review basic concepts of chemistry including combustion, energy and chemical change, writing balanced chemical equations, properties of silane, chemical reactivity of silane, and oxidation-reduction reactions. In addition, the pyrophoric nature of silane is evident with most of these experiments.

Background skills required

Students should be able to:

- generate a gas as learned in Chapter 1.
- know how to manipulate the "silane dispenser" so that no air is accidentally drawn into the syringe.
- use a fume hood for all aspects of these experiments.
- understand fundamental concepts of high school chemistry so that observations can be interpreted.

Time required

These experiments should be done as demonstrations. Each experiment requires a significant amount of time because of the need to use a silane dispenser. The experiments also require other chemicals, including oxygen, chlorine or aqueous potassium hydroxide.

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 SILANE[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.

Toxicity

Silane is spontaneously flammable in air and produces SiO_2 when it burns. Do not breath airborne SiO_2 fumes, as they are known to cause silicosis disease of the lungs. ***These experiments must be done in a fume hood.***

Equipment

- Microscale Gas Chemistry Kit (Chapter 1)
- wide-mouth plastic beverage container
- ring stand and two suitable clamps to hold syringes
- pliers
- pinch clamp or hemostat
- glass disposable pipet

Chemicals

- 0.20 g magnesium silicide, $Mg_2Si(s)$[2]
- 15 mL 1 M HCl(aq)

Silane and Disilane

The gas prepared by the following instructions is mostly $SiH_4(g)$ with small amounts of $Si_2H_6(g)$ and possibly higher silanes as well. For our purposes, this simple method of preparation outweighs the fact that the product is a mixture of silanes. Very pure $SiH_4(g)$ can be prepared by one of several more difficult approaches described in the literature.[3] [4] All of these experiments can be done with one or two syringes full of silane.

Step-by-step instructions for the preparation of silane

Silane is generated by the reaction of magnesium silicide, $Mg_2Si(s)$, with 1 M HCl(aq) by the In-Syringe Method described in Chapter 1.

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[1] Content for this chapter first appeared as "Microscale Gas Chemistry, Part 14. Experiments with Silane" Mattson, B. M., Anderson, M. P., Nguyen, J, Bansal, M., ***Chem13 News***, **281**, January, 2000.

[2] See listing for Aldrich in Appendix E for ordering information

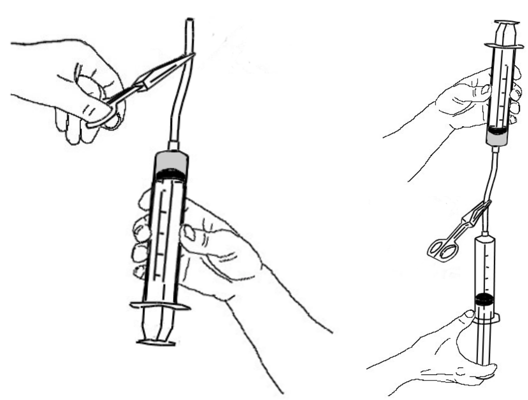
[3] Finholt *et. al.*, ***J. Am. Chem. Soc. 69***, 2692 (1947)

[4] (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; and Bochmann, M.; ***Advanced Inorganic Chemistry***, Sixth Ed., Wiley, 1999; (b) Weiss, H. G. and Fisher, H. D. ***Inorg. Chem.*** 1963, **2** 880.

1. Wear your safety glasses!
2. Make sure the syringe plunger moves easily in the syringe barrel. If it does not, try another combination of plunger and barrel.
3. Measure out 0.20 g solid magnesium silicide, $Mg_2Si(s)$. Place the solid directly into the vial cap.
4. Fill the syringe barrel with water. Place your finger over the hole to form a seal.
5. Float the vial cap containing the solid reagent on the water surface.
6. Lower the cap by flotation. Release the seal made by finger to lower the cap into the syringe barrel without spilling its contents. Allow the syringe to drain into a wide-mouth beverage container.
7. Install the plunger while maintaining the syringe in a vertical position, supported by the wide-mouth beverage bottle or flask.
8. Fill the weighing dish with 1 M HCl(aq). Draw 10 mL of this solution into the syringe.
9. Push the syringe fitting into the syringe cap.
10. Shake the device in order to mix the reagents. Gently help the plunger move up the barrel. Upon mixing the reagents in the syringe with vigorous shaking, gaseous $SiH_4(g)$ is quickly produced. **Note!** You will notice a few flashes of fire inside the syringe as silane is generated and reacts with the small amount of air originally present in the syringe.

The remaining steps are different from the normal sequence of steps for the In-Syringe method used in Parts 1 and 3. After the reaction has stopped, it is necessary to transfer this highly flammable gas to a clean, air-free syringe. Silane is a pyrophoric gas; ***exposure to air will result in instant fire!*** Without air present, silane will not burn.

11. Transfer silane to a clean syringe as follows. Equip a clean syringe with a 15 cm length of tubing. Draw 15 mL water in the syringe. Invert the syringe so that the tubing is facing upward. Discharge 5 mL water to remove bubbles of air. Use a hemostat (or clamp) to close the tubing near the end so that the tubing is filled with water as shown in the figure.

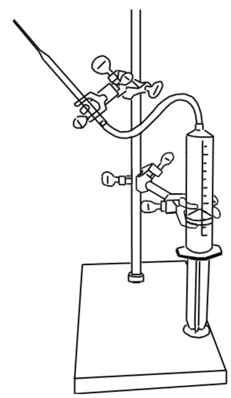


12. Connect the tubing to the silane-preparation syringe as follows. Position the two syringes with the water-filled syringe on top and the silane preparation syringe on the bottom as shown in the figure. Use a ring stand and two clamps (not shown) to

hold the syringes in position. **CAUTION!** Remove the syringe cap from the silane-preparation syringe with a pliers; the contents are likely to be under positive pressure and some flashes of fire with popping noises may be noted. The pliers serves to keep hands a safe distance away. ***Caution: Remove the syringe cap with the cap end of the syringe directed upward so that the reagents will not spray out of the syringe.***

13. After the two syringes are connected as per Step 12, transfer the silane to the water-filled syringe by pushing inward on the lower plunger at the same time as pulling outward on the top plunger at the same rate. When silane transfer is complete, transfer about half of the water (5 mL) from the upper syringe into the lower syringe. This fills the tubing with water. Clamp the tubing shut near the lower end (nearest the silane preparation syringe) so that the tubing remains filled with water. Remove the silane preparation syringe from the tubing and set it aside.

14. ***Silane Dispenser.*** Store silane as shown at right. Connect the tubing to a glass pipet (the diameter of the tubing is such that it fits snugly *inside* the glass pipet.) The lower elbow of the tubing is filled with water and serves as an "air-lock" for the silane. Use a ring stand and two clamps to hold the syringe and the glass pipet in this position. The hemostat can be removed after the apparatus has been clamped in this position because the water trap in the tubing keeps the silane away from air.



Disposal of silane samples

Unwanted samples of SiH_4(g) should be discarded by burning in a fume hood as per Experiment 1A or by reaction with KOH(aq) as per Experiment 5.

Teaching tips

1. Silane spontaneously ignites upon exposre to air. To stop the discharge of silane, draw water into the tubing trap and then pinch the tubing shut with the hemostat. *Never draw air into the silane dispenser.*

2. Work in a fume hood; read the Toxicity warning before attempting the preparation of silane.

Questions

1. Calculate the amount of magnesium silicide used (in moles).

2. Given that magnesium silicide is the limiting reagent, what quantity, in moles, of silane is expected?

3. Use the ideal gas law to convert your answer from Question 2 into a volume, expressed in mL at 25 ^{o}C and standard pressure.

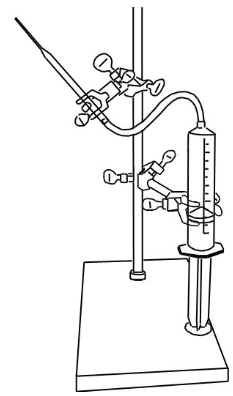
4. Did you observe a small flash of fire in the syringe as the reaction commensed? What caused it?

5. What is the purpose of the water in the upper syringe in Step 12?

6. What is the purpose of the water trap in the "silane dispenser" shown in Step 14?

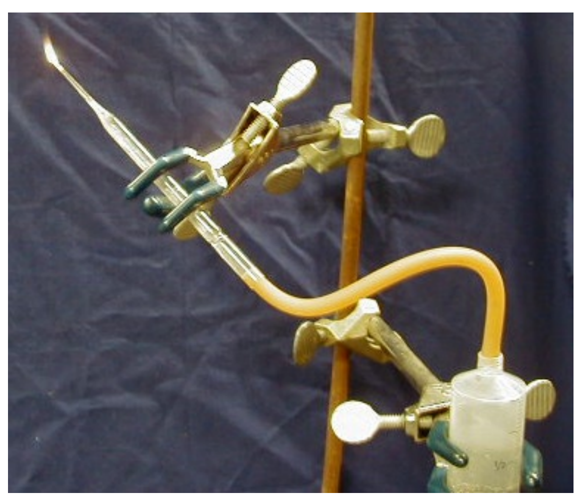
EXPERIMENTS WITH SILANE

All of the experiments described here utilize the silane dispenser apparatus as assembled in Step 14 of the previous section (page 393). The most important feature of this apparatus is the water-filled tubing, held in a curved "U-shaped" position as shown. The "U" holds water and prevents air and silane from coming into contact. The hemostat can be removed after the apparatus has been clamped in this position because the water trap in the tubing keeps the silane away form air.



"silane dispenser" in its proper storage position with the tubing forming a "U" trap airlock

EXPERIMENT 1. SILANES REACT WITH AIR



Equipment

Microscale Gas Chemistry Kit

Chemicals

$SiH_4(g)$, 25 mL (use "silane dispenser" apparatus; see Preparation of Silane)

Suitability

university lab and classroom demonstration

Applications, Topics, Purpose

combustion, pyrophoric substances, energy and chemical change, writing balanced chemical equations, properties of silane, chemical reactivity of silane, oxidation-reduction reactions

Instructions

Part A

Slowly discharge 5 - 10 mL silane from the "silane dispenser" into the air. The gas will bubble through the water and burn with a bright yellow light. The first few mL will burn inside the pipet at the water's surface, but after the oxygen in the pipet has been consumed, the flame will appear at the mouth of the pipet.

Part B

Place a clean, dry medium-size test tube over the end of the pipet. Discharge about 10 mL of silane into the test tube. A white coating of $SiO_2(s)$ will be deposited on the walls of the test tube as the gas burns. As the oxygen becomes depleted, the silane will dissipate to the mouth of the test tube and form a white cloud without flames.

Part C

Discharge some silane through water in a beaker or plastic cup. It is necessary to temporarily reposition the pipet for this procedure. Silane does not dissolve in water and the bubbles rise to the surface where they burst into flames upon contact with the air. Draw 5 mL water back into the tubing in order to re-establish the airlock. Return the pipet to its "silane dispenser" position.

Teaching tips

1. Silane spontaneously ignites upon exposure to air. To stop the discharge of silane, draw water into the tubing trap and then pinch the tubing shut with the hemostat. *Never draw air into the silane dispenser.*
2. Work in a fume hood; read the Toxicity warning before attempting the preparation of silane.

Questions

1. In Part A, why did the bursts of fire first appear inside the pipet, but later appear at the tip of the pipet?
2. The reaction in all three parts is the same. Write the balanced chemical equation for the reaction.
3. What form(s) of energy release were observed?
4. Could silane and air be stored together in the same syringe as was done with hydrogen and oxygen and many other gas combinations?
5. The product of the reaction is silicon dioxide. What is known about this substance? How does it differ from carbon dioxide?

EXPERIMENT 2. SILANE REACTS WITH OXYGEN

Equipment

Microscale Gas Chemistry Kit

Chemicals

SiH_4(g), 10 mL (use “silane dispenser” apparatus; see Preparation of Silane)

25 mL O_2 (See: Chapter 4)

Suitability

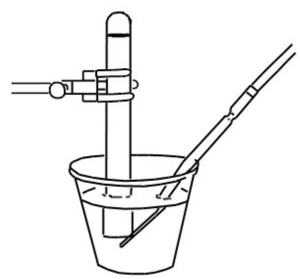
university lab and classroom demonstration

Applications, Topics, Purpose

combustion, pyrophoric substances, energy and chemical change, writing balanced chemical equations, properties of silane, chemical reactivity of silane, oxidation-reduction reactions

Instructions

Fill a medium test tube with water and clamp it in position upside down in a beaker of water. There should be no bubbles of air in the test tube. Deliver 10 mL silane to the test tube via the glass pipet as shown in the figure. Draw 5 mL water back into the tubing in order to re-establish the airlock. Return the pipet to its “silane dispenser” position. Next, bubble 5 mL bursts of O_2(g) into the test tube. Bright flashes of fire inside the test tube will accompany the reaction between silane and O_2(g). The test tube will become full of smoke. The reaction is:



$SiH_4(g) + 2\ O_2(g) \rightarrow SiO_2(s) + 2\ H_2O(l)$

Teaching tips

1. See the teaching tips from the previous experiment.

Questions

1. Why are these maneuvers carried out under water?
2. How would you modify the design of this experiment if the gases involved were both air-sensitive and water soluble (or reactive towards water)?
3. What is the “white smoke”?
4. Why does the test tube not explode?
5. Look up the silicone-oxygen single bond energy in your chemistry book. Is it relatively large or small when compared with typical single bond energies?

6. Sketch the Lewis dot structure for both CO_2 and SiO_2. Be careful! They are quite different. What is the carbon-oxygen bond order? What is the silicon-oxygen bond order?

EXPERIMENT 3. SILANE REACTS WITH CHLORINE

Equipment

Microscale Gas Chemistry Kit

Chemicals

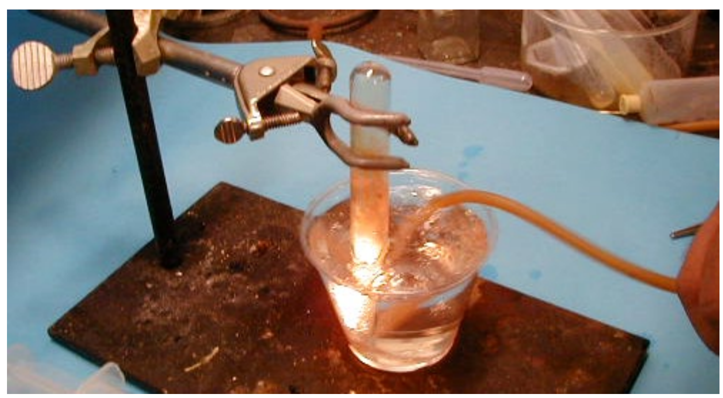
SiH_4(g), 25 mL (use "silane dispenser" apparatus; see Preparation of Silane)
Cl_2(g), 40 mL (See: Chapter 16)
1 M NaOH(aq)
universal indicator, 3 mL
Ag^+(aq) solution, 3 mL

Suitability

university lab and classroom demonstration

Applications, Topics, Purpose

combustion, pyrophoric substances, energy and chemical change, writing balanced chemical equations, properties of silane, chemical reactivity of silane, oxidation-reduction reactions



Instructions

The experimental procedure for this experiment is similar to that used in Experiment 2. Fill a medium test tube with water and clamp it in position upside down in a beaker of water. There should be no air in the test tube. Deliver 10 mL silane to the test tube via the glass pipet. Draw 5 mL water back into the tubing in order to re-establish the airlock. Return the pipet to its "silane dispenser" position. Before adding the Cl_2 to the silane, discharge about 5 mL Cl_2(g) into a fume hood in order to purge the tubing of air. Next, bubble 5 mL bursts of Cl_2(g) into the test tube. Bright flashes of fire and audible pops will accompany the reaction. The test tube will become full of smoke. The reaction produces HCl that can be tested for with universal indicator and/or Ag^+(aq) solution:

$$SiH_4(g) + 4\ Cl_2(g) \rightarrow SiCl_4(l) + 4\ HCl(aq)$$

A more impressive reaction occurs if the $Cl_2(g)$ is delivered directly into the silane gas with a 25 cm length of tubing that has been worked up to the gas phase of the silane-containing test tube. Purge the tubing of air before use.

The tetrachlorosilane produced by the reaction reacts with water to produce $Si(OH)_4$ and HCl(aq).

Teaching tips

1. Chlorine is a toxic substance. Read the toxicity information in Chapter 16. Dispose of excess $Cl_2(g)$ by drawing 10 mL 1 M NaOH(aq) into the syringe.
2. Review the teaching tips given in Experiment 1. *Never draw air into the silane dispenser.*
3. Work in a fume hood; read the Toxicity warning before attempting the preparation of silane.
4. 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 observations, including comments on sight and sound.
2. When designing an experiment to form a useful product, do you think that chemists prefer reactions such as this one where small explosion and fire are involved, or would it be better to design a slower reaction that did not yield as much energy?
3. Do you think of chlorine as being very reactive? Recall some of the experiments we did with chlorine in Chapter 16.

4. The last sentence of the instructions reads “The tetrachlorosilane produced by the reaction reacts with water to produce $Si(OH)_4$ and HCl(aq).” Balance the chemical equation for this reaction.

6. Sketch the Lewis dot structure for $SiCl_4$. What is the silicon-chlorine bond order?

EXPERIMENT 4. THERMAL DECOMPOSITION OF SILANE

Equipment

Microscale Gas Chemistry Kit
propane or butane torch
matches or lighter

Chemicals

SiH_4(g), 20 mL (use “silane dispenser” apparatus; see Preparation of Silane)

Suitability

university lab and classroom demonstration

Applications, Topics, Purpose

combustion, pyrophoric substances, energy and chemical change, writing balanced chemical equations, properties of silane, chemical reactivity of silane, oxidation-reduction reactions, thermal decomposition

Instructions

Silane decomposes to its elements above 400 ^{o}C. Fill a medium test tube with water and clamp it in position upside down in a beaker of water. There should be no air in the test tube. Deliver 20 mL silane to the test tube via the glass pipet. Draw 5 mL water back into the tubing in order to re-establish the airlock. Return the pipet to its “silane dispenser” position. Heat the test tube with the torch in the region that contains the silane gas. Heat gently at first and then strongly in one spot until the glass glows red. A mirror of silicon with brownish edges will be deposited there according to the reaction:

$$SiH_4(g) \rightarrow Si(s) + 2\ H_2(g)$$

Teaching tips

See teaching tips for Experiment 1.

Questions

1. Describe the appearance of silicon metal.

2. Using a ΔH_f table, calculate ΔH_{rxn} for the reaction. Is it endothermic or exothermic?

3. Why was it necessary to provide heat for this reaction?

4. Is the hydrogen produced soluble in water?

5. In previous experiments with hydrogen, a flame or spark was enough to trigger a reaction. Why does the hydrogen not ignite at such high temperatures?

EXPERIMENT 5. REACTION WITH AQUEOUS POTASSIUM HYDROXIDE

Equipment

Microscale Gas Chemistry Kit

Chemicals

SiH_4(g), 20 mL (use “silane dispenser” apparatus; see Preparation of Silane)
25 mL 6 M KOH(aq)
activated platinum sponge (optional)

Suitability

university lab and classroom demonstration

Applications, Topics, Purpose

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

Instructions

Silane hydrolyzes in the presence of base to produce hydrogen. The reaction is not spectacular like the previous reactions.

$$SiH_4(g) + (2+n)\ H_2O(g) \rightarrow SiO_2 \cdot n\ H_2O(s) + 4\ H_2(g)$$

This experiment should be done last because it will destroy all of the silane remaining in the “silane dispenser”. Draw 1 mL 6 M KOH(aq) into a silane dispenser syringe for every 2 mL silane present. Next, draw about 10 mL water up through the pipet in order to remove KOH from the pipet and tubing. Close the tubing with the hemostat. Vigorously shake the contents for about one minute. Discharge the liquid solution. The remaining gas can be tested for silane by discharging some into the air. It should not spontaneously burn upon contact with air as it did in Experiment 1. Discharge some of the gas into a candle flame and it will burn as expected for hydrogen.

The gas can be further tested for hydrogen by pulling an equal volume of air into the syringe (no fire) and then discharging the mixture onto the surface of a small piece of activated platinum sponge (Appendix E). (Note: To activate the platinum sponge, heat the sponge to red heat with a burner flame. Allow the platinum to cool to room temperature before using in the reaction.) The platinum will glow red as it catalyzes the combustion of hydrogen to make water vapor.

Teaching tips

1. See teaching tips for silane, given in Experiment 1.
2. Platinum is an inhalation hazard. Handle with extreme care when working with small particles of platinum

Questions

1. Describe your observations for this reaction.
2. What evidence did you note that a reaction had taken place?
3. Did the volume of gas in the syringe increase or decrease?
4. This reaction is technically an oxidation-reduction reaction. Assign oxidation numbers for the reaction and determine the oxidizing agent and reducing agent.

Clean-up

At the end of the experiments, discharge any unused silane into a fume hood. Place the syringe in a plastic bag and discard in the trash.

Summary of Materials and Chemicals Needed for Chapter 26. Experiments with Silane.

Equipment required

Item	For Demo
Microscale Gas Chemistry Kit	1
pinch clamp or hemostat	1
ring stand	1
suitable clamps to hold syringes	2
glass disposable pipet	1

Materials required

Item	For Demo
wide-mouth plastic beverage container	1
pliers	1
propane or butane torch	
matches or lighter	

Chemicals required

Item	For Demo
magnesium silicide, $Mg_2Si(s)$	1 g
1 M HCl(aq)	50 mL
potassium iodide, KI, powder*	1 g
6% hydrogen peroxide $H_2O_2(aq)$*	20 mL
chlorine, $Cl_2(g)$	a
universal indicator	5 mL
sodium hydroxide, 1 M NaOH(aq)	50 mL
silver nitrate, $AgNO_3(aq)$ solution	5 mL
potassium hydroxide, 6 M KOH(aq)	25 mL
activated platinum sponge**	0.2 g
liquid nitrogen or a dry ice + alcohol bath	b
bromine water	c

a. prepare chlorine by one of the methods described in Chapter 16

* for the preparation of oxygen, O_2 (See: Chapter 4)

** optional