1. The Gas Laws

Objective

The gas laws describe the behavior of ideal gas samples under different pressure, volume, and temperature conditions. Boyle's law (pressure/volume) and Charles's law (volume/temperature) will be investigated. Graham's law, which describes the rates at which ideal gases will diffuse/effuse, will also be studied.

According to Boyle's law, the volume of a sample of ideal gas varies *inversely* with the pressure on the gas sample (at constant temperature). This means, in simple words, if you squeeze harder on a sample of gas, the size of the sample will decrease. In Choice I, a sample of air will be trapped under a column of mercury in a constant-bore glass tube. By adjusting the height of the column of mercury, the pressure on the trapped air sample can be varied. Also, the effect of the pressure on the volume of the gas can be determined by measuring the change in height of the gas sample in the tube.

According to Charles's law, the volume of a sample of ideal gas varies *directly* with the absolute temperature of the gas sample (at constant pressure). This simply means that if you heat a sample of gas, the sample will increase in size. In Choice II, a sample of air will be trapped in a capillary tube beneath a small droplet of mercury. The gas sample will be heated to the temperature of a boiling water bath and then will be allowed to cool spontaneously. The volume of the gas sample will be determined at regular temperature intervals, and the relationship between volume and temperature will be confirmed graphically. The graph will be extrapolated to determine its intercept with the volume axis (absolute zero).

Graham's law, which describes the relative rates at which gases diffuse/effuse, will be investigated in Choice III for the gases ammonia and hydrogen chloride. These gases will be diffused simultaneously into opposite ends of a glass tube, and the appearance of a ring of ammonium chloride will be used to indicate the distances traveled by the gases.

Choice I. Boyle's Law

Introduction

By careful measurement of the volumes of gas samples under different pressure conditions, Sir Robert Boyle determined that the volume of a sample of ideal gas varied inversely with the pressure of the gas sample (at constant temperature). If the pressure on a sample of gas is *increased,* for example, the volume of the sample of gas *decreases.* If the pressure on a sample of gas is decreased, the volume of the sample increases in proportion to the change in the pressure. In particular, if the pressure on a sample of gas is doubled, the volume of the sample will become half of what it had been before the pressure was increased.

Various mathematical statements can be written to describe a gas that follows Boyle's law. Some of these are:

$$P \times V = \text{constant (at constant } T)$$

$$P = \text{constant}/V$$

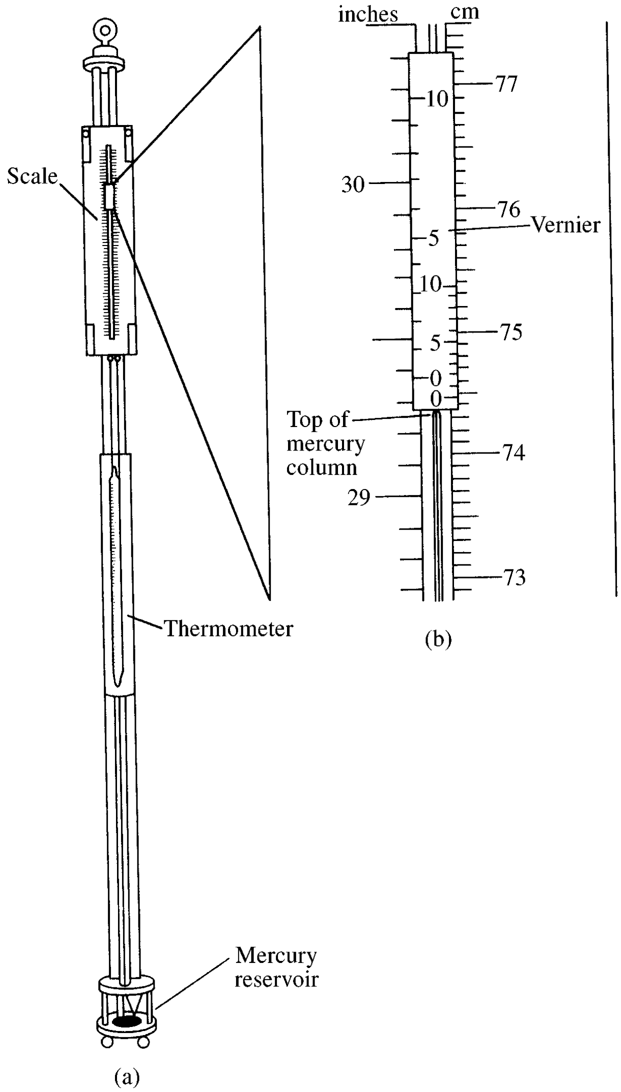
$$P_1 \times V_1 = P_2 \times V_2$$

Each of these statements corresponds to the type of mathematical function known as an **hyperbola**: the algebraic form of the general equation for an hyperbola is $xy = c$.

In this experiment, a sample of gas will be trapped in a sealed constant-diameter glass tube (a buret) beneath a column of mercury. By increasing the height of the mercury column, the pressure on the sample of gas can be increased. Since pressures of gas samples are commonly measured with reference to units of millimeters of mercury (mm Hg, or torr) as derived from the common mercury barometer, the height of the mercury column above the gas in millimeters, combined with the pressure of the atmosphere above the column of mercury, is a direct measure of the pressure of the gas sample. Thus, measuring the height of the column of mercury will provide information about the pressure and volume of the gas sample in the sealed glass tube. Since the glass tube containing the gas sample is of constant diameter, it is geometrically a regular cylinder. The *volume* of a regular cylinder is a constant times the *height* of the cylinder.

Because the apparatus for the measurement of gas volume is open to the atmosphere above the column of mercury, the pressure of the atmosphere is also being applied to the sample of gas and will have to be measured. The most common instrument for the measurement of atmospheric pressure is the **mercury barometer**. The barometer (see Figure 1-1) consists of a glass tube, sealed at one end, that has been filled with mercury and then inverted into a reservoir of mercury. The mercury does not fall out of the glass tube completely because the reservoir into which the tube has been inverted is open to the atmosphere. The pressure of the atmosphere is sufficient to hold most of the mercury in the inverted tube. However, as the pressure of the atmosphere changes from day to day with the weather, the exact height to which the mercury level is held in the tube varies. The height of the mercury in the tube is taken as a direct measurement of the atmospheric pressure at any time and is quoted in units of millimeters of mercury. The average pressure of the atmosphere can support a column of mercury to a level of approximately 760 mm. During periods of clear weather (high pressure), the mercury level in the barometer will be above 760 mm; during periods of stormy weather (low pressure), the mercury level will be below 760 mm. Radio and television stations usually report the barometric pressure in inches of mercury; 760 mm is approximately equivalent to 30 inches.

FIGURE 1-1
The mercury barometer. One standard atmosphere supports a column of mercury to a height of 760 mm. The vernier scale in (b) reads the pressure to a fraction of a millimeter.



SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Mercury is easily spilled, and its vapor is extremely toxic. Mercury can also be absorbed through the skin. For these reasons, Choice I will be performed with the apparatus in a trough in the exhaust hood. The instructor will manipulate the mercury reservoir for you. If any mercury is spilled, the mercury must be cleaned up by suction or a "mercury sponge."**
- **Use glycerine liberally when inserting glass tubing through rubber stoppers. Protect your hands with a towel. Wash the glycerine off before using the glass.**

Apparatus/Reagents Required

Buret, rubber tubing, leveling bulb/mercury reservoir, barometer, meter stick, one-hole stopper to fit mouth of the buret, rubber bands

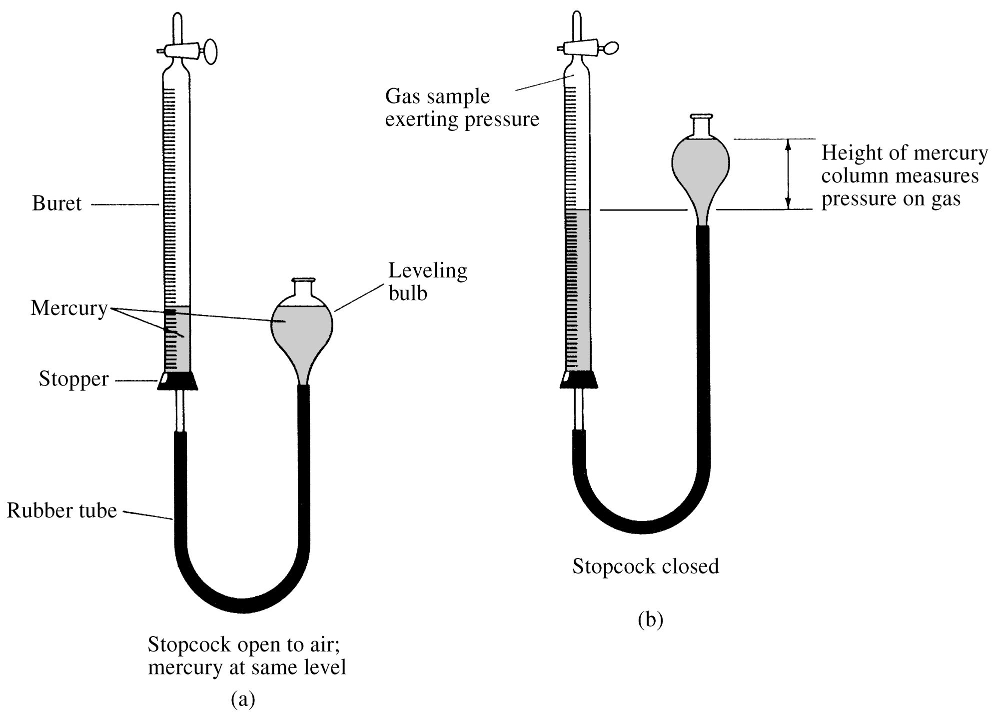
Procedure

Record all data and observations directly in your notebook in ink.

Your *instructor* will manipulate the pressure/volume apparatus for you. Do *not* attempt to operate the apparatus yourself.

The measurements that need to be taken are the *height* of the gas sample in the buret as well as the *difference in height* of the mercury levels in the buret and in the leveling bulb (see Figure 1-2). Therefore, the buret used to contain the gas sample is mounted on a meter stick.

FIGURE 1-2
Boyle's law apparatus. The difference in mercury heights between the buret and leveling bulb represents the difference between the pressure of the gas sample and the barometric pressure.



The height of the gas sample, which is directly proportional to the volume of the sample, is measured from the *top of the mercury meniscus* at the bottom of the gas sample to the *top of the inner chamber of the buret* (directly beneath the stopcock when the buret is in the inverted position).

Your first measurement will be of the *initial* volume of the gas when the system is *open to the atmosphere.* Open the stopcock at the top of the buret. The instructor will then move the leveling bulb of mercury so that the level of mercury in the leveling bulb matches the level of mercury in the buret. While the two levels of mercury match, determine the height of the gas sample in the buret to the nearest mm by reference to the meter stick. When the height reading has been taken, *close the stopcock* on the buret.

The instructor will now move the leveling bulb to a higher position. When the bulb is raised, the gas sample is subjected to a higher pressure because of the difference in heights of the mercury columns in the leveling bulb and in the buret. The volume of the gas sample will decrease because of the additional pressure. After the instructor has moved the leveling bulb, and the system has stood for several minutes, determine the height of the gas sample in the buret to the nearest mm. Also determine the *difference* in height of the mercury columns.

The instructor will then move the leveling bulb to a higher position three more times. Each time the bulb is moved, record the height of the gas sample and the difference in the mercury levels. The instructor may have to add mercury to the leveling bulb to keep the mercury surface within the limits of the bulb itself.

Read the barometric pressure in the laboratory.

From your data, calculate the total pressure exerted on the gas sample at each position of the mercury leveling bulb. The total pressure is equal to the barometric pressure in the laboratory plus the additional pressure exerted by the column of mercury (i.e., the difference in the height of the mercury columns between the leveling bulb and the buret).

Plot a graph of volume (height) versus pressure for your data.

Calculate the *reciprocal* of the pressures ($1/P$) for each of your experimental determinations. Plot a graph of volume versus the reciprocal pressure for your data. Which of the graphs is a straight line?

Choice II. Charles's Law

Introduction

The volume of a sample of an ideal gas is *directly proportional* to the absolute temperature of the gas sample (at constant pressure). The first study of the relationship between gas volumes and temperatures was made in the late eighteenth century by Jacques Charles. Charles's original statement describing his observations was that the volume of a gas sample decreased by the same factor for each degree Celsius (centigrade) the temperature of the sample was lowered. Specifically, Charles found that the volume of a gas sample decreased by 1/273 of its volume for each degree the temperature of the sample was lowered.

The fact that the volume of a gas sample decreases in a regular way when the temperature drops led scientists to wonder what would happen if a gas sample were cooled *indefinitely.* If the gas sample's volume continued to decrease each time the temperature was lowered, then eventually the volume of the gas sample should be so small that lowering its temperature any further would cause the sample of gas to disappear. The temperature at which the volume of an ideal gas would be predicted to approach zero as a limit is called the **absolute zero** of temperature. Absolute zero is the lowest possible temperature. Absolute zero formed the basis for a scale of temperature (Kelvin or absolute), which has zero as its lowest point with all temperatures positive relative to this. The size of the degree on the Kelvin temperature scale was chosen to correspond to that of the Celsius scale. Absolute zero corresponds to -273.15°C; it is a theoretical temperature. Real gases would never reach zero volume but rather would liquefy before reaching this temperature.

Various mathematical statements of Charles's gas law have been made. Some of these are

$$V = \text{constant} \times T \text{ (at constant } P)$$

$$V/T = \text{constant}$$

$$V_1/T_1 = V_2/T_2$$

Mathematically, a graph of volume versus temperature should be a *straight line*. The intercept of this line with the volume axis (i.e., $V = 0$) represents absolute zero. In this experiment, you will measure the volume of a sample of gas at several temperatures that are easily achieved in the laboratory and will plot the data obtained. By *extrapolation*, the intercept of this graph with the volume axis will be calculated.

The gas sample to be determined will be contained in a small glass **capillary tube** beneath a droplet of mercury. Because mercury is a liquid, the droplet will be free to move up and down in the capillary tube as the gas sample is heated or cooled. Because the capillary is of constant diameter, the linear height of the gas sample beneath the mercury drop can be used as a direct index of the gas's volume.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Mercury and its vapor are very toxic. Mercury is absorbed through the skin and should not be handled. Work with mercury in the exhaust hood.**
- **The capillary containing the gas sample is extremely fragile, and if broken, the mercury contained may be released. If the tube is broken, inform the instructor *immediately* so that the mercury can be cleaned up at once.**
- **Use tongs or a towel when handling hot beakers.**

Apparatus/Reagents Required

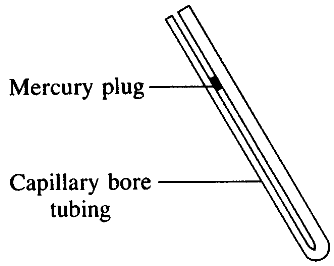
Gas sample (air) trapped beneath a drop of mercury contained in a 2-mm-diameter capillary tube, wooden ruler

Procedure

Record all data and observations directly in your notebook in ink.

Obtain a capillary tube containing the gas sample trapped beneath a droplet of mercury (see Figure 1-3). The capillary tube is extremely fragile and is broken easily. The capillary tube must be handled gently to avoid breaking up the mercury droplet. There must be a *single small unbroken droplet* of mercury in the capillary tube.

FIGURE 1-3
Charles's law apparatus. The mercury droplet moves as the gas is heated or cooled, giving an index as to the volume of the gas sample.



Set up a 600-mL beaker about two-thirds full of water on a ringstand in the exhaust hood and start heating the water to boiling.

Using glycerine as a lubricant, and protecting your hands with a towel, insert the *top* of your thermometer through a rubber stopper so that the thermometer can still be read from 0–100°C.

Attach the capillary tube containing the gas sample to your thermometer with at least two rubber bands (to prevent the capillary from moving during the experiment). Align the *bottom* of the capillary tube with the *mercury reservoir* of the thermometer.

Attach the capillary/thermometer assembly to a millimeter scale *wooden* (not plastic) ruler with several rubber bands. The scale of the ruler will be used for determining the position of the mercury droplet as it moves in the capillary tube.

When the water in the beaker is boiling, clamp the thermometer/capillary/ruler assembly to the ringstand and lower it into the boiling water. Allow the apparatus to heat in the boiling water for 3–4 minutes. Record the temperature of the boiling water bath to the nearest 0.2°C. Notice that the droplet of mercury moves up in the capillary tube as the gas beneath it is heated and expands in volume. While the gas is heating, record the position of the *inside bottom* of the glass capillary tube on the scale of the ruler. This measurement represents the lower end of the cylinder of gas being heated in the capillary.

When the gas sample has been heated in the boiling water for several minutes, record the position of the *bottom* of the droplet of mercury as indicated on the ruler scale. Calculate the height of the cylinder of gas in the capillary tube by subtracting the position of the bottom of the gas capillary from the position of the mercury droplet's lower end. Remove the heat from the beaker and allow the water bath to cool spontaneously while still surrounding the capillary/ruler/thermometer apparatus.

As the water bath cools, the gas sample in the capillary tube will contract in volume, and the mercury droplet will move downward. Determine the position of the lower end of the mercury droplet at approximately 10°C intervals as the gas cools. Record the actual temperature at which each measurement is made (to the nearest 0.2 degree). Continue taking readings in this manner until the temperature has dropped to 30°C.

After the temperature has reached 30°C, begin adding ice to the beaker of water in small portions, with vigorous stirring, and take readings at approximately 20°, 10°, and finally, 0°C. Do not add too much ice at any one time, or the temperature will drop too rapidly.

Construct a graph of your data, plotting the *height of the gas sample* (in mm) versus the *Celsius temperature.* The graph should be a *straight line.* If the graph is not a straight line, you delayed too long before reading the height of the gas sample, thereby allowing the volume of the gas sample to change. If this happens, *repeat* the measurement procedure.

Calculate the slope of the line, as well as the intercept of the line with the volume axis (where $V = 0$), as directed by your instructor.

Calculate the percent error in your determination of absolute zero.

Choice III. Graham's Law

Introduction

Effusion, strictly speaking, describes the passage of the molecules of a gas through a small hole (a "pinhole") into an evacuated chamber. This term is often confused with a similar word—diffusion. **Diffusion** is the spreading out of gas molecules through space when a container of gas is opened, allowing the gas to mix freely with any other gases present. Suppose a balloon were filled with hydrogen sulfide gas (which has the obnoxious odor of rotten eggs): if there were a tiny hole in the balloon, the hydrogen sulfide would *effuse* slowly through the hole and would then *diffuse* into the air of the room.

According to the kinetic-molecular theory of gases, the average velocity (root mean square velocity) of the particles in a sample of gas is inversely related to the square root of the molar mass of the gas

$$u_{\mathrm{rms}} = (3RT/M)^{1/2}$$

While it is not possible experimentally to determine easily and directly the average speed of the molecules in a sample of gas, the average speed at which gases diffuse or effuse can be measured readily. The speed of diffusion in centimeters per second can be determined by measuring how long it takes a gas to pass through a tube of known length.

Thomas Graham, a Scottish chemist, determined experimentally in the nineteenth century that the relative rate of diffusion of two different gases at the same temperature was given by the relationship

$$r_1/r_2 = (M_2/M_1)^{1/2}$$

in which r represents the rate of diffusion of a gas and M its molar mass. This equation, called Graham's law, is consistent with the postulate of the kinetic-molecular theory describing the average speed of molecules in a gas sample.

In this experiment, you will determine the relative rates of diffusion of the gases hydrogen chloride and ammonia, by measuring the *distances* traveled by the two gases in the same time period. For a given period of time, a lighter weight gas should be able to diffuse *farther* than a heavier gas (distance traveled in a given time period is directly related to speed). Cotton balls dipped in concentrated hydrochloric acid (HCl gas in water) and concentrated aqueous ammonia (NH_3 gas in water) will be placed in opposite ends of a glass tube. The two gases will diffuse through the tube toward each other. Hydrogen chloride and ammonia gases *react* with each other, forming the salt ammonium chloride

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

As the gases meet and react, a white *ring* of $NH_4Cl(s)$ will appear in the tube. The position of this white ring along the length of the tube can be used to determine which of the two gases has diffused farther.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while you are in the laboratory.**
- **Concentrated hydrochloric acid and concentrated ammonia solutions are each damaging to skin; wear rubber gloves while handling them.**
- **The fumes of both HCl and NH_3 are extremely irritating and are dangerous to the respiratory tract. *Use these substances only in the exhaust hood.***
- **When cutting glass, protect your hands with a towel and fire-polish all rough edges.**

Apparatus/Reagents Required

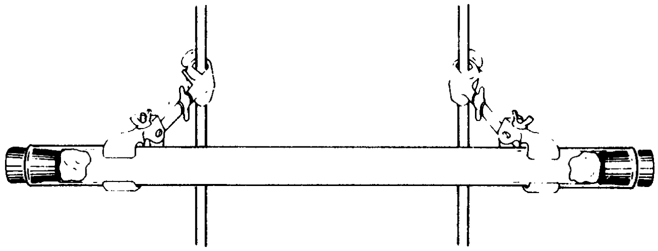
3–4 feet of 1-cm-diameter glass tubing, concentrated HCl, concentrated NH_3, cotton balls, forceps, latex surgical gloves, rubber stoppers that fit the ends of the glass tube, plastic wrap, meter stick, china marker

Procedure

Obtain a length of 1-cm-diameter glass tubing and make certain that the ends have been fire-polished. Obtain two rubber stoppers that will fit snugly in the ends of the tubing. Set up the tubing in the exhaust hood, using two adjustable clamps to hold the tubing in a steady horizontal position (see Figure 1-4).

Wear rubber gloves during the following procedure and work in the exhaust hood.

FIGURE 1-4
Graham's law apparatus. A white ring of ammonium chloride will appear in the tube where the two gases have reacted with each other.



In separate small beakers, obtain 3–4 mL each of concentrated HCl and concentrated NH_3 (*Caution!*). Keep the beakers covered loosely with plastic wrap or a watchglass when not in use. Place a cotton ball in each beaker.

Using forceps, transfer the cotton balls from the beakers to the opposite ends of the glass tubing apparatus. Do this as *quickly* as possible so that one gas will not get too much of a head start over the other (perhaps ask a friend to help you to insert the cotton balls simultaneously). Stopper the ends of the tubing and do *not* disturb or move the glass tube.

Allow the gases to diffuse toward each other until a white ring of ammonium chloride is evident in the tube. Mark the *first* appearance of the ring of ammonium chloride with a china marker before the gases diffuse too much and blur the location of the ring.

Remove the rubber stoppers. Using forceps, remove the cotton balls, and transfer them to a beaker of tap water to dilute the reagents (dispose of the cotton balls in the wastebasket after soaking in water).

Measure the distance diffused by each of the gases to the nearest millimeter, measuring from the respective ends of the glass tube to the center of the ammonium chloride ring.

Rinse out the glass tube with distilled water, allow it to dry, and repeat the determination twice.

Calculate the mean distance diffused by HCl and by NH_3 from your three sets of data.

Realizing that the distances diffused by two gases in the same time period should be directly related to the rates of diffusion of the gases, determine the percent error in your mean experimental data compared to Graham's law as expressed in the introduction to this choice.

The Gas Laws

Date:		Student name:	
Course:		Team members:	
Section:			
Instructor:			

Prelaboratory Questions

Choice I. Boyle's Law

1. Given the following pressure/volume data for a sample of an ideal gas, construct the following two graphs on graph paper:

   a. Plot the volume of the gas versus the pressure.

   b. Plot the volume of the gas versus the reciprocal of the pressure (1/pressure).

Volume, L	Pressure, atm
14.0	1.57
13.0	1.69
12.0	1.83
11.0	2.00
10.0	2.20
9.0	2.44
8.0	2.75
7.0	3.14
6.0	3.66
5.0	4.40

   Attach your graphs to this page.

2. The gas laws are defined only for *ideal* gases. Use your textbook to determine why real gases do not always follow the gas laws exactly. Under what conditions do real gases most closely approximate ideal gases?

Choice II. Charles's Law

1. The volume of a sample of ideal gas at 25°C is 372 mL. What will the volume of the gas be if it is heated at constant pressure to 50°C? What will the volume of the gas be if it is cooled to −272°C?

2. For the following volume/temperature data:

   a. Plot the data on graph paper.

   b. Determine the slope of the line.

   c. Determine the intercept of the line with the volume axis (i.e., $V = 0$)

Volume, mL	Temperature, °C
83.5	30.0
86.2	40.0
88.9	50.0
91.7	60.0
94.4	70.0
97.2	80.0
100.0	90.0

Attach your graphs to this page.

Choice III. Graham's Law

1. How many times faster will helium gas effuse through a pinhole than will nitrogen gas under the same conditions?

2. The fact that gases of different molecular weights effuse and diffuse at different speeds was used during World War II as a means of separating the isotopes of uranium for the first atomic bomb. Use your textbook or an encyclopedia of chemistry to determine in what form the uranium isotopes were separated and how the process was accomplished.

The Gas Laws

Date: ....
Course: ....
Section: ....
Instructor: ....

Student name: ....
Team members: ....
....
....

Results/Observations

Choice I. Boyle's Law

Initial height of gas at atmospheric pressure ....

Barometric pressure ....

Gas height after first movement of leveling bulb ....

Difference in mercury levels ....

Calculated pressure of gas ....

Gas height after second movement of leveling bulb ....

Difference in mercury levels ....

Calculated pressure of gas ....

Gas height after third movement of leveling bulb ....

Difference in mercury levels ....

Calculated pressure of gas ....

Gas height after fourth movement of leveling bulb ....

Difference in mercury levels ....

Calculated pressure of gas ....

Product of pressure $\times$ height of gas for your five sets of data:

Atmospheric pressure ....

First movement ....

Second movement ....

Third movement ....

Fourth movement ....

Mean value of pressure × height of gas ....

Standard deviation ....

Attach your two graphs to this report page.

Questions

1. What effect would have been observed in the pressure/volume of the gas sample if the *temperature* had increased markedly during the course of your measurements?

2. Why is it that the *height* of the gas sample can be used in the determination of Boyle's law in this experiment, rather than the actual volume of the gas in milliliters or liters?

The Gas Laws

Date:	....	Student name:	....
Course:	....	Team members:	....
Section:	....		....
Instructor:	....		....

Results/Observations

Choice II. Charles's Law

Height of gas sample	*Temperature*
....	....
....	....
....	....
....	....
....	....
....	....
....	....
....	....
....	....
....	....
....	....

Attach your graph to this report form.

Slope of volume versus temperature graph ....

Intercept of graph with volume axis ....

Percent error in absolute zero determination ....

Questions

1. Occasionally, when the glass tubes containing the gas sample are prepared, water vapor is inadvertently trapped beneath the mercury plug. What error in the volumes measured would the presence of water vapor cause?

2. Why were you able to use the height of the gas sample in the glass tube, rather than the actual volume of the gas, in the plotting of the Charles's law graph?

3. In this experiment, you *extrapolated* data over several hundred degrees to calculate a value for absolute zero. What errors might be introduced in an experiment by such a large extrapolation?

The Gas Laws

Date:	....	Student name:	....
Course:	....	Team members:	....
Section:	....		....
Instructor:	....		....

Results/Observations

Choice III. Graham's Law

Observation of NH_4Cl appearance

Distance of NH_4Cl ring from ends of tube

	NH_3 end	HCl end
Trial 1	....	....
Trial 2	....	....
Trial 3	....	....
	Mean	Mean ....

Ratio predicted from Graham's Law for rates of diffusion for NH_3/HCl ....

Experimental ratio for diffusion of NH_3/HCl based on mean distances ....

Percent error ....

Questions

1. The two gases used diffused into air, rather than into a vacuum. Is any error likely to be introduced into the experiment by this?

2. You were told to try to introduce the cotton balls containing HCl and NH_3 into the glass tube simultaneously. What error would be introduced if one substance had been introduced to the glass tube substantially before the other substance?

3. What effect on the distances measured would have occurred if the experiment had been done at a higher temperature?