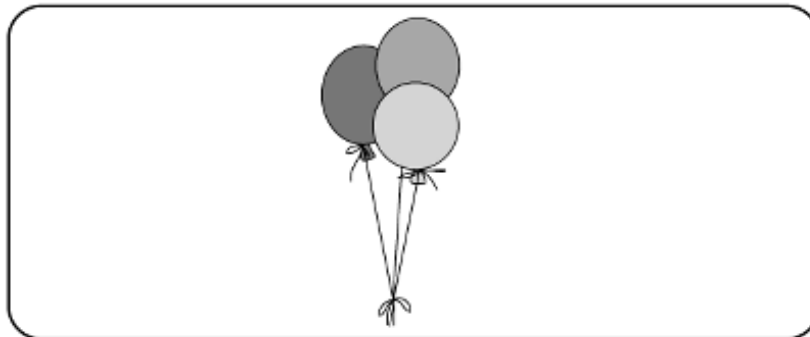


Name _____ Date _____ Partners _____

THE IDEAL GAS LAW AND ABSOLUTE ZERO OF TEMPERATURE



. . . the hypothesis, that supposes the pressures and expansions to be in reciprocal proportions . . .

—Robert Boyle

OBJECTIVES

- To understand how a gaseous system may be characterized by temperature, pressure, and volume.
- To examine the relationship between any two of these variables when the third is kept constant.
- To understand and be able to use the ideal gas law, which describes the relationship between pressure, volume and temperature.
- To use the ideal gas law and helium gas in a constant volume thermometer for a wide range of temperatures to determine the absolute zero of temperature.

OVERVIEW

In introductory physics, we often talk about matter as if it were continuous. We don't need to invent aluminum atoms to understand how a ball rolls down a track. As early as the fifth century B.C., Greek philosophers, such as Leucippus and Democritus, proposed the idea of "atomism." They pictured a universe in which everything is made up of tiny "eternal" and "incorruptible" particles, separated by "a void." Today, we think of these particles as atoms and molecules.

In terms of everyday experience, molecules and atoms are hypothetical entities. In just the past forty years or so, scientists have been able to "see" molecules and atoms using electron microscopes and scanning probe microscopes. But long before atoms and molecules could be "seen," nineteenth-century scientists, such as James Clerk Maxwell and Ludwig Boltzmann in Europe and Josiah Willard Gibbs in the United States, used these imaginary, small-scale *microscopic* entities to construct models that account for the large-scale *macroscopic* properties of thermodynamic systems.

Even a small container filled with a gas contains a very large number of molecules, on the order of 10^{23} ! Because it is impossible to use Newton's laws of motion to keep track of what each of these molecules is doing at any moment, we must characterize the behavior of a gas by the macroscopic quantities: volume V ; pressure p ; and temperature T . *Kinetic theory* is the area of physics that uses Newton's laws and averages of molecular behavior to explain the relationship between p , V , and T .

In this lab, you will determine experimentally how p , V , and T are related. First, you will carry out experiments to relate p and V at constant temperature. You will use these results to verify *Boyle's Law*.

Then you will first study temperatures and thermometers. You will use a constant-volume thermometer and measure pressure for well-known temperatures. Using the *ideal* gas law you will extrapolate these results to zero pressure to determine the absolute zero of temperature.

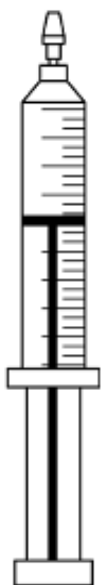
INVESTIGATION 1: BEHAVIOR OF A GAS IN TERMS OF P , V , AND T

How do the three variables, pressure p , volume V , and temperature T , of a gas depend on each other? It is straightforward to measure pressure and temperature with computer-based pressure and temperature sensors, so we can explore the relationships between these quantities. To simplify this investigation, you will look at the behavior of any two of these variables, while the third is kept constant.

Comment: In SI units, pressure is measured in Pa (N/m^2) and volume is measured in m^3 . Temperature can be measured in $^{\circ}\text{C}$ (degrees Celsius) or in K (kelvin). It turns out that the relationships that involve temperature appear simpler if temperature is measured in K, the Kelvin or absolute temperature scale. The reason for this can be traced back to the definition of temperature and its meaning on a microscopic scale. We will talk more about this later. For now, you can simply set up your software to display the readings of your temperature sensor in K.

You will start by examining the relationship between pressure p and volume V by doing measurements on the air in a syringe. Since the syringe is in thermal contact with the surrounding air, if you change the volume of the gas relatively slowly, the gas in the syringe remains in thermal equilibrium with the surroundings. Another way of referring to a process that takes place at constant temperature is to call it *isothermal*. First make a prediction.

Prediction 1-1: As you compress the air in a syringe by pushing the piston in *slowly*, what will happen to the pressure? What do you think will be the mathematical relationship between pressure p and volume V ?



To test your prediction you will need

- 20-mL plastic syringe (with the needle removed)
- short piece of Tygon tubing (to attach syringe to pressure sensor)
- pressure sensor

Activity 1-1: Isothermal Volume Change for a Gas

The approach to obtaining measurements is to trap a volume of air in the syringe and then compress the air slowly to smaller and smaller volumes by pushing in the piston. The gas should be compressed slowly so it will always have time to come into thermal equilibrium with the room (and thus be at room temperature). You should take pressure data for about 5 different volumes.

1. Attach the end of an unsealed syringe to the pressure sensor using the Tygon tubing. Start with the piston at 20 mL.

- Open the experiment file called **L12.1-1.Pressure vs. Volume**. This will also set up the software in **prompted event mode** so that you can continuously measure pressure and decide when you want to keep a value. Then you can **enter** the measured volume.
- The volume of the pressure sensor and associated tubing in this experiment is estimated to be 1.0 cm³. Enter this value in the second column of Table 1-1.
- Start the computer. As you squeeze down on the piston slowly, the computer will display the pressure. When the pressure reading is stable, you can **keep that value** and then **enter the total volume** of air from Table 1-1.
- Repeat this in steps of 2 mL down to 6 mL. It goes rather quickly, but you have to communicate with your partners to indicate that the person holding the piston is ready for the computer person to click on **Keep**.
- Use the **fit routine** to find a relationship between p and V .

Table 1-1

Volume of air in syringe (cm ³)	Volume of sensor and tubing (cm ³)	Total volume of air in system (cm ³)

- Print** one graph for your group report.

Question 1-1: What is the relationship between p and V ? Is it proportional, linear, inversely proportional, or something else? Did this agree with your prediction?

Question 1-2: Write down the relationship between the initial pressure and volume (p_i, V_i) and the final pressure and volume (p_f, V_f) for an isothermal (constant-temperature) process.

The relationship that you have been examining between p and V for a gas with the temperature and the number of molecules of gas held constant is known as *Boyle's law*.

INVESTIGATION 2: THERMOMETERS AND TEMPERATURE SCALES

It is easy enough to grasp the concept of **temperature** intuitively: something that feels ‘cold’ has a low temperature whereas something that feels ‘hot’ has a high temperature. However, it is not at all trivial to translate such a qualitative understanding into a scientifically sound or even a scientifically practical quantitative definition of temperature.

The most widely used temperature scale today is the **Celsius Scale** (A. Celsius, 1701-1744). One useful representation of the temperature t (in °C) is

$$t = 100 \frac{X_t - X_0}{X_{100} - X_0} [\text{°C}], \quad (1)$$

where X is a *property of a material* that varies with temperature. X_0 and X_{100} are, respectively, the values of that property at the temperatures of freezing and boiling water. The temperature of freezing water is defined as 0°C and that of boiling water is defined as 100°C. X_t is the value of the property at the temperature being measured.

The property X can be the length of a metal rod, the electrical resistance of a wire, the pressure of a gas, or one of many other quantities. Each of the resulting ‘thermometers’ would have provided its own scale of temperature which need not have agreed with any other. Of all these thermometers, gas thermometers are unique in providing, under suitable conditions, a scale that is not only (almost) independent of the gas used, but that is also based on well understood physical phenomena and that comes closest to providing an ‘absolute’ temperature scale.

Water is chosen to define the temperature scale because it is widely available and easy to purify, and because its freezing and boiling points straddle the temperature range of greatest importance to human existence. They also mark **phase transitions**. Matter in general, and water in particular, exists in three **phases: solid, liquid and gaseous**. When heat energy is continuously imparted to a solid, the temperature of that solid will rise to a particular value, the **melting point**, where it remains constant until all the solid has been converted to liquid. Then the temperature will rise again until a second stationary value, the **boiling point**, is reached. Here again the temperature will remain constant as heat energy is added until all the liquid is vaporized. Only then will the temperature of the gas rise with the continued application of heat. The reason for this is that at the phase transitions (melting and boiling points) the added energy serves to change the phase of the material rather than to raise its temperature. A mixture of two phases of the same material, e.g. ice and water, is thus capable of absorbing heat as well as of giving it off without changing temperature. For this reason, such mixtures are very useful as temperature standards.

There is one caveat: The boiling point of water (indeed of any liquid), and to a much smaller degree its freezing point, are dependent on the ambient pressure which is usually the atmospheric pressure. For the precise calibration of a Celsius thermometer, it is thus necessary to work at one standard atmosphere of pressure (760 Torr)¹. In our simple experiments, we need not be so punctilious but you should know that considerable precautions are necessary to obtain precisely reproducible fixed points.

We will use a **constant volume gas thermometer**, which consists of a fixed volume that is filled with a given mass of gas whose pressure p is used as a measure of temperature. In this case (constant volume), the temperature in degrees Celsius [°C] is given by

$$t = 100 \frac{P_t - P_0}{P_{100} - P_0} [\text{°C}]. \quad (2)$$

¹The international unit of pressure is the Pascal (1 Pa = 1 Nm⁻²), but the pressure gauges in this laboratory read in Torr, where 760 Torr = 760 mm Hg = 1 atm = 1.013 × 10⁵ Pa.

The resulting Celsius scale is called the **ideal gas Celsius scale**.² An ideal gas is one in which the interaction between molecules is negligible. This is the case when two conditions are met:

1. The molecules of the gas collide only (relatively) rarely with each other. This happens if the gas is dilute, i.e. if the volume available to the gas molecules is large compared to the volume they would fill if they were tightly packed.
2. During a collision, the molecules just exchange energy and momentum but do not stick to each other. This condition is satisfied by all gases at temperatures well above their condensation point, i.e. the point at which the gas is liquefied.

Helium is an excellent approximation to an ideal gas: it is monatomic, its atoms are small, and its condensation point is the lowest of all known substances. It is for this reason that we shall use helium to fill our **gas thermometer**.

We shall study in this activity the **Ideal Gas Law**

$$pV = nRT, \quad (3)$$

where p is the gas pressure, V is the volume of the container holding the gas, n is the number of moles³ of the gas filling the container, R is the **Universal Gas Constant**,

$$R = 8.3145 \text{ J/(mol} \cdot \text{K)}, \quad (4)$$

and T is the temperature measured on an **absolute scale** (e.g., the **Kelvin scale**). Just what this absolute scale is you will find out below. For the moment, we just note that we can fix n and V . Since R is a constant, the ideal gas law implies a simple proportionality between temperature and pressure,

$$p = \frac{nR}{V}T = CT, \quad (5)$$

where C is a constant (for a given n and V).

Kinetic Gas Theory tells us that the molecules of a gas are in constant thermal motion. As the temperature of the gas is lowered, the thermal motion becomes slower and slower. Since a molecule cannot move slower than not at all, there must exist a lowest temperature, an absolute zero of temperature, at which all thermal motion has come to a stop. In an **Absolute Temperature Scale**, this point is chosen as zero. For the **Kelvin Scale** (Lord Kelvin, 1824 - 1907), the increments are taken over from the Celsius scale, i.e. a temperature difference of one Kelvin (notation: 1 K, *not* 1 degree K or °K) is the same as a temperature difference of 1 °C.⁴ The Celsius and Kelvin scales (see Fig. 1) are related by the following expression:

$$T_{(\text{Kelvin})} = t_{(\text{Celsius})} + 273.15 \text{ K} \quad (6)$$

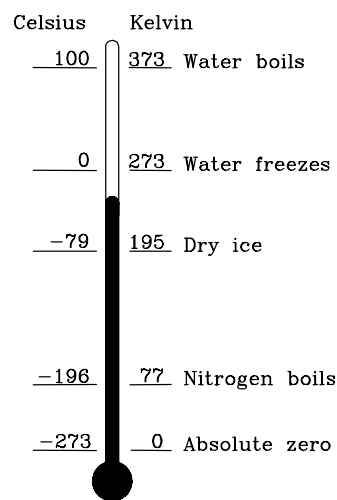


Fig. 1

² The zero of the Celsius scale is defined as the temperature at which ice and water coexist at atmospheric pressure. The triple point of water (where all three phases of water – solid, liquid, gas – are in equilibrium) is at 0.01°C.

³ One mole of gas consists of Avagaddo's constant ($N_A = 6.022 \times 10^{23}$) molecules.

⁴ This account of the definition of the Kelvin scale is somewhat simplified. The actual definition of the scale is based on thermodynamic considerations.

In an absolute scale, the ratio of two temperatures becomes a meaningful quantity. A temperature, for instance, of 400 K is indeed twice as high as a temperature of 200 K. A similar statement made using Celsius or Fahrenheit temperatures would be quite nonsensical. Liquid nitrogen boils at a very frigid 77 K. It is, nevertheless, almost 20 times 'hotter' than liquid helium, which boils at 4.2 K. In the same sense, a temperature of 0.01 K is 100 times colder than one of 1 K and indeed there are physical phenomena that are unnoticeable at, say, 0.1 K but become obvious at 0.001 K. The quest for lower and lower temperatures goes on. According to the **Third Law of Thermodynamics**, it is not possible to ever reach 'absolute zero'. However, it has been approached to less than 10^{-6} K.

The pressure that a gas exerts on the walls of its container is due to the change in momentum of the gas molecules bouncing off of these walls. At the absolute zero of temperature, there is no thermal motion and the pressure of the gas must drop to zero. The ideal gas thermometer will thus register zero at the temperature of 0 K.

The materials you will need for this investigation are

- Gas thermometer
- Kitchen-type thermometer
- Hot water pot
- Dewar
- Nalgene container
- Plastic buckets
- Safety goggles (one for each student, **WEAR THEM!!!**)
- Dry ice (frozen carbon dioxide)
- Methanol
- Liquid nitrogen

Activity 2-1: Constant volume thermometer

1. The hot water bath needs about half an hour to come to a boil. Before you do anything else, **top it off with water and plug it in**. Make sure to leave enough space in the hot water bath to completely submerge the spherical ball of the gas thermometer without boiling water spilling over the top.

CAUTION!
PUT ON SAFETY GOGGLES!!!

Liquid nitrogen and the dry ice - methanol mixture are extremely cold and can damage skin and eyes so **be very careful** while using them. (Boiling water is not particularly good for you either.)

Question 2-1: You will be using helium gas in this activity. Is this a good gas to use for this experiment? Explain. Why not just use air, which is composed of mostly nitrogen and oxygen?

2. Open the experimental file **L12.2-1.Absolute Zero** Note that you can enter data for temperature and pressure into the table. Measure room temperature and insert that value in the computer and in Table 2-1 now.

3. *Data Studio* is already set up for you to take three sets of data for different initial pressures. Enter your data into the tables in this manual and into *Data Studio*.
4. With the sphere of the gas thermometer *completely* immersed in the ice bath, your instructor will pump it out and then fill it with helium gas to a pressure of about 1060 Torr at the pump station. This is about 300 Torr above atmospheric pressure (p_{atm}) of 760 Torr. Do not fill the sphere to a pressure greater than 300 Torr above p_{atm} . You can obtain the atmospheric pressure by reading the barometer provided in the lab. **Hold the gas thermometer by the handle while the sphere is in any of the baths!** The sphere tends to float and can readily jump out of the container and break the gauge. Whenever you dip the gas thermometer sphere into any of the temperature baths move it around **gently** to stir the liquid and insure good thermal contact. Tap the gas thermometer gauge with your finger because the needle may stick slightly. Read the pressure carefully and write it in your journal. Enter your values into Table 2-1 and into the computer.
5. Next, dip the gas thermometer into the boiling water, make sure the sphere is completely covered, move it about gently until the water boils again vigorously. Read the pressure, tapping the pressure gauge gently to help overcome the friction in the meter movement. Enter your data results into Table 2-1 and into the computer.
6. Measure the temperature of the room temperature bath with the kitchen type thermometer. Run cold water over the bulb until it is near room temperature. Now, dip the gas thermometer into the room temperature bath, move it about and wait for the temperature to equilibrate, and then read the pressure and the bath's temperature (again). (Take care to keep this temperature constant!) Record the bath's temperature in Table 2-1
7. Repeat the procedures for the ice bath and the dry ice and methanol bath.

CAUTION!
WIPE UP ANY METHANOL SPILLS IMMEDIATELY!

8. Dry off the sphere with a paper towel then dip it into the liquid nitrogen, move it about until the nitrogen has stopped boiling vigorously and read the pressure. Rinse the sphere under running water until all the ice has melted.
9. Referring to the temperatures of the baths in Table 2-2, the computer will graph the measured pressures against the Celsius scale ranging from $-300\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$. This experiment with initial pressure near 1060 torr will be labeled Run 1 in the computer. Do not erase these data.

Table 2-1 Data for initial pressure near 1060 torr

Temperature Bath	T ($^{\circ}\text{C}$)	Pressure (torr)
Ice water (initial fill)		
Boiling water		
Room temperature		
Ice water		
Dry ice/methanol		
LN ₂		

10. You are now ready to work on the next pressure. While one of you is doing that, another student should be preparing a linear fit to the data in Run 1. Expand the axes so you can see the fit to at least $-300\text{ }^{\circ}\text{C}$.

Table 2-2. Temperatures of Various Baths in Celsius and Kelvin Scales

Temperature	t [$^{\circ}\text{C}$]	T [K]
Boiling water	100	373
Room Temperature (water Bath)	(Measured with a thermometer)	
Ice Water	0	273
Dry ice + methanol	-78	195
Liquid nitrogen	-196	77

11. Your instructor may want to do this step for you. Ask him or her to find out. Immerse the bulb in the ice water bath, and after the pressure has become stable open the valve slightly and slowly until the helium begins to escape. Reduce the pressure to about 960 Torr and close the valve. (If you overshoot, go on to the next pressure and return to this pressure later.) Again, tap the gauge with your finger. Write down the exact value of the pressure. This will represent a new value of n for the number of moles of He in the constant volume gas thermometer. Repeat steps 3) through 8) and determine the pressure for all six temperatures again. Enter the data for this initial pressure of 960 torr in to Run 2.

Table 2-3 Data for initial pressure near 960 torr

Temperature Bath	T ($^{\circ}\text{C}$)	Pressure (torr)
Ice water (initial fill)		
Boiling water		
Room temperature		
Ice water		
Dry ice/methanol		
LN ₂		

12. Repeat step 11) for an initial pressure of 860 (Run 3) in the ice water bath. Take the data for all six temperatures again. Enter your data in the tables here and in the computer. Perform Linear Fits on all.

13. Print out one graph with all linear fits and data points on it. Include this with your group report.

Table 2-4 Data for initial pressure near 860 torr

Temperature Bath	T (°C)	Pressure (torr)
Ice water (initial fill)		
Boiling water		
Room temperature		
Ice water		
Dry ice/methanol		
LN ₂		

Question 2-2: Your linear fits should pass through the pressure $p = 0$ point. At this point we believe the temperature should be absolute zero. At what temperatures do your lines pass through $p = 0$? Do they all go through zero at the same position? Discuss.

Question 2-3: Use these data to get an initial estimate for the absolute zero temperature (in Celsius):

$$T_{ABS} = \text{_____ } ^\circ\text{C}$$

Activity 2-2: Correction to constant volume thermometer

In your plot, you will notice that for each n , your data do not quite line up on a straight line as you would expect from Eq. (5). This is, in part, because of the design of the gas thermometer, for which we must make a correction. Indeed, the gauge, whose temperature does not change as the bulb is placed in the various baths, contains about 6% of the internal volume of the apparatus. We wish to find the correction to the pressure which relates the pressure measured by the gauge to the pressure measured by an ideal gauge containing no volume of air. Let us define the following quantities:

- n_g = the number of moles of gas in the gauge
- n_s = the number of moles of gas in the sphere
- n = $n_g + n_s$, the total number of moles of gas in the apparatus
- V_g = the volume of the gauge = 19.4 cm³
- V_s = the volume of the sphere = 523.3 cm³
- T_g = the **absolute** temperature of the gauge (room temperature)
- T_s = the **absolute** temperature of the sphere

The gas law applied to the gas *in the gauge* is

$$p_g V_g = n_g R T_g \quad \text{or} \quad n_g = \frac{p_g V_g}{R T_g}. \quad (7)$$

The gas law applied to the gas in the sphere is

$$p_s V_s = n_s R T_s. \quad (8)$$

Note that while the temperature of the gas in the sphere changes, the temperature in the gauge remains at room temperature ($T_g = T_{RT}$). Furthermore, the pressure is the same throughout the apparatus (i.e. in both the sphere and the gauge so that $p = p_g = p_s$) at any particular time. Using this observation along with the relation $n = n_g + n_s$, we can rewrite Eq. (8)

$$p_s = p = \frac{n_s R T_s}{V_s} = (n - n_g) \frac{R T_s}{V_s}, \quad (9)$$

which simplifies to

$$P_{\text{corrected}} = p \left[1 + \frac{V_g T_s}{V_s T_{RT}} \right] = \frac{n R T_s}{V_s} \quad (10)$$

making use of Eq. (7). The quantity in the bracket is the desired correction factor with which one must multiply the *measured* values of the pressure in order to get the pressure that an *ideal gauge* would measure.

1. We have already programmed most of this correction for you in the computer. To make this correction, look under Data on the far left of the screen and double click on the calculator icon that says Pressure Corrected. The calculator screen appears. Note the definition of Pressure Corrected in the window. Look at this equation carefully and compare it to Equation (10) above. We need the value in the bracket of Eq. (10). We have included T_s in the equation, so you need to determine the value of $V_g/(V_s T_{RT})$. Calculate your value of this constant, which we have called C . You enter the value of C by clicking on the + sign at the bottom of the window next to Experimental Constants. An additional window opens up, and you should enter C as a decimal number, not using exponents. The “precision number” should remain at 7, but do not enter a number that has more than 7 digits. The value of C should appear above in the window. Close the calculator window.
 2. The corrected data tables and graphs have been minimized at the bottom of the screen. Restore both of them so you can see the corrected pressure and new graphs. Make sure you have linear fits for all three sets of data.
1. Verify the ideal gas law in the form of Eq. (5). What this means is 1) that for each n corresponding to the two initial pressures, the corrected data should form a straight line, and 2) that all three lines (one for each n) should intersect each other at a single point, within experimental error.
 2. Print out all three data tables and one graph with all three sets of data with the linear fits shown.

Question 2-4: Do the linear fits pass through the corrected data better than before? Can you believe that pressure is linearly proportional to temperature for a constant volume?

Question 2-5: For which data points is the correction the largest? Does this make sense? Were these the data points that were furthest off the linear line before? Explain.

Question 2-6: On the Celsius scale, what is the absolute zero of temperature according to your data? Do the three sets of data come together near the zero pressure? Should they? Explain.

Question 2-7: How does your value for absolute zero compare with the known value? (Refer to Eq. (6).) Is it within experimental uncertainty?

INVESTIGATION 3: MYSTERY GAS

To do this investigation you will need

- Constant volume thermometer with mystery gas
- Liquid nitrogen in dewar

Your instructor has a special constant volume thermometer just like the one you have been using, but it is filled with a “mystery” gas. If your instructor has time, he may want to go through this investigation with you. If not, please ask the instructor for this thermometer and proceed through the following activity.

1. What is the pressure of the thermometer at room temperature? The exact value is not important; we just want to make sure that you realize there is gas pressure inside the metal sphere. Reading the gas pressure in the room air is fine.

Pressure _____ mm Hg

2. Now carefully place the metal sphere in the liquid nitrogen dewar and watch the pressure carefully as it decreases.

Question 3-1: What happens to the gas pressure as the metal sphere becomes cooler? Does this behavior follow that of an ideal gas?

Question 3-2: Explain the phenomenon that you just observed. Discuss this among yourselves and perhaps with the other group sharing your temperature baths. The following questions may be helpful to you in figuring out what you just observed. We do believe the ideal gas law is valid. Keeping the ideal gas law, Eq. (3), in mind, we can solve for the pressure: $p = nRT / V$. Did the temperature go to zero? Did the volume become infinite? What is n ? Now explain the physics of your observation.

3. Warm up the metal sphere and clean it off so another group can use it. Place it in front of the room where the instructor wants to keep it.

Question 3-3: In light of the mystery gas activity, was hydrogen a good gas to use in this experiment? Why would you not want to just use air?